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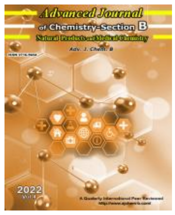

Original Research Article

A brief overview of the preparation and application of additives in lubricating oils in industry

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ABSTRACT

Mineral lubricants which are derived from crude oil are relatively inexpensive products used in very expensive engines and industrial machinery. Likewise, they have a direct impact on the efficiency and life of these devices, so the correct operation of machinery should be ensured. The quality of the utilized oils is quite good, however it has been seen unfortunately that this important issue is not paid enough attention even by technical experts, and in our country, the oil quality as well as the way of its control is underestimated. Petroleum products are the most complex in terms of the relationship between physical and chemical properties and practical efficiency. We know that the type and ratio of different existed compounds in crude oil in different parts of the world, a country or a region, is significantly variable. Even in an oil well, especially at different depths, there are different types and percentages of chemicals in crude oil. Therefore, petroleum lubricating oils contain a wide variety of hydrocarbons and their derivatives, especially as the components of lubricating oils are generally composed of very large molecules (C_{15} to C_{30}).

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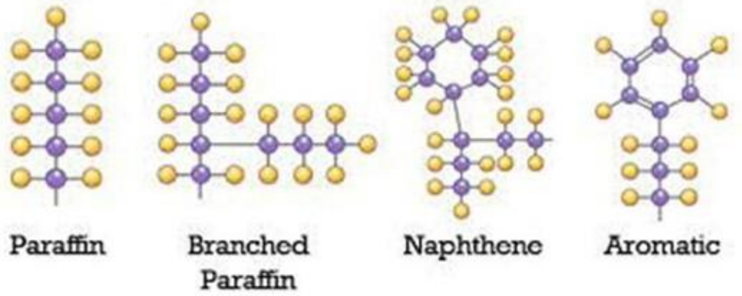
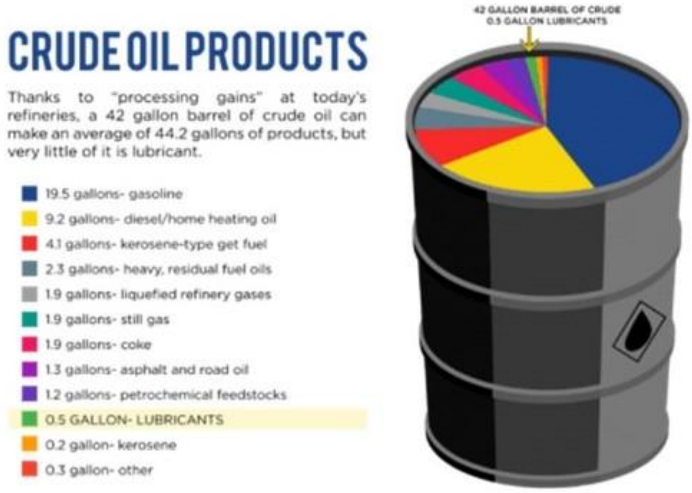
GRAPHICAL ABSTRACT





INTRODUCTION

The human endeavor to obtain effective lubricants has a long history. A lot of materials have been tested for this purpose over the time, and then they were discarded and replaced by better materials, but some lubricants used to date are surprisingly old-fashioned. In 1400 BC, the Egyptians boiled a mixture of animal fat and calcareous soap and used it as grease on chariot wheels, but the recent lubricants used in industrial world can be classified into four types of lubricants as gaseous liquids, liquid lubricants, semi-solid lubricants and finally, solid lubricants [1].

A) Gas lubricants, especially air, are used for lubrication in applications where the desired high-speed, low load, and radial stability of the rotational axis, or create the unusual temperature conditions or the presence of nuclear radiation.

B) Liquid lubricants include a wide range of fluids from pressurized liquefied gases to a variety of synthetic oils. Liquid lubricants are used in hydrodynamic lubrication with a thick or thin layer of lubricant and for this occasion, the most common type of lubricant is used. The most important and widely used liquid lubricant is mineral oil obtained from crude oil refining. Liquid lubricants also include natural, animal, and vegetable oils which have their own special lubricating uses (Figure 1) [2].

C) Semi-solid lubricants, including greases, solids, and waxes in cases in which it is difficult to seal the lubrication area for the use of liquid ones, the light and discontinuous working conditions or the lack of a single lubricant for the life of the mechanism that is is used in ball and roller bearings where lubrication of electrohydrodynamic type is predominant. Grease, the most widely used semi-solid lubricant, consists of oil or synthetic oil, and a filler or hardener.

D) Solid lubricants are used for lubrication in special working conditions such as complete vacuum or high load and heat, and in cases where lubrication is limited. Solid lubricants include graphite, mica, talc, molybdenum sulfide, lead oxide, sulfur mud, and plastics [3].

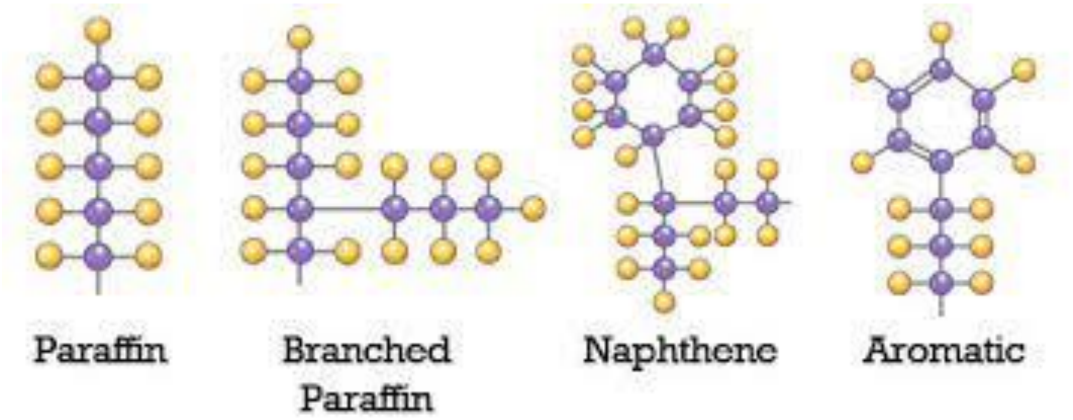


Figure 1. Fundamentals of Mineral Base Oil Refining

It has been previously mentioned that the quality of each commodity means that it is suitable for consumption in a certain application, so the first step to enter the quality field of these oils is their usage consideration. Mineral lubricating oils have many applications. Consumption may be more than the types of engines and industrial machinery used, but it is only mentioned here that oils are classified in one sense as engine oils, industrial machinery, and aircraft. The separation of specific aircraft oils in a particular class may be due to different ground, the air operating conditions, and drastic changes in these conditions [4].

Functions of lubricating oils

The difference between the mechanism of engine and industrial machinery from tribology viewpoint requires the performance of multiple and complex tasks of oils, besides fortunately with all the complexities of this mechanism, there are many commonalities between them and therefore, based on the functions of oil can be reminded a few sentences (Figure 2) [5].

A) Lubrication (formation of an oil layer among the moving parts and reducng their friction and wear).

B) Heat transfer and cooling of moving parts.

C) Prevent the effects of the parts on each other.

D) Sealing the intervals of the parts and in some cases, the force transmission in hydraulic oils.

E) Acting as a carrier of chemicals called additives by which machine parts as well as the oil itself are protected against oxidation, abrasion, rust, corrosion, dirt, etc.

F) Keep parts clean by transporting particles due to wear of parts and materials resulting from the decomposition of oil and fuel outside the parts area as well as prevent the accumulation of contaminants and the above-mentioned materials on car parts (especially in engines). With the exception of Tier 6, which deals mainly with motor oils and some special industrial oils, almost all other oils are responsible. Of course, not all of these tasks are performed with the same intensity in all cases, and depending on each specific usage, one or more of them may be considered as the main functions of the oil and the rest of its ancillary tasks. The important point is that in order for oils to be able to perform their functions properly, they should have certain conditions and characteristics, and in fact, these are the properties which distinguish different oils and their quality from each other [6-8].

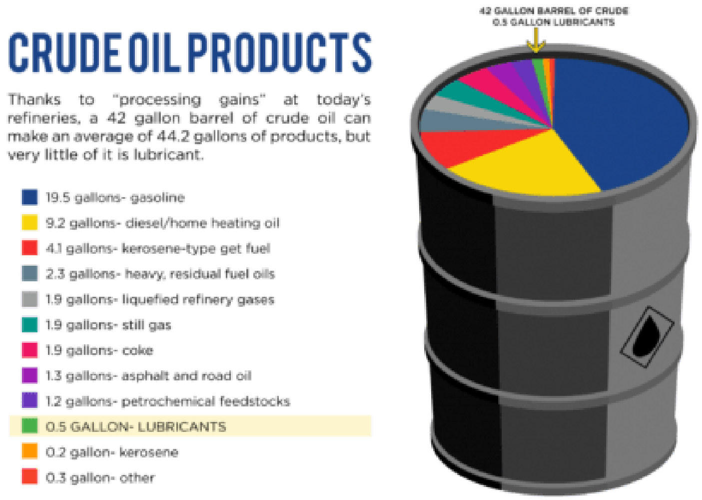


Figure 2. molecules sink to the bottom. After the hydrocarbons with 26-40 carbon atoms are separated, they are sent to a refining process specific to lubricants

Essential properties of lubricating oils

Lubricating oils should:

A) Have a good viscosity, perform the formation of oil layer and reduce friction and abrasion as well as heat transfer, shock, seal, and transfer of force.

B) Maintain their viscosity within the working temperature range sufficiently so as not to impair the performance of their duties. The term is said to have a sufficiently high viscosity index (VI).

C) Be sufficiently resistant to heat and air oxygen (thermal decomposition and oxidation).

D) Avoid rusting, corrosion by acidic materials and excessive abrasion of parts (in cases where the base oil is not able to form a thick layer and prevent abrasion).

E) Contain cleaning and suspending materials and prevent the deposition of sediments in the labia of the parts.

F) Hold in the cold enough to be easy to start and continue moving parts.

G) If they are in contact with non-metallic parts, they will not have an adverse effect on them.

H) In general, they do not have adverse effects on the parts with which they are in contact, as well as on their internal components, and there is compatibility between their components.

I) From the viewpoint of factors such as escape, fire and the like are in good condition.

J) Do not work while functioning.

K) Be able to neutralize the adverse effects of the device as much as possible.

L) Foreign contaminants such as dust, dirt, water and so forth should not be with oil.

Most of the above properties are essential for almost all oils together. Of course, in each particular case, certain items may have priority. In addition to these properties, each oil may have a specific property necessary for it [9-11]. For example, cleaning power is important for gasoline, diesel engines and the like, or soluble turning oils should be able to form a stable emulsion with water. Heating turbine oils should be separated from water vapor which has been converted into water and mixed with them within a short period of time. For this, turbine oils should not be mixed with contaminants such as cleaners from engine oils, which cause emulsions and water and oil separation. Transformer oils and the like should have a high degree of electrical insulation and hydraulic oils must perform the transmission power efficiently [12-15].

Mineral lubricating oil compounds

The above properties should be somehow created in the oil. The important fact is that lubricating oils are made up of two main components:

A) Base oil, as a substance obtained from crude oil after a series of refining operations. Base oils make up an average of 90% of the volume of oils.

B) Chemicals called additives which make up about 10% of the average volume of oils.

There are only a limited number of essential properties of oils in base oils, and additives are added to lubricating oils to have all the necessary properties and to be able to perform their functions perfectly [16]. The important point is that the readers should note that today's lubricating oils are very complex sets of base oils and additives without which the design and use of modern and sophisticated machines is not possible. Creating a balance between the base oil and the oil additives and maintaining the conditions to avoid the possible adverse effects of these components on each other as well as obtaining the best combination is a complex and delicate technique of human knowledge, however unfortunately it is very simple to look at oils. For instance, automatic gear oils or shock absorber oils are products that sometimes have to have up to 15 different additives, while in Iran, due to lack of awareness and attention of consumers, many people use base oil (without any additives) with diesel and paint [17]. They mix and sell this at an exorbitant price, called automatic transmission oil, or pour it into the springs, unaware of how much damage the same diesel does to the springs or how quickly the base oil in the automatic gear wears them out.

Lubricating oil tests

Various types of tests are used to control the quality of oils.

A) Tests called Banch Tests: In this type of test, lubricating oils are exposed to the conditions similar to the actual working conditions of the resulting oil with greater intensity and generally only in one dimension of those conditions, the oil changes, and its effects on the standard parts are examined. Tests such as thermal stability, oxidation stability, corrosion, rust prevention, etc. which are usually performed in laboratory glassware and with special simple devices, are of this type. The so-called Bench test is among physical and chemical tests and motor and instrumental tests, and in fact, one difference with motor tests is that they are performed on the laboratory table, while this similarity they have engine tests and a device that, like them, checks the condition of the oil in practice [18].

B) Engine & Rig tests: To evaluate oils under practical and actual operating conditions, such as those in engines, gearboxes, etc. certain mechanical tests are performed to evaluate the effects of various oil properties. Certain standardized motors and devices are usually installed or located in large laboratories on the ground and in which several tests are performed under well-defined and controlled conditions. At the end of the tests, changes in the oil properties and its effects on the engine or device parts are evaluated. Such tests are designed in such a way that the results generally determine and predict the situation in the real service, but for those products marketed for the first time, usually after the above-mentioned mechanical tests, a series of tests on devices is carried out as the field tests [19].

Classifications and standards of oil

As mentioned in the previous sections, scientific and governmental organizations and institutes, as well as manufacturers of automobiles and industrial machinery, and manufacturers of additives and oils, have come together to create a very effective and efficient system for controlling the quality of lubricating oils. One of the foundations of this system is the classification of oils as well as the development and dissemination of relevant standards, which play a vital role in establishing the right relationship between producers, testers and consumers of oils.

In general, engine oils and industrial machinery are classified in two ways.

A) Viscosity classification: Viscosity classification helps consumers to choose the right oil only in terms of suitable viscosity. Viscosity classification tables generally classify oils according to viscosity in relation to temperature. Of course, manufacturers recommend factors such as load, pressure, speed, friction, etc. when recommending their proper viscosity or their own machine, in addition to temperature, but they generally recommend only the same viscosity alone or in relation to the temperature.

B) Classification in terms of performance (Efficiency): Classification of oils in terms of efficiency, in fact, provides the main criterion for the correct choice of oil. In this type of classification, oils according to the specific use case, the intensity of work in that case, the type of metallurgy and mechanical design in which oil is used, the type of fuel consumed by these devices, and other ancillary points, type of work or equipment, working environment, the desired repair life, and so on are classified. It is quite clear that such a subtle classification requires really complex experience and tests. It should be noted that the manufacturers of automobiles and industrial machinery, which are the most reputable sources for the recommendation of used oils, list their required oils in the catalogs of machinery both in terms of viscosity and performance, but in the past it has been seen that due to the unfamiliarity of oil gas consumers, only the viscosity of oils has been considered and their type and quality level, which is specified in the performance classification, has not been considered, and therefore the oil has been used inappropriately. Briefly, the choice of oil is made using two types of classifications:

A) In terms of viscosity: That is not the reason for the oil advantages and disadvantages and only helps to choose the right viscosity.

B) In terms of efficiency: which is actually the classification of the oil actual quality.

Additives to lubricating oils

With the increasing necessity of oil for lubricating and also for power transmission, numerous researches are conducted to expand and improve the performance of oils. Not only petroleum-based oils, but also synthetic oils such as organic esters, silicone liquids, and polyphenyl ethers need additives to improve their lubrication performance. Including oxidation inhibitors, which are mainly composed of organic compounds as sulfur, nitrogen, phosphorus and some phenyls. In practice, these compounds react with the primary hydroperoxides formed by the oxidation of the oil, which leads to a chain reaction and the formation of organic acid in the engine. In this way, corrosion of babbitts and accessories made of zinc and copper bearings can be reduced to a minimum. Combinations of zinc, barium, and calcium thiophosphate can be used for difficult working conditions of internal combustion engines. Anti-abrasion agents minimize friction and abrasion by lubrication by forming a surface film by physical and chemical adsorption mechanism. A variety of anti-abrasive agents contain compounds of oxygen, sulfur, chlorinated wax, phosphorus, and organic compounds of lead. TCP tricycle phosphate and ZDDP zinc diecyl dithiophosphate are widely used to minimize abrasion in hydraulic pumps, gears, and transmitters. In cases in which the pressure is high and where the metal is in contact with the metal, chlorine, and lead activated sulfur compounds should be used. These compounds react chemically to form a relatively stable surface film such as lead sulfide, iron chloride, or iron sulfide. Oil cleaners prevent fouling of combustion engine components and turn them into oil-suspended sludges in the form of varnishes, carbon, and lead deposits. Barium, calcium sulfonates, and fanatics are used as cleaning agents in diesel and gasoline engine oils. Many ash-free cleaners are based on methacrylate alkyls, which often contain polar nitrogen groups in their side chains or polyamino derivatives of succinic acid. In addition to their cleaning properties, this type of compound also prevents rust and improves the oil viscosity index and its pour point. Common types of viscosity index enhancers include polymethacrylates, polyisobutylene, and polyalkyl citrons. These compounds primarily increase the viscosity of light oils. These materials are used in the preparation of multigrade engine oils. Much research has been done to improve the mechanical fracture toughness of these materials so that the oil remains viscous for a long time. The properties of petroleum oils depend on the type of crude oil and the refining operation. After distillation, solvent purification and waxing, the base oil is still a mixture of millions of chemical compounds with different characteristics, which in general do not have suitable properties for use in most industrial and engine applications. Intensified refining to separate the most suitable compounds for lubrication in the base oil indicates that only a paraffin compound with 20 carbon can have about 20 million isomers, economically due to the low amount of product and practically the reason for the lack of technology is not possible and therefore, in general, petroleum oils are not pure compounds and their characteristics are average of the components' characteristics of the base oil, which include good, medium, and bad compounds for lubrication. Synthetic or synthetic oils, although often petroleum-based, are synthesized by synthesizing one or more low-molecular-weight organic compounds, and the final product contains one or a limited number of chemical compounds with physical and chemical properties as well as definite, suitable, and desirable properties for lubrication. Therefore, synthetic oils are used for lubrication in harsh and unconventional conditions in which petroleum oils are not able to function properly. The effect of low temperature on oil lubrication, miscibility with water, high thermal stability, non-flammability, and no gum formation due to the oxidation are some of the properties of synthetic oils which widen their range of application compared to petroleum oils. While the use of synthetic oils in the aerospace industry and some industrial applications has a long history. In recent years, due to the use of these oils in gasoline engines, this industry has changed. While the use of synthetic oils in the aerospace industry and in industrial applications has been limited, the growth rate of synthetic oils consumption in relation to the lubrication of gasoline engines in some countries has been reported to be more than 15% per year [19].

Sources of alkalinity and its effects in oils

The resulting alkalinity of the components in the cleaning agents in the engine oils directly affects its cleanliness and durability. Increasing the alkalinity of the cleaners causes scale and abrasion throughout the life of the engine and controls oil consumption. Careful selection of the cleaner is essential to control the bearings cleanliness in diesel engines. To understand the source of alkalinity in diesel engine oil, all materials in the oil must be considered.

A) Suspended ash-free builders: Two types of ash-free suspending materials, namely succinimides and Monich type, can be involved in the alkalinity of engine oils. Polyisobutylene reacts with maleic anhydride to form the succinic anhydride polyisobutylene PIBSA, which then combines with a polyallylamine to form the suspended succinimide. The ratio of the amount of nitrogen to the amount of acidity derived from PIBSA can determine the presence or absence of succinimide alkalinity. In alkyl phenol, formaldehyde and an amine, which are mostly alkaline, react. Succinimide suspending agents include nitrogenous substances that can exist in two different forms, one is the imide structure and the other is the amino structure, which is the type of amino structure that contains the alkalinity in the oil.

$$(CH_3)_3N: + H_2SO_4 \longrightarrow (CH_3)_3N - H_2SO_4$$

Polyether and polyurethane additives, which have good antioxidant properties and anti-corrosion effect, can also be used as a suspending agent.

Properties and formulas of various additives used in engine oils

A) Viscosity index enhancers VI-MPROVERS: These materials are mainly oil-soluble polymers with a molecular weight between 10,000 and 1,000,000. By these materials, the base oil with a lower viscosity can be utilized to make a certain degree of SAE. The soluble polymer molecule is swollen by oil. The volume of this swollen material determines the increase rate in viscosity. The higher the temperature, the more volume and concentration increases, and the oil lose its tendency to decrease at high temperatures. The quality of polymers depends on their degree of resistance to mechanical breakage. As the molecular weight increases, this stability decreases. As a result, the viscosity of the oil also decreases. On the other hand, the increasing concentrating power of the viscosity index increases [20]. The figure below displays that the viscosity dependence on temperature is significantly lower for multigrade oils than for mono-grid oils. The viscosity of lubricating oils increases with increasing temperature, decreasing or decreasing temperature, but the rate of change in viscosity is not the same for different oils. Oils whose molecules are mainly paraffinic type show slight changes in viscosity in the face of temperature changes and, on the contrary, the aromatic compounds are very weak in terms of increasing and decreasing viscosity due to temperature change. Makes a significant difference. Naphthenic oils (containing saturated cyclic molecules) are intermediate in this respect. The rate of change in viscosity due to temperature change is denoted by an experimental number called the viscosity index, or VI for short. The higher the VI of the oil, the less changes in its viscosity due to changes in temperature. For the first time in the United States, oils from crude oils from two different points, one predominantly naphthenic (VI=o) and the other predominantly paraffinic (VI=100), were conventionally assigned VI zeros and one hundred, and VI other oils relative to this Two types were measured and determined. This method, which is still common today, uses the following formula:

$$VI = \frac{L-U}{L-H} \times 100$$

- U shows the viscosity of the oil tested in100 degrees Fahrenheit.
- L indicates the viscosity at 100 degrees Fahrenheit.
- H demonstrates the viscosity at 100 degrees Fahrenheit.

Of course, oils with a VI above 100 are now being made. To calculate VI for this type of oil, the above formula changes slightly. Of course, the calculation of the new formula for VI is based on oil viscosities at 40 °C and 100 °C. VI Oil is important in two general ways. First, base oil is an indication of the amount and depth of refining of that base oil. From a specific lobe cut, different base oils with different VIs can be obtained. Among these base oils, the one with higher VI is more refined and its viscosity resistance due to temperature change as well as its thermal stability and oxidation is higher and therefore it is better. Of course, it should be noted that the base oil VI alone cannot indicate the advantages and the disadvantages of the base oil, and it is not correct to compare the VIs of the base oil obtained from various lobes and crude oil. Because what matters is the amount by which the base oil VI is elevated relative to its corresponding lobe cut VI, not the VI number itself. VI can be used to compare base oils from a type of crude oil and of lob cut. It should be noted that VI base oils are mostly used to control oil production in the refinery and engine oils, etc. due to additives may have VI different from VI base oils and therefore should be judged with caution. For instance, with a base oil of Medium VI and the use of additive VI Improver, it is possible to create more than 110 for oil VI, malt oils or a few degrees with base oil (90-100 VI) to 180. Base oils are not usually made with a VI above 105. It has been mentioned for reasons that VI is generally not included as a mandatory feature of official oils standards. The second importance of VI is that the oil may need to work well over a wide range of temperatures. Of course, it should not be too flowing in the heat and uneven in the cold weather. Therefore, in these cases, if VI is higher, it is better [21].

B) Dispersants: During the combustion process, large amounts of soot particles, SOOT and materials from incomplete combustion are generated. These oil-insoluble contaminants lead to the formation of piston deposits or can even cause the rim and piston to stick. In the form of sludge, they can also block the filters and prevent the oil from flowing through narrow passages, and finally cause ENGINE SEIZURE. The type of these additives is effective on the SEQUENCE V-D engine test. For example, these materials have a polar end that is rapidly absorbed by contaminated particles, and the other end is a hydrocarbon chain that is soluble in oil. Thus, during the formation of sludge and velocity in the engine, the potential for impurities is taken. High quality engine oils contain about 4-8% of these ash-free additives [22-24].

Ash-free suspending agents are classified into two general types:

- High molecular weight polymer suspenders.
- Suspenders with lower molecular weight.

Practically ash-free suspenders are more effective than metal cleaners in controlling sludge deposits in low-temperature gasoline engines. In order to achieve these goals, beneficial compounds are obtained by a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group contains one or more elements such as nitrogen, oxygen, and phosphorus. Soluble chains have a higher molecular weight than their metal counterparts. Polyhydric alcohols such as glycerol, pentaerythritol, and sorbitol are used in this type of substance [25].

Detergents

Alkyl salicylates, fanatics, and sulfonates are used in engine oil formulations to prevent the formation of deposits at high temperatures, corrosion, abrasion, and rust of engines. They are usually composed of organometallic compounds that use elements such as calcium and magnesium in their construction. Determination of chemical elements is generally done to control the number of additives in the oil [26-28]. Of course, the application of the results of these tests for the above purpose is possible provided that the oil additives and their chemical analysis have already been clarified. Some of these elements are also important from other points of view. For example, chlorine is important in additives related to gear oils, lathes, etc. that work under high load and pressure [29-31]. If it is too small, the additive may not be able to conduct its function and if it is too much, it will cause corrosion. Phosphorus is also present in many additives. Its amount is important in that it may be the catalyst of exhaust gas converters to non-polluting compounds. Some metals, such as Zn, Ca, Mg, etc., are indications of the type and amount of anti-corrosion and detergent additives and are widely used to control these substances, provided they are already known [32-34].

Types of cleaners

A) Sulfonates:

$$MOH \longrightarrow R-SO_3M + H_2O \; R-SO_3H + MO$$

Commercial sulfonates are of two types:

A) Petroleum sulfonates: By using by-products of sulfuric acid treatment, oil extraction is obtained in the manufacture of white oils. With high demand for cleaning oils, sulfonate production is considered as a basic product. The structure of petroleum sulfonates is not fully understood and depends on the crude oil used in its preparation. Because the ratio of naphthenic and aromatic aliphatic hydrocarbons is different [35].

B) Synthetic sulfonates: The most popular sulfonate cleaners are in the form of barium, magnesium and calcium. Alkaline background of sulfonates can provide the conditions for the direct reaction of sulfonic acid with metal oxide or metal hydroxide [36].

B1) Thiophosphates: A commercial product derived from this type of acidic substance is derived from the reaction between polybutene and phosphorus pentasulfide. The reaction between polybutene with a molecular weight between 1000-500 and phosphorus pentasulfide is catalyzed by sulfur or phosphates. The reaction products are neutralized with metal hydroxide or metal oxide in a dry environment or in the presence of water or alcohol. Free salts can be obtained from mineral phosphorus compounds by hydrolysis of polybutene phosphopentasulfide.

B2) Phenol salts and phenol sulfide: Prominent class in metal mortates include salts of phenyl alkyl, alkyl phenol sulfide, and alkyl phenol aldehydes. To dissolve them in phenol base oil, they are alkylated with olefins which have eight or more carbon atoms. Sulfur replacement in the construction of fans is done by the reaction of phenyl alkyl with chlorine sulfide or sulfur of another element. The formation of sulfide bridges or methyl reduces the corrosion of the product and increases its antioxidant properties. Calcium and barium mortars are the most widely used types. They are made by the substitution reaction of phenols or metal oxides and hydroxides. If the metal base is used too much, its acid neutralizing property will increase. Such products contain two to three times more metal than conventional mortars. All of the above types of cleaners form stable micelles by incorporating the large amounts of metal carbonate by creating strong bases. The cleaning concentration in the oil formulation varies from about one percent in gasoline engines to 10 percent in heavy diesel engines. Compounds with their alkalinity source can neutralize the acids contamination resulting from the combustion of high-sulfur fuels [37].

C) Petroleum sulfonates:

The main action of these inhibitors is to eliminate free radicals or to react with peroxides formed in the oil. It is certain that the oil heats up in the engine and oxidizes in contact with the atmosphere. Oxidized oils come into contact with metal catalysts such as iron and copper, which are part of the engine, and become contaminated with active combustion products, becoming dusty and thin film in the crankcase. The extent of oxidation changes in the base oil and additives depends on the intensity of the engine operation. The oil rings on the surface of the belt due to contamination and oxidation of carbon deposits, and in places where there is high temperature and oxidation conditions are more difficult, deposits form on the tip of the piston. Improper cooling of the top of the piston initially results in the formation of resin deposits, but the resulting polymers quickly become coke-like materials which can accumulate due to the adhesion of the ring and the piston and overheating of the piston. Lubricating oils that are exposed to air and resulting in oxygen, and despite their low affinity for oxygen due to their high operating temperature and the presence of metals such as copper and iron as catalysts, the oxidation reaction of oils occurs. Falls and these substances are oxidized. The oil resistance to oxidation depends on the rate at which it is refined, so that the more refined the oil and the less resistant its aromatic materials, the aromatic hydrocarbons, are the later the oil will oxidize. However, well-refined oils are not able to withstand high temperatures for a long time and are oxidized [38]. Therefore, oxidation inhibitors were added to the oils, which are very effective in prolonging the life of the oils.

Oxidation of oils leads to two types of unwanted substances:

- Oil-insoluble materials such as resins, glazes, or sludge.
- Oil-soluble substances, which are mainly organic acids and peroxides.

The important point is that these oxidation products themselves, especially peroxides, are catalysts for the oxidation reaction and greatly increase the rate of the oil oxidation. In fact, inhibitory additives prevent the formation of these substances or decompose them after formation. And prevent their chain growth. Paraffin-based oils are more resistant to oxidation, but instead precipitate harder to oxidize [39]. Oxidation of oils increases their viscosity. Oxidation deposits may cause the parts to stick together, wear out, and clog filter holes and narrow oil passageways. Oils that work in closed systems and generally for long periods of time should have the desired oxidation stability, especially if the oil temperature is high and the catalytic metals (i.e., copper and iron), water, and dust with oil [40]. This is especially true of steam turbine oils. Because the bearings are destroyed as a result of oxidative damage to the oil. Gear oils, transformers, hydraulics, heat transfer, and most engine oils also require high oxidation resistance, formation of sludge, acid, excessive foaming, and separation of oil from water that may be mixed with it. Corrosion and viscosity (lack of oil flow) are considered as oxidation damages of oil. The result of the oxidation process is the formation of acidic substances in the engine oil, which causes corrosion in the copper, lead, and cadmium in the engine bearings. Basically, suspended solids in oil play a major role in reducing corrosion by neutralizing corrosive acids. Amines and diphenols are oxidation inhibitors that are mostly used in the production of industrial oils. Among ZDDP oxidation inhibitors, it is widely used in engine oils [41].

Anti-corrosion additives

One of the significant uses of oil, especially in marine engines and locomotives, is their ability to prevent rusting of metal engine parts. Such rusting is often due to the presence of moisture in the atmosphere, which collects in the form of droplets inside the engine or in short travel services in winter, the engine is driven cold and water enters the engine oil. If the engine oils do not contain anti-corrosion additives, they will not be able to prevent rusting of metal surfaces inside the engine. To ensure the oil quality in this case should be able to pass the engine test well. To prevent rusting, the oil should be able to perform the following actions.

- Formation of a strong absorbent film on the metal surface.
- Neutralization of acidic substances in the oil.

Alkaline cleaning additives can provide sufficient protection against staining of metal surfaces by neutralizing the resulting acids, but to complete the process it is necessary to add additional components to the oil.

Anti-wear additives

Engines that operate in harsh conditions and that have lubrication with particular boundaries may occur on certain engine components such as valves, sprockets, tubes, valve and camshafts, abrasion, and scaffolding. Anti-abrasion additives prevent such wastes. In this way, if the oil film is broken, the temperature of the fracture zone increases and at that temperature, the additive reacts with the metal surface and creates a strong protective film. Zinc compounds of di-alkyl or di-aryl thiophosphates are used as anti-corrosion additives in motor oils and industrial oils. In the preparation of these compounds, the reaction between monobasic alcohol and pentasulfide phosphorus is used and the product of the action is increased with zinc oxide. Alkyls used are: propyl, butyl, hexyl, octyl, and mixtures thereof. The longer the alcohol chain, the greater the anti-abrasion stability. Branched chains reduce the stability of the compound. Abrasion is the reduction of metal between two moving surfaces, the factors which affect it, the contact between metals, the presence of certain abrasives, and the attack of corrosive acids. The reaction mechanism of anti-abrasion compounds is not fully understood, but it is suggested that the decomposed products, including sulfur and phosphorus, react chemically with metal surfaces to form a resistant protective film such as:

- It has load bearing properties.
- Disables metal oxidizing catalysts.
- Prevents bearing wear.

Friction improvers

In order to reduce friction in the moving parts of the engine and improve the fuel economy in the formulation of engine oils, various types of metal soaps, esters, and amides or their sets are used. These materials have a lot of tension compared to metal surfaces and by being placed on these surfaces, they create a friction reduction film. By consuming one percent of friction improvers, up to 4 percent of fuel consumption is saved.

Falling point reducers

Many oils need to be able to perform their functions in cold and low temperatures. In this regard, in addition to check the viscosity at low temperatures, three other tests are used:

A) Spill point: Used exclusively for oils used in refrigerators. The pour point is the lowest temperature at which oil can flow. The oil spill is due to the formation of large wax crystals in the oils.

B) Cloudy point: The point of formation of a cloud mass.

The point of cloudiness, which is related to the formation of the first wax crystals (usually microcrystals) in the oil, is the temperature at which the oil darkens. This test can only be done carefully for clear oils. Also, the point of cloudiness should not be confused with the cloudiness of oil due to the possible presence of water in it. In other words, the presence of small amounts of water increases the cloud point and therefore, may be used to detect the presence of small amounts of water. The method of measuring Pour Pt and Cloud Pt is that the oil is gradually cooled under the standard conditions to determine the temperature at which the oil is no longer flowing or cloudy. The importance of these tests is that the ability of an oil to flow easily at low temperatures in many cases determines its effective use in the device. When another oil is not flowing, or its viscosity is inherently very high, or wax crystals have formed in it, such oil will not reach the engine parts or the device, because although the pump may break the wax crystals and pump the oil, in many places the oil should move due to gravity. The pour point of an oil, which is related to the presence of normal chain waxes with a larger molecular mass, depends greatly on the origin and type of crude oil from which the oil is made. Paraffin-based oils generally have a high Pour Pt, but can be pumped at the point of shedding by the pump, and secondly, solid waxes can be separated by further refining methods. The resulting oil spill can also be reduced with special additives, however naphthenic base oils flow abnormally in the cold, not due to the presence of wax, rather for high viscosity, and therefore cannot be pumped in this case. They move them and at the same time, the drop-lowering additive has no effect on them. However, naphthenic oils have a lower pour point than paraffin oils and are therefore, used as cooling compressor oils. For the first time in 1931, the initial drop-down additive was developed for commercial use. This additive is a combination of chlorine wax with naphthalene. The various compounds used on an industrial and commercial scale are mostly organic polymer compounds. However, some monomer compounds such as tetra silicate, etc. have also been effective in lowering the pour point. At present, all additives lowering the pour point of compounds are from one of the following families:

- Polymethacrylate, which is a polymer compound of methacrylate alcohol with different chain structure and molecular weight.
- Polyacrylamides.
- Materials obtained by mixing and distilling paraffin wax compounds with naphthalene, which are obtained by condensing a paraffin wax with naphthalene by Friedel Kraft.
- Materials obtained by combining and distilling paraffin wax with phenol, which are also obtained by adding an alkane to the phenol ring by the Friedel Kraft method.
- nitroparaffins phenol phenolate.
- Vinyl carboxylate.

Mechanism of action of additives lowering the drop point

The last and most precise mechanism proposed in this case is the result of a study by Lawrence et al. It grows in different directions and forms compact homogeneous wax crystals. Such crystals are usually not able to form interconnected networks of wax which cause oil to leak. Aliphatic polymers with the molecular structure of side chains such as compounds “a” and “b” change the formation of wax crystals in a similar way to the previous case, but their mechanism of action is based on the simultaneous crystallization of these compounds with wax and their adsorption.

Floor pregnancies

Depending on the mechanical working conditions of the parts with which the oil is in contact and the intensity of the rotation, the air may be mixed with the oil and foam may form. The presence of surfactants such as anti-corrosion additives, detergents and oxidation agents, dust, etc. especially in the presence of water, help to create the stable foam. Foaming of the oil causes non-lubrication (lack of oil film formation), oil leakage, lack of force transfer (in hydraulic oils), trapping air in the oil surface and helping to accelerate the oxidation of the oil, etc. Therefore, anti-foaming additives are added to the oil. The foam test in the factory reveals the presence or absence of anti-foam in the oil. It should also be noted that hydraulic oils have a special status in terms of foam properties. Because these oils, on the one hand, should have the property of releasing air so that they can transfer the force well, and on the other hand, they should not create foam, so a balance should be established between these two properties. The air entering the oil can form the stable foam in it. The presence of this foam affects the lubrication of various parts and its gradual reduction on the parts causes this which can cause irreparable damage to the engine or parts. Consumption of foam inhibitor additive, which is usually a silicone compound with different molecular weights, prevents foam formation in very small amounts. The mechanism of action of this material is not entirely clear, but it is stated that silicon adheres to air bubbles and increases its surface tension so that they burst quickly as soon as the bubble reaches the surface of the oil.

How to control oils while working

An oil begins to lose its properties from the moment it is served, because substances are firstly mixed and contaminate it, and its additives are secondly gradually consumed. Obviously, the better the oil quality, the longer it will work under the same conditions, however it should be noted that factors other than oil quality generally play a role in reducing it. Among these factors, the following can be mentioned:

- Improper storage of oil and contamination before consumption.
- Wrong choice of oil for the desired application and mixing of oils which are not compatible with each other.
- Improper lubrication (incomplete lubrication system, time and place, and the incorrect amount of oil).
- Improper operation of the device (such as not adjusting the engine, for example, moving too much in the cold and stopping quickly, which leads to mixing of gasoline and oil, or changing the gear awkwardly, etc.).
- Inadequate working environment of the device (being too hot or cold and not balancing the temperature, the presence of a lot of dust).
- Not paying attention to the equipment related to the device, such as not choosing the right air and oil filter and not changing them in time, etc.

Conclusion

However, the following points can be used to assess the condition of the oil during operation. It is worth to note that it is generally only possible to determine the useful life of oil by comparing the results of successive tests at regular intervals, unless the oil is so contaminated that it can be mentioned by testing once which can no longer be used. The oil oxidizes while working and the most important damage is usually due to this issue, because it produces oxidation of oil, sludge, glaze, etc. Oils which contain antioxidants oxidize very little below 60, but over the mentioned rate of oxidation almost double with every 10 degrees increase in temperature. The presence of water, iron and copper greatly increase the oxidation rate. In addition to its role in oil oxidation, heat also causes oil to crack and polymerize. Excessive oil damage can be detected with some simple inspections.

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