FRICTION, WEAR AND LUBRICATION

MEMM 1343

Oils can be of two different origins, biological and non-biological, and this provides a vast array of hydrocarbon compounds.

These substances are usually present as complex mixtures and can be used for many other purposes besides lubrication, that is, the control of wear and friction. Modern technology places severe and varied demands on lubricants, so the selection and formulation of appropriate mixtures of hydrocarbons for the purposes of lubrication are skilled and complex processes.

Most natural oils contain substances which can hinder their lubrication properties, but they also contain compounds essential to the lubrication process. Lubricants made from natural or mineral oils are partly refined and partly impure. The balance between impurity and purity is critical to the oxidation stability of the oil and it varies depending on the application of the lubricant.

Chemicals which are deliberately added to an oil in order to improve its properties are called additives. Additives can radically change the properties of a lubricant and are essential to its overall performance. They also dictate specific characteristics of the lubricant such as corrosion tendency, foaming, clotting, oxidation, wear, friction and other properties.

There are two fundamental aspects of lubricant performance: achieving the required level of friction and wear rates, and maintaining these standards despite continuous degradation of the lubricant.

Chemical reaction of the lubricant with atmospheric oxygen and water is inevitable since the lubricant is essentially a hydrocarbon. Additives present in the oil also deteriorate during operation since they react with the metallic parts of the machinery and with the environment. The degradation of the lubricant is inevitable and must be postponed until the required lifetime is achieved. In fact, a large part of lubricant technology is devoted to the preservation of lubricating oils when in use.

A typical lubricating oil is composed of 95% base stock and 5% additives. Base stock is the term used to describe plain mineral oil. The physical properties of an oil depend on its base stock. In most cases it is chemically inert.

There are three sources of oils: biological, mineral and synthetic. The oils manufactured from these sources exhibit different properties and they are suitable for different applications.

Biological oils are used in applications where the risk of contamination must be reduced to a minimum, for example, in the food or pharmaceutical industry. They are usually applied to lubricate kilns, bakery ovens, etc. There can be two sources of this type of oil: vegetable and animal. Examples of vegetable oils are palm oil, castor and rape-seed oils while the examples of animal oils are sperm, fish and wool oils from sheep (lanolin).

Mineral oils are the most commonly used lubricants throughout industry. They are petroleum based and are used in applications where temperature requirements are moderate. Typical applications of mineral oils are to gears, bearings, engines, turbines, etc.

Synthetic oils are artificial substitutes for mineral oils. They are specifically developed to provide lubricants with superior properties to mineral oils. For example, temperature resistant synthetic oils are used in high performance machinery operating at high temperatures. Synthetic oils for very low temperature applications are also available.

Greases are not fundamentally different from oils. They consist of mineral or synthetic oil, but the oil is trapped in minute pockets formed by soap fibres which constitute the internal structure of the grease. Hence a grease is classified as "mineral" or "synthetic" according to the base stock used in its production.

Greases have been developed especially to provide semipermanent lubrication since the oil trapped in the fibrous structure is unable to flow away from the contacting surfaces. For this reason greases are widely used despite certain limitations in performance.

Mineral oils are the most commonly used lubricants. They are manufactured from crude oil which is mined in various parts of the world.

There are certain advantages and disadvantages of applying mineral oil to lubricate specific machinery, and these must be carefully considered when selecting a lubricant and designing a lubrication system.

The cost of mineral oils is low and even with the rapid development of synthetic oils, solid lubricants and wear-resistant polymers, their continued use in many industries seems certain.

The commonly accepted hypothesis about the origins of mineral oils is the fossil fuel theory. The theory states that the mineral oils are the result of decomposition of animal and plant matter in salt water.

According to the theory the remains of dead plants and animals were collected in sedimentary basins, especially in places where the rivers dump silt into the sea. Over time they were buried and compressed. Under these conditions the organic matter transformed into tar-like molecules called kerogen.

As the temperature and pressure increased, the kerogen gradually transformed into the complex hydrocarbon molecules which are the basic constituents of crude oil. When the temperature and pressure became sufficiently high methane was produced from the kerogen or crude oil and hence natural gas is often found together with crude oil.

About 60% of the known world oil resources are in the Middle East, concentrated in 25 giant fields.

It seems, according to the conventional theory, that the Persian Gulf was a vast sink for plant and animal life for millions of years. Over the years, plants and animals deposited there were covered by impermeable layers which formed a sort of rock cap. In order for such a system to remain intact it must be left undisturbed, i.e., free of earthquakes, faultings, etc., for millions of years, and this creates some serious doubts in the validity of the fossil fuel hypothesis as the only source of mineral oils.

To begin with it is quite difficult to believe that, in ancient times, most of the plant and animal life on the Earth was concentrated in the Persian Gulf region.

It is very unlikely that the Persian Gulf was free from earthquakes since it is known that most of the Middle East oil deposits lie along continental plate boundaries where the African, Eurasian and Arabian plates are pushing and pulling each other, and the probability for earthquakes occurring in this region is quite high in comparison to other regions.

Interestingly, most of the rich oil deposits have been found along the most seismically active regions such as from Papua New Guinea through Indonesia and Burma to China. Despite these facts the fossil fuel theory is still widely accepted, perhaps because we do not have a valid, experimentally confirmed replacement.

There is another hypothesis about the origin of mineral oils suggested by Gold. It has been known for some time that many hydrocarbons are present in meteorites and that these hydrocarbons cannot possibly originate from any plant or animal life.

The hydrocarbons are also quite common on the other planets of the solar system. For example, Jupiter, Saturn, Uranus and Neptune have atmospheres rich in some forms of hydrocarbons. Even Titan, one of Saturn's moons, has large quantities of methane and ethane in its atmosphere.

The hypothesis suggests that, although a proportion of oil and gas deposits may originate from biological sources, a proportion of hydrocarbons on the Earth have originated from non-biological sources, in the same way as on most of the other planets.

If the material from which the Earth was formed resembled some of the meteorites, then the Earth would release hydrocarbons when heated. The hydrocarbons would then accumulate under layers of rock and would generate very high pressures. This would lead to the migration of hydrocarbons through cracks and fissures in the Earth's crust.

Although at high temperatures oil molecules break down to their most stable form, methane, at the very high pressures which occur several thousand metres below the surface of the Earth, some of the oil molecules would survive.

It has been shown, in experiments with laser heated diamond anvil cells, that when methane is exposed to pressures higher than 2 (GPa) and temperatures in the range between 1,000K to 1,500K (conditions comparable to those in the upper mantle), it partially reacts to form saturated hydrocarbons containing as many as 4 carbon atoms (i.e., ethane, propane and butane) and molecular hydrogen and graphite.

This indicates that hydrocarbons heavier than methane can be produced in the upper mantle.

They could then migrate upwards along faults, deep rifts, continental plate boundaries and other fissures in the Earth's crust and form deposits.

Although the pressure would decrease, these places are also cooler, so the probability that the oil molecules would survive is very much higher.

Some of the hydrocarbon molecules would dissolve, some of them would create or enrich coal deposits while some of them would be trapped under rock caps and create reservoirs. Some of the oil would be trapped about 3,000 (m) below the surface, and much of this has already been found.

There seems to be a very strong correlation between fault and rift zones and the known reservoirs of oil and gas. There is also a strong pattern of trace elements occurring in the oil.

For example, along the west coast of South America the oil is rich in vanadium, oils from the Persian Gulf, the Ural Mountains, and parts of West Africa have a constant ratio of nickel to vanadium.

This seems to indicate that the origin of these oil deposits is deep within the Earth.

According to the hypothesis huge reservoirs of gas and oil might still be waiting to be discovered.

They are buried several thousand metres below the Earth's surface and an efficient deep drilling technology will be required to exploit them. This hypothesis, however plausible, has not yet been proved, but if true then there are still major oil and gas reservoirs yet to be discovered.

Crude oil exhibits a complex composition which is separated into a number of fractions by a distillation process which is called fractional distillation.

The process of fractional distillation involves heating the crude oil to turn it into a vapor which is then passed through a tall vertical column (fractional tower) containing a number of trays at various levels.

The vapor passes through the column and at each successive tray the temperature gradually drops. The fraction whose boiling point corresponds to the temperature at a particular tray will condense.

In this manner the most volatile compounds will condense at the highest trays in the column while those with the highest boiling points condense at the lower trays. The condensed fractions are then tapped. There are certain temperature limits to which crude oil can be pre-heated.

If the temperature is too high, then some of the crude may decompose into coke and tarry matter. This problem is overcome by employing another distillation tower which operates at a lower pressure.

By lowering the pressure the heavy fractions of crude can be vaporized at much lower temperatures. Thus, in the manufacture of mineral oils and petroleum, fuels distillation takes place at atmospheric pressure and also at significantly reduced pressures.

At atmospheric pressures, the following fractions of crude oil distillate are obtained in ascending order of boiling point: gas, petrol, naphtha, white spirit, light and heavy gas oils and residue.

The unvaporized fraction will sediment at the bottom of the column as a residue. This unvaporized residue from the "atmospheric column" is then placed in the "vacuum column" and heated.

At the lower distillation temperatures which result from using low pressures, the risk of decomposition is eliminated.

The vapor condenses on subsequent trays and the distillation products are extracted by vacuum pumps.

The following fractions of the remaining residue are obtained by this method in ascending order of boiling point: gas oil, lubricant fraction and short residue.

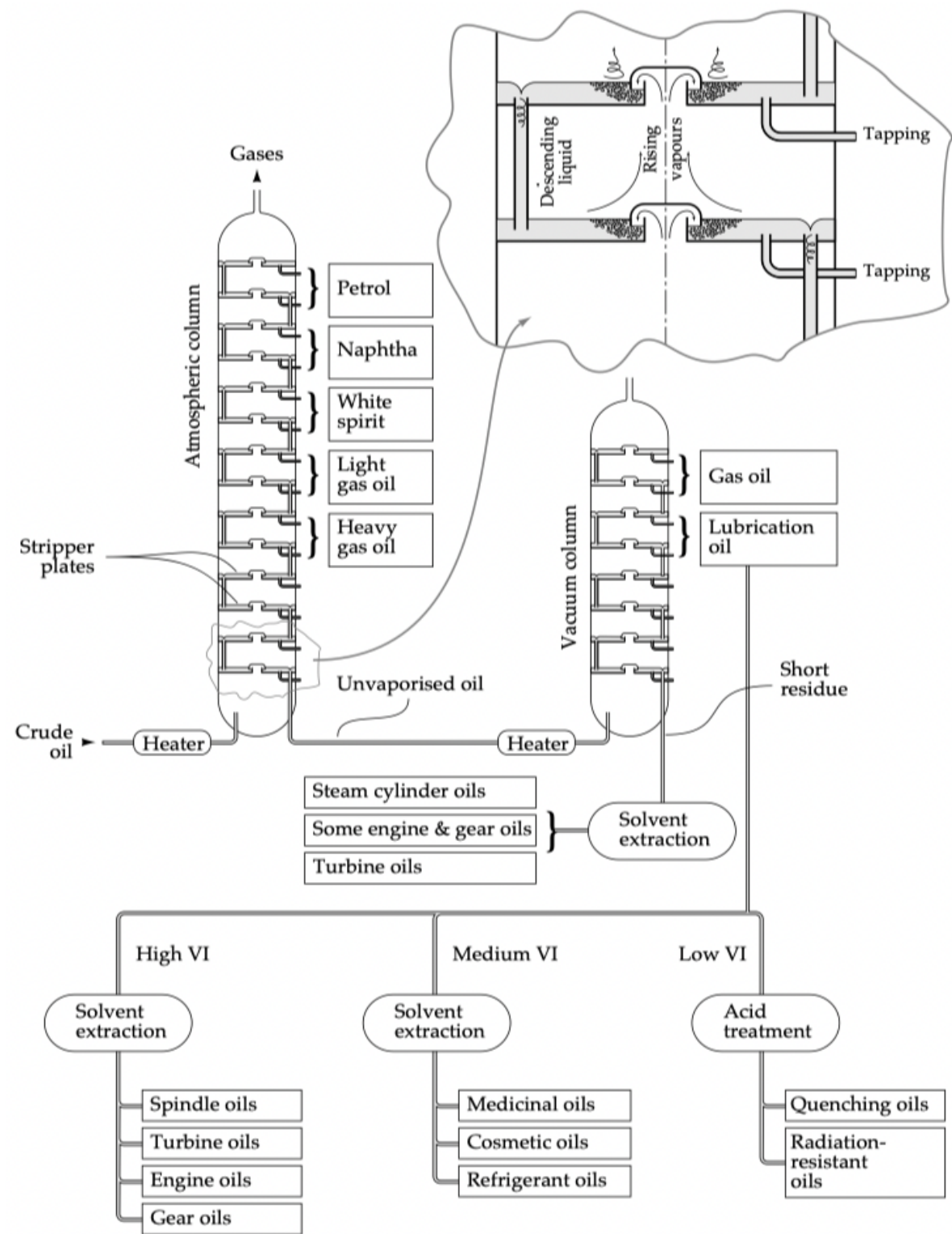The schematic diagram of a crude oil distillation process is shown in Figure 1.

Figure 1: Schematic diagram of a crude oil distillation process.

Not all crude oils have to be treated in two stages.

Depending on the origin, some of the crude oils are light enough to be heated to a temperature sufficient for their complete distillation at atmospheric pressure.

After the distillation, the lubricating oil fractions of the distillate are then subjected to several stages of refining and various treatments which result in a large variety of medical, cosmetic, industrial and automotive oils and lubricants.

The refining process involves further distillation of impure lubricating oils and mixing with organic solvents for preferential leaching of impurities. The purpose of refining is to remove high molecular weight waxes, aromatic hydrocarbons and compounds containing sulphur and nitrogen.

The waxes cause the oil to solidify or become near solid at inconveniently high temperatures.

The aromatic compounds accentuate the decrease in viscosity of the oil with temperature.

The sulphur or nitrogen compounds can cause corrosion of wearing surfaces, resulting in accelerated wear.

They may also contribute to some other problems such as corrosion of seals. Filtration of the oil through absorbent clays and hydrogenation of the oil in the presence of a catalyst are applied at the later stages of refining. The lubricant may also be mixed with concentrated sulphuric acid as this is a very effective way of removing complex organic compounds as esters of sulphuric acid. This treatment, however, causes a severe waste disposal problem. For this reason, the sulphuric acid treatment is used only for special high purity oils, such as pharmaceutical oils.

As already underlined, the salient feature of refining is that crude oil is a variable and extremely complex mixture of hydrocarbons and that refining imposes only an approximate control on the final product.

The objective of the process is not to produce a pure compound, but a product with specific characteristics which are desirable for a particular application.

It is possible to over-refine a lubricating oil, which does not happen very often in practice. In fact most lubricating oils have trace compounds deliberately left in. Many trace aromatic compounds are anti-oxidants, hence an over-refined oil is prone to rapid oxidation.

Trace compounds, however, are usually a source of sludge and deposits on contacting surfaces therefore a balance or optimization of refining is necessary. In practice the crude oil and refining process are selected to give the desired type of lubricating oil.

The composition of mineral oils is very complex.

For example, a detailed analysis of crude oil revealed 125 different compounds of which only 45 have been analysed in detail. An interesting consequence of this is that since it is not possible to give a precise analysis of mineral oil, wear and friction studies of lubricated contacts are often being conducted in the presence of pure organic fluids of known composition such as hexadecane.

The results obtained can then be compared between various research groups.

The major part of mineral oils consists of hydrocarbons with approximately 30 carbon atoms in each molecule. The structure of each molecule is composed of several aliphatic (straight) chains and cyclic carbon chains bonded together.

Almost any composition of cyclic and aliphatic chains may occur and a large number of the possible forms of the complex molecule are present in any single oil sample.

The mineral oils are also impure. The impure nature of mineral oils results in a range of useful and harmful properties such as the trace compounds provide anti-oxidants and boundary lubrication properties but they also cause deposits which can impede lubrication.

There are also many other compounds present in mineral oils such as waxes which are virtually useless and can easily be oxidized to form harmful organic acids. Special additives are needed to neutralize these waxes and related compounds.

Therefore, mineral oils differ from each other depending on the source of crude oil and refining process. The fundamental differences between mineral oils are based on:

chemical forms

sulphur content and

viscosity.

There are three basic chemical forms of mineral oil:

Paraffinic
Naphthenic and
Aromatic.

They originate from crudes from different sources and correspond to an exact chemical type. As shown in Figure 2, paraffinic implies straight chain hydrocarbons, naphthenic means cyclic carbon molecules with no unsaturated bonds and aromatic oils contain benzene type compounds.

Oils are distinguished based on the relative proportions of paraffinic, naphthenic and aromatic components present.

The aromatic oil is present only as a minor component of naphthenic or paraffinic oils. The subtlety of the lubricant engineering definition of these terms is that the lubricant is named depending on which chemical type makes up its major proportion.
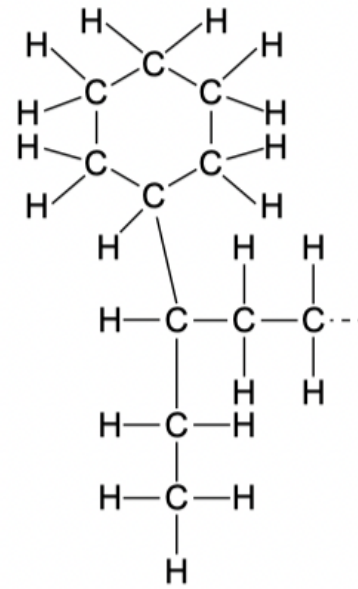
For example, a paraffinic oil means that the majority of the hydrogen and carbon atoms are present as paraffinic chains. These paraffinic chains are then linked by carbon atoms bonded in a cyclic manner to form a more complex molecule.
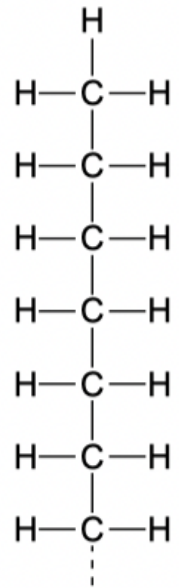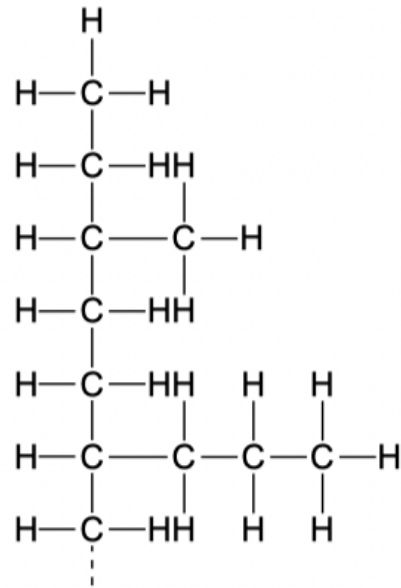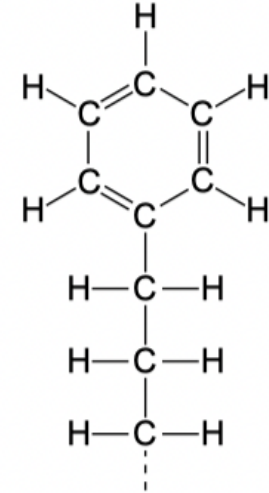
Figure 1: Types of mineral oils: a) straight paraffin, b) branched paraffin, c) naphthene, and d) aromatic.

A naphthenic oil has much smaller paraffinic chains in each hydrocarbon molecule and most carbon is incorporated in cyclic molecules. There is also a limited quantity (about 20%) of simple paraffins (alkanes) present in the oil.

The presence of one type or the other of these molecules determines some of the physical properties of the lubricants, i.e., pour point, viscosity index, pressure-viscosity characteristics, etc.

For example, there are significant differences in viscosity-temperature characteristics and viscosity-pressure characteristics between paraffinic and naphthenic oils and care must be taken in distinguishing between them.

Paraffinic oils are also generally more expensive since they require a few more stages of refining than naphthenic oils.

Sulphur content

Sulphur content in mineral oils varies, depending on the source of the crude oil and the refining process.

Small amounts of sulphur in the oil are desirable to give good lubrication and oxidation properties. It has been demonstrated, for example, that between 0.1% and 1% of natural sulphur content ensures reduced wear.

On the other hand, too much sulphur is detrimental to the performance of the machinery, e.g., it may accelerate the corrosion of seals.

Excess sulphur can be removed from oil by refining, but this can be expensive.

The sulphur content varies with the source of crude oil and the range of concentration lies between 0% and 8%.

For example, sulphur content of Pennsylvanian oil is <0.25%, Venezuelan ~2%, Middle East ~1%, Mexican 5%.

Mineral oils can also be classified by viscosity, which depends on the degree of refining.

For commonly used mineral oils, viscosity varies from about 5 (cS) to 700 (cS) at room temperature.

For example, the viscosity of a typical spindle oil is about 20 (cS), engine oil between 30 and 300 (cS) and bright stock about 600 (cS).

Synthetic oils

Synthetic lubricants were originally developed early last century by countries lacking a reliable supply of mineral oil. These lubricants were expensive and initially did not gain general acceptance.

The use of synthetic oils has increased gradually, especially in more specialized applications for which mineral oils are inadequate. Despite many positive features such as availability and relatively low cost, mineral oils also have several serious defects, such as oxidation and viscosity loss at high temperatures, combustion or explosion in the presence of strong oxidizing agents and solidification at low temperatures.

These effects are prohibitive in some specialized applications such as gas turbine engines where a high temperature lubricant is required, but occasionally very low temperatures must be sustained.

In other applications such as vacuum pumps and jet engines, low vapor pressure lubricant is needed.

In food processing and the pharmaceutical industry, low toxicity lubricant is required.

In recent years, the strongest demand has been for high performance lubricants, especially for applications in the aviation industry with high performance gas turbine engines.

This led to the development of synthetic lubricants that can withstand high temperatures without decomposing and at the same time will provide a reduced fire hazard.

The recent trend towards high operating temperatures of machinery has created a second and probably more durable period of interest in these lubricants.

Synthetic lubricants can generally be divided into two groups:

   1) Fluids intended to provide superior lubrication at ambient or elevated temperatures and
   2) Lubricants for extremes of temperature or chemical attack.

There is also a clear distinction between exotic lubricants with high performance but high cost and more economical moderate performance lubricants.

For example, the price of a halogen based synthetic lubricant reached $450/kg in 1987 which was close to the price of silver.

There are three basic types of synthetic lubricant currently in use:

1) Synthetic hydrocarbon lubricants,
2) Silicon analogues of hydrocarbons and
3) Organohalogens.

All of the hundred or more specific types of synthetic lubricant available on the market conform to one of these broad categories.

Phosphates, as in polyphenyl phosphate, deviate from the pattern as they are generally associated with simple hydrocarbons.

These three groups of synthetic lubricants have distinct characteristics which sustain the usefulness of this form of classification. These are:

1) Synthetic hydrocarbons provide a lubricant that is similar in price to mineral oil but has superior performance,
2) Silicon analogues or silicones are resistant to extremes of temperature and vacuum but do not provide good adsorption or extreme-pressure lubrication (sometimes known as "boundary characteristics") and are expensive, and
3) Organohalogens can offer effective lubrication by adsorption and extreme-pressure lubrication mechanisms and resist extremes of temperature or chemical attack, but are also expensive.

In most cases synthetic hydrocarbon lubricants are produced from low molecular weight hydrocarbons which are derived from the "cracking" of petroleum.

The process of cracking is performed in order to reduce the range of molecules present in the oil.

Through the application of high pressures and catalysts, large complex molecules present in the oil are decomposed to simpler, smaller and more uniform molecules. The low molecular weight hydrocarbons are then polymerized under carefully controlled conditions to produce fluids with the required low volatility and high viscosity.

The polymerization is carefully limited otherwise a solid polymer results and, in strict technical terms, an oligomer as opposed to a polymer is produced. A prime example of this method of lubricant synthesis is the production of a polyolefin synthetic lubricant oil from olefins (alkenes).

Halogenated lubricants are also manufactured on a large scale; these are appropriate for low temperatures or where there is an extreme fire risk.

These lubricants are made from ethylene and halogen compounds in a process of simultaneous halogenation and polymerization within a solvent.

Not all synthetic lubricants are produced by polymerization, some monomers, e.g., dibasic acid esters, are also useful for many applications.

Organohalogens and silicones are produced using catalysts.

Organohalogens are manufactured by reacting hydrocarbon gas, i.e., methane and hydrogen chloride, under pressure and temperatures of about 250°C or more in the presence of a catalyst such as alumina gel or zinc chloride.

During the process low molecular weight organohalogens (i.e., methyl-chloride) are formed which can later be polymerized, resulting in high molecular weight organohalogens.

Silicones, on the other hand, are produced from methyl chloride (CH_3Cl) which is reacted with 3 silicon in the presence of copper catalysts at 380°C to form dimethyl-silicon-chloride ($(2CH)-2-SiCl_2$).

Secondary treatment with hydrochloric acid causes the removal of the chloride radicals to form a silicone.

After neutralizing and dewatering the original stock, the polymerization of silicones is then induced by alkali, resulting in the finished product.

Hydrocarbon synthetic lubricants

There is an almost infinite variety of hydrocarbons that could be utilized as lubricants. The economics of production, however, severely restricts their range.

The oils presently advocated as the optimum synthetic lubricants by various oil refiners are not necessarily ideal as lubricants, but they are relatively cheap to produce and therefore are economic for large volume applications such as engine oils. Engine oils constitute almost half the entire lubricating oil usage and there is a large profit to be made from a synthetic oil which costs only a little more than mineral oil but can improve engine performance, durability and prolong draining periods.

Synthetic oils that can be classified as synthetic hydrocarbons are polyalphaolefins, esters, cycloaliphatics and polyglycols.

Of course, the list is incomplete and future advances in refining and synthesis may extend it.

The oxidation stability of a synthetic hydrocarbon depends on the structure of the hydrocarbon chain.

The bond energy of the C-C linkage (360 (MJ/kg.mole)) is the fundamental limitation and higher oxidation stability can be achieved by applying various oxidation inhibitors.

Oxidation stability can also be improved by replacing weakly bonded structures with branched hydrocarbons.

The hydrocarbons can be optimized for their viscosity-temperature characteristics, low temperature performance and volatility.

Polyalphaolefins

Polyalphaolefins are among the most promising general purpose synthetic lubricants.

Olefins or alkenes are unsaturated hydrocarbons with the general formula $(-CH_2-)n$.

They consist of a straight carbon chain with an unsaturated carbon at one end of the chain. A typical example is polybutene.

The presence of unsaturated carbons allows polymerization or oligomerization to form a lubricating oil. The preferred alkene is decene which produces an oil with a low minimum operating temperature (pour point).

Higher molecular weight compounds such as dodecenes have a higher viscosity index but also a higher pour point.

The viscosity of polydecenes can be varied from 0.3 (mPas) to 100 (mPas).

Their viscosity index is about 130 and pour point about -30°C.

Polydecenes are highly resistant to oxidation, have a low volatility due to the lack of small molecular weight substances and are not toxic or corrosive. These properties ensure the use of polydecenes as a general purpose synthetic lubricant.

Polyphenyl ethers exhibit better boundary characteristics than silicone oils.

They have very high oxidation and thermal stability, but are limited by poor viscosity-temperature characteristics.

Thermal stability of these compounds is about 430°C and oxidation stability is also quite high at about 290°C.

They are used as lubricants in aircraft hydraulic pumps.

A very important group of synthetic hydrocarbons are the esters.

They are produced by reacting alcohol with organic or inorganic acids.

For applications such as lubrication, inorganic acids are widely used in their production. The linkages of esters are much more stable than those of typical hydrocarbons with their C-C bonds.

The ester linkages have a much higher bond energy, thus they are more resistant to heat.

Esters usually have good oxidation stability and excellent viscosity-temperature and volatility characteristics.

Emulsions and aqueous lubricants

Water is an attractive extender of lubricating oils; cheap, good heat transfer characteristics and non-flammability are all useful attributes.

Water by itself is a very poor lubricant but when mixed with oils to form emulsions or when mixed with water-soluble hydrocarbons to produce an aqueous solution, some useful lubricants can be developed.

These liquids are used as coolants in metalworking where the combination of the lubricity of oil, high conductivity and the latent heat of water provide the optimum fluid for this application.

Mining machinery is also lubricated by water-based fluids to minimize the risk of fire from leakage of lubricants. It has been observed that during the lubrication process by emulsions, water is excluded from the loaded contacts and as a result the performance of an emulsion is close to that of a pure mineral oil.

The most severe limitation of these lubricants is the temperature range at which they can successfully be applied. They are limited to the temperature range of water, which lies between the melting point of ice and the boiling point of water. This excludes these lubricants from many applications, for example, engine oils.

Emulsions are produced by mixing water and oil with an emulsifier. An example of this relatively simple process, which usually occurs inadvertently, is when water contaminates a lubricating oil sump (most lubricating oils contain natural emulsifiers).

The mixing must be sufficiently intense to disperse one of the liquids as a series of small droplets within the other liquid. About 1 - 10% by weight of emulsifier is added to stabilize the dispersed droplets and stop their coagulation.

A "water in oil" emulsion, commonly abbreviated to "W/O", is a suspension of water droplets in oil. The converse, oil in water, contains oil droplets dispersed in water and is usually referred to as an "O/W" emulsion.

The "W/O" and "O/W" emulsions have different lubrication characteristics.

The "W/O" emulsions are used as fire-resistant hydraulic fluids, while the "O/W" emulsions are suitable as metalworking coolants. A novel type of water-based emulsion involves suspensions of nanoparticles in water. It was found that titanium dioxide nanoparticles, with diameters in the range of 20–40 (nm) and with an adsorbed coating of oleic acid (cis-9-octadecenoic acid), perform as an effective lubricating agent when combined with a dispersant and added to water in concentrations around 0.5% by weight.

Despite some limitations, water-based fluids constitute an important and specialized form of lubricant.

Characteristics

The apparent viscosity of emulsions declines with increasing shear stress, and their viscosity index is usually high. "W/O" emulsions have a high viscosity, several times that of the base oil. They exhibit an interesting behavior in concentrated contacts operating in the elastohydrodynamic lubrication regime (EHL).

The size of an EHL contact is comparable to the droplet size, or the volume of fluid within the contact is similar to the average droplet volume.

This suggests that the elastohydrodynamic films generated would be unstable or fluctuate when an emulsion is used. This, however, is not confirmed experimentally, and in fact it is known that a low stability emulsion gives the best lubrication.

It has been suspected for a long time that the emulsion is temporarily degraded at the EHL contact and releases oil for lubrication. It was suggested that the typically oleophilic metal surfaces drew oil into the EHL contact but excluded water.

Measurements showed that EHL film thickness does not vary with water concentration and maintains a value close to that of the constituent mineral oil. The pressure-viscosity coefficient of water is negligibly small, so that without forming an entrapment of oil around the EHL contact, elastohydrodynamic lubrication would not be possible.

Although it is generally accepted that the temperature limit of emulsions is dictated by the boiling point of water, i.e., around 100°C at ambient pressure.

The emulsions can effectively function at much higher temperatures.

When a water-based emulsion is in contact with a surface significantly hotter than the ambient boiling point of water then film boiling or Leidenfrost boiling occurs. Thus, when an emulsion is placed on a hot surface, its oil component is released and transferred across the vapor film reaching the hot surface and providing lubrication.

In general, the boiling point of most oils is higher than that of water. At greatly elevated temperatures, the vapor film may become too thick or continuous in nature and the lubricant transfer ceases.

At the temperature where the vapor film becomes established, known as the critical temperature, which is often more than 200°C, the emulsion effectively fails as a lubricant.

Apart from a limited temperature range emulsions exhibit poor storage capability and they may not only be degraded by oil oxidation but also by bacterial contamination of water.

Emulsions and aqueous solutions are mostly used as cutting fluids in the metal working industry and as fire resistant lubricants in the mining industry.

Aqueous solutions of polyglycols are often used as fire resistant hydraulic oils with the added advantage of low viscosity and low pour points, e.g., -40°C.

As a lubricant, however, polyglycol solutions offer only mediocre performance. The pressure-viscosity coefficient of a polyglycol solution is only 0.45×10^{-8} (Pa^{-1}) compared to 2.04×10^{-8} (Pa^{-1}) for a mineral oil.

Even small quantities of water can significantly reduce the pressure-viscosity coefficient. Thus the primary applications of these fluids are as fire resistant lubricants because even if all the water were evaporated from the lubricant, the polyglycol would burn only with difficulty.

Polyelectrolytes are polymers containing groups that can be positively or negatively ionized by dissociation in polar solvents such as water. Polyelectrolyte-based aqueous solutions are the basis of lubrication systems found in nature.

In these solutions naturally occurring polyelectrolytes perform a function similar to that of boundary additives in oils, i.e., charged polyelectrolyte molecules can adsorb on surfaces or interfaces and modify friction.

Examples of biological systems where the polyelectrolyte lubricants operate are eyes or synovial joints. In the low-loaded eye interfaces it is thought that friction is mediated by the adsorbed brushlike polyelectrolyte layers.

The lubrication mechanism is more complicated in synovial joints where self-assembled mixtures of polyelectrolytes and proteins seem to provide effective aqueous lubrication over a wide range of load and speed conditions.

In recent years, the concept of making synthetic polyelectrolyte lubricants has been explored. Of special interest are polyelectrolyte-surfactant systems that self assemble to form semi-solid, brush-like layers on the contacting surfaces that reduce friction.

Very low coefficient of friction, $\mu < 0.001$, at low sliding velocities was measured in the presence of polyelectrolyte brushes grafted onto the surfaces in aqueous media.

Pin-on-disk experiments were conducted on polyelectrolyte lubricants composed of a copolymer of poly(L-lysine) grafted to poly(ethylene glycol), PLL-g-PEG.

Poly(L-lysine) is a natural polyelectrolyte produced by bacterial fermentation and is noted for its adhesion to both cell membranes and glass surfaces. It was found that in water PLL-g-PEG adsorbed on the silicon oxide surfaces reducing friction coefficients of steel sliding against glass to values as low as 0.1.

When excess PLL-g-PEG was dissolved in the solution self-healing properties of the lubricant were observed with a continuous exchange between the surface film and the dissolved PLL-g-PEG molecules repairing the film damage caused by wear.

Short lifetime of polyelectrolyte brushes at high loads and large distances are the main disadvantages that must be overcome before wider applications can be considered.