3

Fundamental Properties of Lubricants

3.1 INTRODUCTION

Lubricants are various substances placed between two rubbing surfaces in order to reduce friction and wear. Lubricants can be liquids or solids, and even gas films have important applications. Solid lubricants are often used to reduce dry or boundary friction, but we have to keep in mind that they do not contribute to the heat transfer of the dissipated friction energy. Greases and waxes are widely used for light-duty bearings, as are solid lubricants such as graphite and molybdenum disulphide (MoS_2). In addition, coatings of polymers such as PTFE (Teflon) and polyethylene can reduce friction and are used successfully in light-duty applications.

However, liquid lubricants are used in much larger quantities in industry and transportation because they have several advantages over solid lubricants. The most important advantages of liquid lubricants are the formation of hydrodynamic films, the cooling of the bearing by effective convection heat transfer, and finally their relative convenience for use in bearings.

Currently, the most common liquid lubricants are *mineral oils*, which are made from petroleum. Mineral oils are blends of *base oils* with many different additives to improve the lubrication characteristics. Base oils (also referred to as *mineral oil base stocks*) are extracted from crude oil by a vacuum distillation process. Later, the oil passes through cleaning processes to remove undesired components. Crude oils contain a mixture of a large number of organic compounds, mostly hydrocarbons (compounds of hydrogen and carbon). Various other compounds are present in crude oils. Certain hydrocarbons are suitable for lubrication; these are extracted from the crude oil as base oils.

Mineral oils are widely used because they are available at relatively low cost (in comparison to synthetic lubricants). The commercial mineral oils are various base oils (comprising various hydrocarbons) blended to obtain the desired properties. In addition, they contain many additives to improve performance, such as oxidation inhibitors, rust-prevention additives, antifoaming agents, and high-pressure agents. A long list of additives is used, based on each particular application. The most common oil additives are discussed in this chapter.

During recent years, synthetic oils have been getting a larger share of the lubricant market. The synthetic oils are more expensive, and they are applied only whenever the higher cost can be financially justified. Blends of mineral and synthetic base oils are used for specific applications where unique lubrication characteristics are required. Also, greases are widely used, particularly for the lubrication of rolling-element bearings and gears.

3.2 CRUDE OILS

Most lubricants use mineral oil base stocks, made from crude oil. Each source of crude oil has its own unique composition or combination of compounds, resulting in a wide range of characteristics as well as appearance. Various crude oils have different colors and odors, and have a variety of viscosities as well as other properties. Crude oils are a mixture of hydrocarbons and other organic compounds. But they also contain many other compounds with various elements, including sulfur, nitrogen, and oxygen. Certain crude oils are preferred for the manufacture of lubricant base stocks because they have a desirable composition. Certain types of hydrocarbons are desired and extracted from crude oil to prepare lubricant base stocks. Desired components in the crude oil are saturated hydrocarbons, such as paraffin and naphthene compounds. Base oil is manufactured by means of distillation and extraction processes to remove undesirable components.

In the modern refining of base oils, the crude oil is first passed through an atmospheric-pressure distillation. In this unit, lighter fractions, such as gases, gasoline, and kerosene, are separated and removed. The remaining crude oil passes through a second vacuum distillation, where the lubrication oil components are separated. The various base oils are cleaned from the undesired components by means of solvent extraction. The base oil is dissolved in a volatile solvent in order to remove the wax as well as many other undesired components. Finally, the base oil is recovered from the solvent and passed through a process of hydrogenation to improve its oxidation stability.

3.3 BASE OIL COMPONENTS

Base oil components are compounds of hydrogen and carbon referred to as *hydrocarbon compounds*. The most common types are paraffin and naphthene compounds. Chemists refer to these two types as *saturated mineral oils*, while the third type, the *aromatic compounds* are *unsaturated*. Saturated mineral oils have proved to have better oxidation resistance, resulting in lubricants with long life and minimum sludge. A general property required of all mineral oils (as well as other lubricants) is that they be able to operate and flow at low temperature (low pour point). For example, if motor oils became too thick in cold weather, it would be impossible to start our cars.

In the past, Pennsylvania crude oil was preferred, because it contains a higher fraction of paraffin hydrocarbons, which have the desired lubrication characteristics. Today, however, it is feasible to extract small desired fractions of base oils from other crude oils, because modern refining processes separate all crude oils into their many components, which are ultimately used for various applications. But even today, certain crude oils are preferred for the production of base oils. The following properties are the most important in base-oil components.

3.3.1 Viscosity Index

The viscosity index (VI), already discussed in Chapter 2, is a common measure to describe the relationship of viscosity, μ, versus temperature, T. The curve of log μ versus log T is approximately linear, and the slope of the curve indicates the sensitivity of the viscosity to temperature variations. The viscosity index number is inversely proportional to the slope of the viscosity–temperature ($\mu - T$) curve in logarithmic coordinates. A high VI number is desirable, and the higher the VI number the flatter the $\mu - T$ curve, that is, the lubricant's viscosity is less sensitive to changes in temperature. Most commercial lubricants contain additives that serve as *VI improvers* (they increase the VI number by flattening the $\mu - T$ curve). In the old days, only the base oil determined the VI number. Pennsylvania oil was considered to have the best thermal characteristic and was assigned the highest VI, 100. But today's lubricants contain VI improvers, such as long-chain polymer additives or blends of synthetic lubricants with mineral oils, that can have high-VI numbers approaching 200. In addition, it is important to use high-VI base oils in order to achieve high-quality thermal properties of this order. Paraffins are base oil components with a relatively high VI number (Pennsylvania oil has a higher fraction of paraffins.) The naphthenes have a medium-to-high VI, while the aromatics have a low VI.

3.3.2 Pour Point

This is a measure of the lowest temperature at which the oil can operate and flow. This property is related to viscosity at low temperature. The pour point is determined by a standard test: The pour point is the lowest temperature at which a certain flow is observed under a prescribed, standard laboratory test. A low pour point is desirable because the lubricant can be useful in cold weather conditions. Paraffin is a base-oil component that has medium-to-high pour point, while naphthenes and aromatics have a desirably low pour point.

3.3.3 Oxidation Resistance

Oxidation inhibitors are meant to improve the oxidation resistance of lubricants for high-temperature applications. A detailed discussion of this characteristic is included in this chapter. However, some base oils have a better oxidation resistance for a limited time, depending on the operation conditions. Base oils having a higher oxidation resistance are desirable and are preferred for most applications. The base-oil components of paraffin and naphthene types have a relatively good oxidation resistance, while the aromatics exhibit poorer oxidation resistance.

The paraffins have most of the desired properties. They have a relatively high VI and relatively good oxidation stability. But paraffins have the disadvantage of a relatively higher pour point. For this reason, naphthenes are also widely used in blended mineral oils. Naphthenes also have good oxidation resistance, but their only drawback is a low-to-medium VI.

The aromatic base-oil components have the most undesirable characteristics, a low VI and low oxidation resistance, although they have desirably low pour points. In conclusion, each component has different characteristics, and lubricant manufacturers attempt to optimize the properties for each application via the proper blending of the various base-oil components.

3.4 SYNTHETIC OILS

A variety of synthetic base oils are currently available for engineering applications, including lubrication and heat transfer fluids. The most widely used are poly-alpha olefins (PAOs), esters, and polyalkylene glycols (PAGs). The PAOs and esters have different types of molecules, but both exhibit good lubrication properties. There is a long list of synthetic lubricants in use, but these three types currently have the largest market penetration.

The acceptance of synthetic lubricants in industry and transportation has been slow, for several reasons. The cost of synthetic lubricants is higher (it can be 2–100 times higher than mineral base oils). Although the initial cost of synthetic lubricants is higher, in many cases the improvement in performance and the longer life of the oil makes them an attractive long-term economic proposition. Initially, various additives (such as antiwear and oxidation-resistance additives) for mineral oils were adapted for synthetic lubricants. But experience indicated that such additives are not always compatible with the new lubricants. A lot of research has been conducted to develop more compatible additives, resulting in a continuous improvement in synthetic lubricant characteristics. There are other reasons for the slow penetration of synthetic lubricants into the market, the major one being insufficient experience with them. Industry has been reluctant to take the high risk of the breakdown of manufacturing machinery and the loss of production. Synthetic lubricants are continually penetrating the market for motor vehicles; their higher cost is the only limitation for much wider application.

The following is a list of the most widely used types of synthetic lubricants in order of their current market penetration:

1. Poly-alpha olefins (PAOs)
2. Esters
3. Polyalkylene glycols (PAGs)
4. Alkylated aromatics
5. Polybutenes
6. Silicones
7. Phosphate esters
8. PFPEs
9. Other synthetic lubricants for special applications.

3.4.1 Poly-alpha Olefins (PAOs)

The PAO lubricants can replace, or even be applied in combination with, mineral oils. The PAOs are produced via polymerization of olefins. Their chemical composition is similar to that of paraffins in mineral oils. In fact, they are synthetically made pure paraffins, with a narrower molecular weight distribution in comparison with paraffins extracted from crude oil. The processing causes a chemical linkage of olefins in a paraffin-type oil. The PAO lubricants have a reduced volatility, because they have a narrow molecular weight range, making them superior in this respect to parrafinic mineral oils derived from crude oil, which have much wider molecular weight range. A fraction of low-molecular-weight paraffin (light fraction) is often present in mineral oils derived from crude oil. This light fraction in mineral oils causes an undesired volatility, whereas this fraction is not present in synthetic oils. Most important, PAOs have a high viscosity index (the viscosity is less sensitive to temperature variations) and much better low-temperature characteristics (low pour point) in comparison to mineral oils.

3.4.2 Esters

This type of lubricant, particularly polyol esters (for example, pentaerithritol and trimethyrolpropane) is widely used in aviation fluids and automotive lubricants. Also, it is continually penetrating the market for industrial lubricants. Esters comprise two types of synthetic lubricants. The first type is dibasic acid esters, which are commonly substituted for mineral oils and can be used in combination with mineral oils. The second type is hindered polyol esters, which are widely used in high-temperature applications, where mineral oils are not suitable.

3.4.3 Polyalkylene Glycols (PAGs)

This type of base lubricant is made of linear polymers of ethylene and propylene oxides. The PAGs have a wide range of viscosity, including relatively high viscosity (in comparison to mineral oils) at elevated temperatures. The polymers can be of a variety of molecular weights. The viscosity depends on the range of the molecular weight of the polymer. Polymers of higher molecular weight exhibit higher viscosity. Depending on the chemical composition, these base fluids can be soluble in water or not. These synthetic lubricants are available in a very wide range of viscosities—from 55 to 300,000 SUS at 100°F (12–65,000 centistoke at 38°C). The viscosity of these synthetic base oils is less sensitive to temperature change in comparison to petroleum oils. The manufacturers provide viscosity vs. temperature charts that are essential for any lubricant application. In addition, polyalkylene-glycols base polymers have desirably low pour points in comparison to petroleum oils. Similar to mineral oils, they usually contain a wide range of additives to improve oxidation resistance, lubricity, as well as other lubrication characteristics. The additives must be compatible with the various synthetic oils.

Figure 3-1 presents an example of viscosity vs. temperature charts, for several polyalkylene-glycol base oils. The dotted line is a reference curve for petroleum base oil (mineral oil). It is clear that the negative slope of the synthetic oils is less steep in comparison to that of the mineral oil. It means that the viscosity of synthetic oils is less sensitive to a temperature rise. In fact, polyalkylene-glycol base oils can reach the highest viscosity index. The viscosity index of polyalkylene-glycols is between 150 and 290, while the viscosity index of commercial mineral oils ranges from 90 to 140. In comparison, the viscosity index of commercial polyol esters ranges from 120 to 180.

Another important property is the change of viscosity with pressure, which is more moderate in certain synthetic oils in comparison to mineral oils. This characteristic is important in the lubrication of rolling bearings and gears (EHD lubrication). The change of viscosity under pressure is significant only at very high pressures, such as the point or line contact of rolling elements and races. Figure 3-2 presents an example of viscosity vs. pressure charts, for several

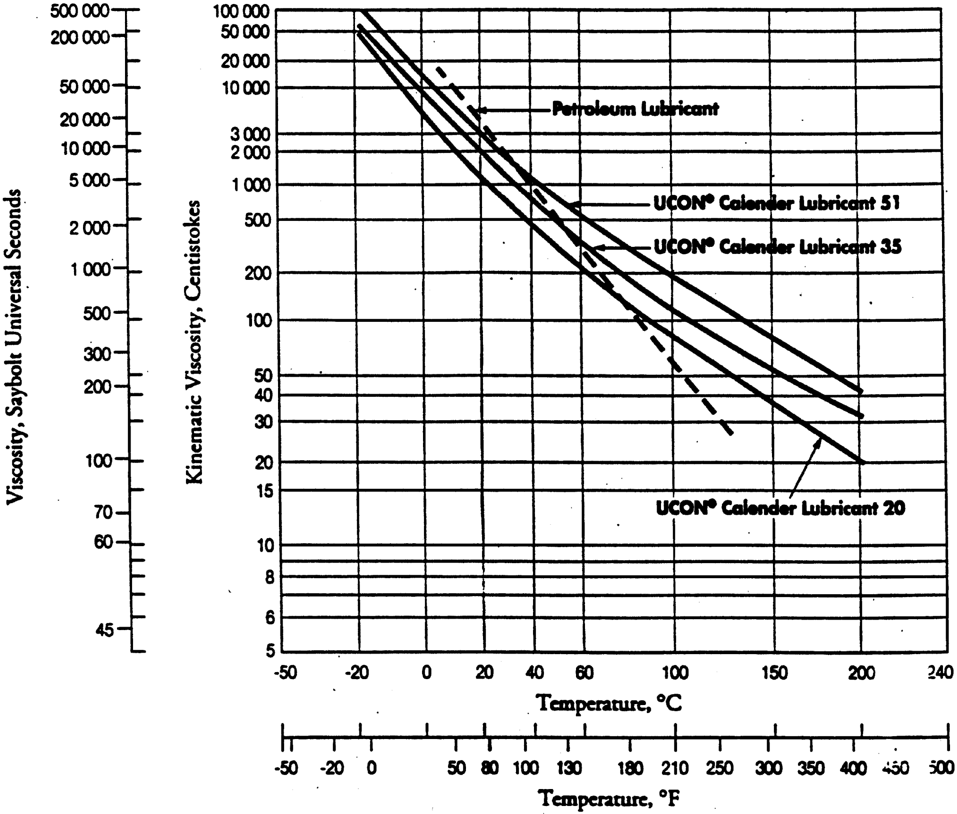

FIG. 3-1 Viscosity vs. temperature charts of commercial polyalkylene-glycol lubricants. (Used by permission of Union Carbide Corp.)

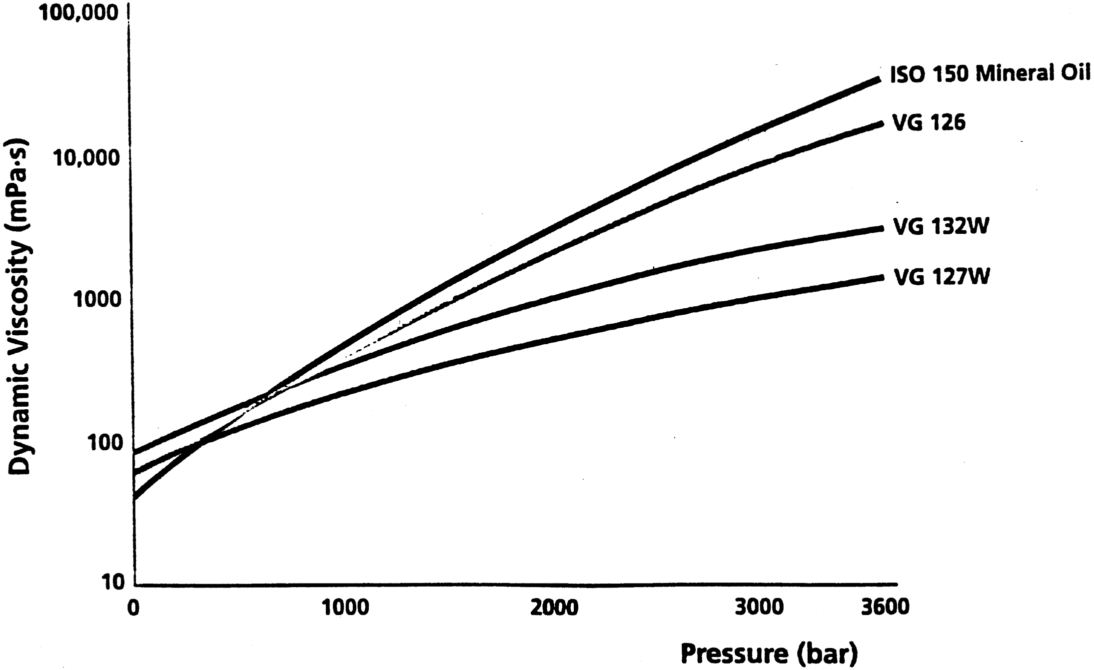

FIG. 3-2 Viscosity vs. pressure charts of commercial polyalkylene-glycol lubricants. (Used by permission of ICI Performance Chemicals.)

commercial polyalkylene-glycols as compared with a mineral oil. This chart is produced by tests that are conducted using a high-pressure viscometer.

3.4.4 Synthetic Lubricants for Special Applications

There are several interesting lubricants produced to solve unique problems in certain applications. An example is the need for a nonflammable lubricant for safety in critical applications. Halocarbon oils (such as polychlorotrifluoroethylene) can prove a solution to this problem because they are inert and nonflammable and at the same time they provide good lubricity. However, these lubricants are not for general use because of their extremely high cost. These lubricants were initially used to separate uranium isotopes during World War II.

In general, synthetic oils have many advantages, but they have some limitations as well: low corrosion resistance and incompatibility with certain seal materials (they cause swelling of certain elastomers). However, the primary disadvantage of synthetic base oils is their cost. They are generally several times as expensive in comparison to regular mineral base oils. As a result, they are substituted for mineral oils only when there is financial justification in the form of significant improvement in the lubrication performance or where a specific requirement must be satisfied. In certain applications, the life of the synthetic oil is longer than that of mineral oil, due to better oxidation resistance, which may result in a favorable cost advantage over the complete life cycle of the lubricant.

3.4.5 Summary of Advantages of Synthetic Oils

The advantages of synthetic oils can be summarized as follows: Synthetic oils are suitable for applications where there is a wide range of temperature. The most important favorable characteristics of these synthetic lubricants are: (a) their viscosity is less sensitive to temperature variations (high VI), (b) they have a relatively low pour point, (c) they have relatively good oxidation resistance; and (d) they have the desired low volatility. On the other hand, these synthetic lubricants are more expensive and should be used only where the higher cost can be financially justified. Concerning cost, we should consider not only the initial cost of the lubricant but also the overall cost. If a synthetic lubricant has a longer life because of its better oxidation resistance, it will require less frequent replacement. Whenever the oil serves for a longer period, there are additional savings on labor and downtime of machinery. All this should be considered when estimating the cost involved in a certain lubricant. Better resistance to oxidation is an important consideration, particularly where the oil is exposed to relatively high temperature.

3.5 GREASES

Greases are made of mineral or synthetic oils. The grease is a suspension of oil in soaps, such as sodium, calcium, aluminum, lithium, and barium soaps. Other thickeners, such as silica and treated clays, are used in greases as well. Greases are widely used for the lubrication of rolling-element bearings, where very small quantities of lubricant are required. Soap and thickeners function as a sponge to contain the oil. Inside the operating bearing, the sponge structure is gradually broken down, and the grease is released at a very slow rate. The oil slowly bleeds out, continually providing a very thin lubrication layer on the bearing surfaces. The released oil is not identical to the original oil used to make the grease. The lubrication layer is very thin and will not generate a lubrication film adequate enough to separate the sliding surfaces, but it is effective only as a boundary lubricant, to reduce friction and wear.

In addition to rolling bearings, greases are used for light-duty journal bearings or plane-sliders. Inside the bearing, the grease gradually releases small quantities of oil. This type of lubrication is easy to apply and reduces the maintenance cost. For journal or plane-slider bearings, greases can be applied only for low PV values, where boundary lubrication is adequate. The oil layer is too thin to play a significant role in cooling the bearing or in removing wear debris.

For greases, the design of the lubrication system is quite simple. Grease systems and their maintenance are relatively inexpensive. Unlike liquid oil, grease does not easily leak out. Therefore, in all cases where grease is applied there is no need for tight seals. A complex oil bath method with tight seals must be used only for oil lubrication. But for grease, a relatively simple labyrinth sealing (without tight seals) with a small clearance can be used, and this is particularly important where the shaft is not horizontal (such as in a vertical shaft). The drawback of tight seals on a rotating shaft is that the seals wear out, resulting in frequent seal replacement. Moreover, tight seals yield friction-energy losses that add heat to the bearing. Also, in grease lubrication, there is no need to maintain oil levels, and relubrication is less frequent in comparison to oil.

When rolling elements in a bearing come in contact with the grease, the thickener structure is broken down gradually, and a small quantity of oil slowly bleeds out to form a very thin lubrication layer on the rolling surfaces.

A continuous supply of a small amount of oil is essential because the thin oil layer on the bearing surface is gradually evaporated or deteriorated by oxidation. Therefore, bleeding from the grease must be continual and sufficient; that is, the oil supply should meet the demand. After the oil in the grease is depleted, new grease must be provided via repeated lubrication of the bearing. Similar to liquid oils, greases include many protective additives, such as rust and oxidation inhibitors.

The temperature of the operating bearing is the most important factor for selecting a grease type. The general-purpose grease covers a wide temperature range for most practical purposes. This range is from −400°C to 1210°C (−400°F to 2500°F). But care must be exercised at very high or very low operating temperatures, where low-temperature greases or extreme high-temperature greases should be applied. It would be incorrect to assume that grease suitable for a high temperature would also be successful at low temperatures, because high-temperature grease will be too hard for low-temperature applications. Greases made of sodium and mixed sodium–calcium soaps greases are suitable as general-purpose greases, although calcium soap is limited to rather low temperatures. For applications requiring water resistance, such as centrifugal pumps, calcium, lithium, and barium soap greases and the nonsoap greases are suitable. Synthetic oils are used to make greases for extremely low or extremely high temperatures. It is important to emphasize that different types of grease should not be mixed, particularly greases based on mineral oil with those based on synthetic oils. Bearings must be thoroughly cleaned before changing to a different grease type.

3.5.1 Grease Groups

a. *General-purpose greases*: These greases can operate at temperatures from −40°C to 121°C (−40°F to 250°F).
b. *High-temperature greases*: These greases can operate at temperatures from −18°C to 149°C (0°F to 300°F).
c. *Medium-temperature greases*: These greases can operate at temperatures from 0°C to 93°C (32°F to 200°F).
d. *Low-temperature greases*: These greases operate at temperatures as low as −55°C (−67°F) and as high as 107°C (225°F).
e. *Extremely high-temperature greases*: These greases can operate at temperatures up to 230°C to (450°F).

These five groups are based only on operating temperature. Other major characteristics that should be considered for the selection of grease for each application include consistency, oxidation resistance, water resistance, and melting point. There are grease types formulated for unique operating conditions, such as heavy loads, high speeds, and highly corrosive or humid environments. Grease manufacturers should be consulted, particularly for heavy-duty applications or severe environments. In the case of dust environments, the grease should be replaced more frequently to remove contaminants from the bearing. Greases for miniature bearings for instruments require a lower contamination level than standard greases.

Grease characteristics are specified according to standard tests. For example, the consistency (hardness) of grease, an important characteristic, is determined according to the ASTM D-217 standard penetration test. This test is conducted at 25°C by allowing a cone to penetrate into the grease for 5 seconds, higher penetration means softer grease. Standard worked penetration is determined by repeating the test after working the grease in a standard grease worker for 60 strokes. Prolonged working is testing after 100,000 strokes. The normal worked penetration for general-purpose grease is approximately between 250 and 350. Roller bearings require softer grease (ASTM worked penetration above 300) to reduce the rolling resistance. Other characteristics, such as oxidation stability, dropping point, and dirt count, apply in the same way to grease for roller bearings or ball bearings.

The selection of grease depends on the operating conditions, particularly the bearing temperature. The oxidation stability is an important selection criterion at high temperature. Oxidation stability is determined according to the ASTM D-942 standard oxidation test. The sensitivity of grease oxidation to temperature is demonstrated by the fact that a rise of 8°C (14°F) nearly doubles the oxidation rate. Commercial high-temperature greases are usually formulated with oxidation inhibitors to provide adequate oxidation resistance at high temperature.

3.6 ADDITIVES TO LUBRICANTS

Lubricants include a long list of additives to improve their characteristics. Lubricating oils are formulated with additives to protect equipment surfaces, enhance oil properties, and to protect the lubricant from degradation. Manufacturers start with blends of base oils with the best characteristics and further improve the desired properties by means of various additives. The following is a general discussion of the desired properties of commercial lubricants and the most common additives.

3.6.1 Additives to Improve the Viscosity Index

Multigrade oils, such as SAE 10W-40, contain significant amounts of additives that improve the viscosity index. Chapter 2 discusses the advantage of flattening the viscosity–temperature curve by using viscosity index improvers (VI improvers). These additives are usually long-chain polymeric molecules. They have a relatively high molecular weight, on the order of 25,000–500,000 molecular weight units, which is three orders of magnitude larger than that of the base-oil molecules. Examples of VI improvers are ethylene-propylene copolymers, polymethacrylates, and polyisobutylenes.

It is already recognized in the discipline of multiphase flow that small solid particles (such as spheres) in suspension increase the apparent viscosity of the base fluid (the suspension has more resistance to flow). Moreover, the viscosity increases with the diameter of the suspended particles.

In a similar way, additives of long-chain polymer molecules in a solution of mineral oils increase the apparent viscosity of the base oil. The long-chain molecules coil up into a spherical shape and play a similar role to that of a suspension of solid spheres. However, the diameter of the coils increases with the temperature and tends to raise the apparent viscosity more at higher temperatures. At higher temperatures, polymeric molecules are more soluble in the base because they interact better with it. In turn, the large molecules will uncoil at higher temperature, resulting in a larger coil diameter, and the viscosity of the lubricant increases. On the other hand, at lower temperatures, the polymeric molecules tend to coil up, their diameter decreases, and, in turn, the viscosity of the oil is reduced. This effect tends to diminish the stronger effect of viscosity reduction with increasing temperature of base oils.

In summary: When polymer additives are dissolved in base oils, the viscosity of the solution is increased, but the rise in viscosity is much greater at high temperatures than at low temperatures. In conclusion, blending oils with long chain polymers results in a desirable flattening of the viscosity–temperature curve.

The long-chain molecules in multigrade oils gradually tear off during operation due to high shear rates in the fluid. This reduces the viscosity of the lubricant as well as the effectiveness of polymers as VI improvers. This phenomenon, often referred to as *degradation*, limits the useful life of the lubricant. Permanent viscosity loss in thickened oils occurs when some of the polymer molecules break down under high shear rates. The shorter polymer molecules contribute less as VI improvers. The resistance to this type of lubricant degradation varies among various types of polymer molecules. Polymers having more resistance to degradation are usually selected. The advantage of synthetic oils is that they have relatively high VI index, without the drawback of degradation. In certain lubricants, synthetic oils are added to improve the VI index, along with polymer additives. Long-chain polymer additives together with blends of synthetic lubricants can improve significantly the VI numbers of base oils. High VI numbers of about 200 are usually obtained for multigrade oils, and maximum value of about 400 for synthetic oils.

3.6.1.1 Viscosity–Shear Effects

The long-chain molecule polymer solution of mineral oils is a non-Newtonian fluid. There is no more linearity between the shear stress and the shear-rate. Fluids that maintain the same viscosity at various shear rates are called *Newtonian fluids*. This is true of most single-viscosity-grade oils. However, multigrade oils are non-Newtonian fluids, and they lose viscosity under high rates of shear. This loss can be either temporary or permanent. In addition to the long-term effect of degradation, there is an immediate reduction of viscosity at high shear rates. This temporary viscosity loss is due to the elongation and orientation of the polymer molecules in the direction of flow. In turn, there is less internal friction and flow-induced reduction of the viscosity of the lubricant. When the oil is no longer subjected to high shear rates, the molecules return to their preferred spherical geometry, and their viscosity recovers. Equations (2-7) and (2-8) describe such non-Newtonian characteristics via a power-law relation between the shear rate and stress.

3.6.1.2 Viscoelastic Fluids

In addition to the foregoing nonlinearity, long-chain polymer solutions exhibit viscoelastic properties. Viscoelastic flow properties can be described by the Maxwell equation [Eq. (2-9)].

3.6.2 Oxidation Inhibitors

Oxidation can take place in any oil, mineral or synthetic, at elevated temperature whenever the oil is in contact with oxygen in the air. Oil oxidation is undesirable because the products of oxidation are harmful chemical compounds, such as organic acids, that cause corrosion. In addition, the oxidation products contribute to a general deterioration of the properties of the lubricant. Lubricant degradation stems primarily from thermal and mechanical energy. Lubricant degradation is catalyzed by the presence of metals and oxygen.

The organic acids, products of oil oxidation, cause severe corrosion of the steel journal and the alloys used as bearing materials. The oil circulates, and the corrosive lubricant can damage other parts of the machine. In addition, the oxidation products increase the viscosity of the oils as well as forming sludge and varnish on the bearing and journal surfaces. Excessive oil oxidation can be observed by a change of oil color and also can be recognized by the unique odors of the oxidation products.

At high temperature, oxygen reacts with mineral oils to form hydroperoxides and, later, organic acids. The oxidation process is considerably faster at elevated temperature; in fact, the oxidation rate doubles for a nearly 10°C rise in oil temperature. It is very important to prevent or at least to slow down this undesirable process. Most lubricants include additives of oxidation inhibitors, particularly in machines where the oil serves for relatively long periods of time and is exposed to high temperatures, such as steam turbines and motor vehicle engines. The oxidation inhibitors improve the lubricant's desirable characteristic of oxidation resistance, in the sense that the chemical process of oxidation becomes very slow.

Radical scavengers, peroxide decomposers, and metal deactivators are used as inhibitors of the oil degradation process. Two principle types of antioxidants that act as radical scavengers are aromatic amines and hindered phenolics. The mechanistic behavior of these antioxidants explains the excellent performance of the *aromatic amine* type under high-temperature oxidation conditions and the excellent performance of the *hindered phenolic* type under low-temperature oxidation conditions. Appropriate combinations of both types allow for optimum protection across the widest temperature range. Other widely used additives combine the two properties of oxidation and corrosion resistance, e.g., zinc dithiophosphates and sulfurized olefins. There are several companies that have specialized in the research in and development of oxidation inhibitors. Lubricants in service for long periods of time at elevated temperature, such as engine oils, must include oxidation inhibitors to improve their oxidation resistance. As mentioned earlier, synthetic oils without oxidation inhibitors have better oxidation resistance, but they also must include oxidation inhibitors when used in high-temperature applications, such as steam turbines and engines.

For large machines and in manufacturing it is important to monitor the lubricant for depletion of the oxidation inhibitors and possible initiation of corrosion, via periodic laboratory tests. For monitoring the level of acidity during operation, the *neutralization number* is widely used. The rate of increasing acidity of a lubricating oil is an indication of possible problems in the operation conditions. If the acid content of the oil increases too fast, it can be an indication of contamination by outside sources, such as penetration of acids in chemical plants. Oils containing acids can also be easily diagnosed by their unique odor in comparison to regular oil. In the laboratory, standard tests ASTM D 664 and ASTM D 974 are used to measure the amount of acid in the oil.

3.6.3 Pour-Point Depressants

The pour point is an important characteristic whenever a lubricant is applied at low temperatures, such as when starting a car engine on winter mornings when the temperature is at the freezing point. The oil can solidify at low temperature; that is, it will loose its fluidity. Saturated hydrocarbon compounds of the paraffin and naphthene types are commonly used, since they have a relatively low pour-point temperature. Pour-point depressants are oil additives, which were developed to lower the pour-point temperature. Also, certain synthetic oils were developed that can be applied in a wide range of temperatures and have a relatively very low pour point.

3.6.4 Antifriction Additives

A bearing operating with a full hydrodynamic film has low friction and a low wear rate. The lubricant viscosity is the most important characteristic for maintaining effective hydrodynamic lubrication operation. However, certain bearings are designed to operate under boundary lubrication conditions, where there is direct contact between the asperities of the rubbing surfaces. The asperities deform under the high contact pressure; due to adhesion between the two surfaces, there is a relatively high friction coefficient. Measurements of the friction coefficient, f, versus the sliding velocity U (*Stribeck curve*) indicate a relatively high friction coefficient at low sliding velocity, in the boundary lubrication region (see Chapter 16). In this region, the friction is reducing at a steep negative slope with velocity. Under such conditions of low velocity, there is a direct contact of the surface asperities. The *antifriction* characteristic of the lubricant, often referred to as *oil lubricity*, can be very helpful in reducing high levels of friction. A wide range of oil additives has been developed to improve the antifriction characteristics and to reduce the friction coefficient under boundary lubrication conditions.

Much more research work is required to fully understand the role of antifriction additives in reducing boundary lubrication friction. The current explanation is that the additives are absorbed and react with the metal surface and its oxides to form thin layers of low-shear-strength material. The layers are compounds of long-chain molecules such as alcohol, amines, and fatty acids. A common antifriction additive is oleic acid, which reacts with iron oxide to form a thin layer of iron-oleate soap. Antiwear additives such as zinc dialkyldithiophosphate (ZDDP) are also effective in friction reduction.

Theory postulates that the low shear strength of the various long-chain molecular layers, as well as the soap film, results in a lower friction coefficient. The thin layer can be compared to a deck of cards that slide easily, relative to each other, in a parallel direction to that of the two rubbing surfaces. But at the same time, the long-chain molecular layers can hold very high pressure in the direction normal to the rubbing surfaces. The thin layers on the surface can reduce the shear force required for relative sliding of the asperities of the two surfaces; thus it reduces the friction coefficient.

The friction coefficient, f, in boundary lubrication is usually measured in friction-testing machines, such as four-ball or pin-on-disk testing machines. But these friction measurements for liquid lubricants are controversial because of the steep slope of the $f-U$ curve. Moreover, it is not a “clean” measurement of the effect of an antifriction additive. The friction reduction is a combination of two effects, the fluid viscosity combined with the surface treatment by the antifriction additive. A much better measurement is to record the complete Stribeck curve, which clearly indicates the friction in the various lubrication regions. The antifriction performance of various oil additives is tested under conditions of boundary lubrication. A reduction in the maximum friction coefficient is an indication of the effectiveness in improving the antifriction characteristics of the base mineral oil. Experiments with steel sliding on steel indicate a friction coefficient in the range of 0.10–0.15 when lubricated only with a regular mineral oil. However, the addition of 2% oleic acid to the oil reduces the friction coefficient to the range of 0.05–0.08. Lubricants having good antifriction characteristics have considerable advantages, even for hydrodynamic bearings, such as the reduction of friction during the start-up of machinery.

3.6.5 Solid Colloidal Dispersions

Recent attempts to reduce boundary lubrication friction include the introduction of very small microscopic solid particles (powders) in the form of colloidal dispersions in the lubricant. More tests are required to verify the effectiveness of colloidal dispersions. These antifriction additives are suspensions of very fine solid particles of graphite, PTFE (Teflon), or MoS_2, and the particle sizes are much less than 1 μm. More research is required, on the one hand, for testing the magnitude of the reduction in friction and, on the other hand, for accurately explaining the antifriction mechanism of solid colloidal dispersions in the lubricant. Theory postulates that these solid additives form a layer of solid particles on the substrate surface. The particles are physically attracted to the surface by adhesion and form a thin protective film that can shear easily but at the same time can carry the high pressure at the contact between the surface asperities (in a similar way to surface layers formed by antifriction liquid additives).

3.6.6 Antiwear Additives

The main objective of antiwear oil additives is to reduce the wear rate in sliding or rolling motion under boundary lubrication conditions. An additional important advantage of antiwear additives is that they can reduce the risk of a catastrophic bearing failure, such as seizure, of sliding or rolling-element bearings. The explanation for the protection mechanism is similar to that for antifriction layers. Antiwear additives form thin layers of organic, metal-organic, or metal salt film on the surface. This thin layer formed on the surface is sacrificed to protect the metal. The antiwear additives form a thin layer that separates the rubbing surfaces and reduces the adhesion force at the contact between the peaks of the asperities of the two surfaces. Oil tests have indicated that wear debris in the oil contain most of the antiwear-layer material.

Zinc dialkyldithio-phosphate (ZDDP) is an effective, widely used antiwear additive. It is applied particularly in automotive engines, as well as in most other applications including hydraulic fluids. Zinc is considered a hazardous waste material, and there is an effort to replace this additive by more environmentally friendly additives. After ZDDP decomposes, several compounds are generated of metal-organic, zinc sulfide, or zinc phosphate. The compounds react with the surface of steel shafts and form iron sulfide or iron phosphate, which forms an antiwear film on the surface. These antiwear films are effective in boundary lubrication conditions. Additional types of antiwear additives are various phosphate compounds, organic phosphates, and various chlorine compounds. Various antiwear additives are commonly used to reduce the wear rate of sliding as well as rolling-element bearings.

The effectiveness of antiwear additives can be measured on various commercial wear-testing machines, such as four-ball or pin-on-disk testing machines (similar to those for friction testing). The operating conditions must be close to those in the actual operating machinery. The rate of material weight loss is an indication of the wear rate. Standard tests, for comparison between various lubricants, should operate under conditions described in ASTM G 99-90.

We have to keep in mind that laboratory friction-testing machines do not always accurately correlate with the conditions in actual industrial machinery. However, it is possible to design experiments that simulate the operating conditions and measure wear rate under situations similar to those in industrial machines. The results are useful in selecting the best lubricant as well as the antifriction additives for minimizing friction and wear for any specific application. Long-term lubricant tests are often conducted on site on operating industrial machines. However, such tests are over a long period, and the results are not always conclusive, because the conditions in practice always vary with time. By means of on-site tests, in most cases it is impossible to compare the performance of several lubricants, or additives, under identical operation conditions.

3.6.7 Corrosion Inhibitors

Chemical contaminants can be generated in the oil or enter into the lubricant from contaminated environments. Corrosive fluids often penetrate through the seals into the bearing and cause corrosion inside the bearing. This problem is particularly serious in chemical plants where there is a corrosive environment, and small amounts of organic or inorganic acids usually contaminate the lubricant and cause considerable corrosion. Also, organic acids from the oil oxidation process can cause severe corrosion in bearings. Organic acids from oil oxidation must be neutralized; otherwise, the acids degrade the oil and cause corrosion. Oxygen reacts with mineral oils at high temperature. The oil oxidation initially forms hydroperoxides and, later, organic acids. White metal (babbitt) bearings as well as the steel in rolling-element bearings are susceptible to corrosion by acids. It is important to prevent oil oxidation and contain the corrosion damage by means of corrosion inhibitors in the form of additives in the lubricant.

In addition to acids, water can penetrate through seals into the oil (particularly in water pumps) and cause severe corrosion. Water can get into the oil from the outside or by condensation. Penetration of water into the oil can cause premature bearing failure in hydrodynamic bearings and particularly in standard rolling-element bearings. Water in the oil is a common cause for corrosion. Only a very small quantity of water is soluble in the oils, about 80 PPM (parts per million); above this level, even a small quantity of water that is not in solution is harmful. The presence of water can be diagnosed by the unique hazy color of the oil. Water acts as a catalyst and accelerates the oil oxidation process. Water is the cause for corrosion of many common bearing metals and particularly steel shafts; for example, water reacts with steel to form rust (hydrated iron oxide). Therefore in certain applications that involve water penetration, stainless steel shafts and rolling bearings are used. Rust inhibitors can also help in reducing corrosion caused by water penetration.

In rolling-element bearings, the corrosion accelerates the fatigue process, referred to as *corrosion fatigue*. The corrosion introduces small cracks in the metal surface that propagate into the metal via oscillating fatigue stresses. In this way, water promotes contact fatigue in rolling-element bearings. It is well known that water penetration into the bearings is often a major problem in centrifugal pumps; wherever it occurs, it causes an early bearing failure, particularly for rolling-element bearings, which involve high fatigue stresses.

Rust inhibitors are oil additives that are absorbed on the surfaces of ferrous alloys in preference to water, thus preventing corrosion. Also, metal deactivators are additives that reduce nonferrous metal corrosion. Similar to rust inhibitors, they are preferentially absorbed on the surface and are effective in protecting it from corrosion. Examples of rust inhibitors are oil-soluble petroleum sulfonates and calcium sulfonate, which can increase corrosion protection.

3.6.8 Antifoaming Additives

Foaming of liquid lubricants is undesirable because the bubbles deteriorate the performance of hydrodynamic oil films in the bearing. In addition, foaming adversely affects the oil supply of lubrication systems (it reduces the flow rate of oil pumps). Also, the lubricant can overflow from its container (similar to the use of liquid detergent without antifoaming additives in a washing machine). The function of antifoaming additives is to increase the interfacial tension between the gas and the lubricant. In this way, the bubbles collapse, allowing the gas to escape.

Problems

3-1 Find the viscosity of the following three lubricants at 20°C and 100°C:

a. SAE 30
b. SAE 10W-30
c. Polyalkylene glycol synthetic oil

List the three oils according to the sensitivity of viscosity to temperature, based on the ratio of viscosity at 20°C to viscosity at 100°C.

3-2 Explain the advantages of synthetic oils in comparison to mineral oil. Suggest an example application where there is a justification for using synthetic oil of higher cost.

3-3 List five of the most widely used synthetic oils. What are the most important characteristics of each of them?

3-4 Compare the advantages of using greases versus liquid lubricants. Suggest two example applications where you would prefer to use grease for lubrication and two examples where you would prefer to use liquid lubricant. Justify your selection in each case.

3-5 a. Explain the process of oil degradation by oxidation.
b. List the factors that determine the oxidation rate.
c. List the various types of oxidation inhibitors.