

# LUBRICANTS, COMPOSITION AND ADDITIVES

Lubrication is simply the use of a material to improve the smoothness of movement of one surface over another; the material which is used in this way is called a lubricant. Lubricants are usually liquids or semi-liquids, but may be solids or gases or any combination of solids, liquids, and gases.

The smoothness of movement is improved by reducing friction. This is not, however, always the case, and there may be situations in which it is more important to maintain steady friction than to obtain the lowest possible friction.

In addition to reducing or controlling friction, lubricants are usually expected to reduce wear and often to prevent overheating and corrosion.

## BASIC TYPES OF LUBRICANT

Lubricants are usually divided into four basic classes.

- (a) Oils: A general term used to cover all liquid lubricants, whether they are mineral oils, natural oils, synthetics, emulsions, or even process fluids.
- (b) Greases: Technically these are oils, which contain a thickening agent to make them semi-solid. It is convenient, however, to include the anti-seize pastes and the semi-fluid greases under the same heading.
- (c) Dry lubricants: These include any lubricants, which are used in solid form, and may be bulky solids, paint-like coatings, or loose powders.
- (d) Gases: The gas usually used in gas bearings is air, but any gas can be used which will not attack the bearings, or itself decompose.

The advantages and disadvantages of oils stem from their ability to flow easily. Thus, on the credit side, it is very easy to pour them from a container, to feed them into a bearing by dripping, splashing or pumping, and to drain them out of a machine when no longer fit for use. Other advantages are the cooling of a bearing by carrying away heat, and cleaning it by removing debris.

The behavior of greases is very similar to that of oils, but the former are used where the advantages of easy flow are outweighed by the disadvantages. Thus grease do not easily leak out of a machine, or container, do not migrate away, and will form an effective seal against contaminants.

The advantages and disadvantages of solid lubricants are rather like the extremes for greases, where the lubricant will not flow at all. Similarly, the advantages and disadvantages of gas lubricants are like the extremes of oils, where the flow properties are almost too good.

## (a)OILS

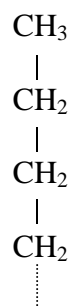
### MINERAL OIL

Mineral oils are easily the most widely used lubricating oils. Consequently, they are often the standard with which other oils are compared. It may be helpful to consider first what mineral oils are.

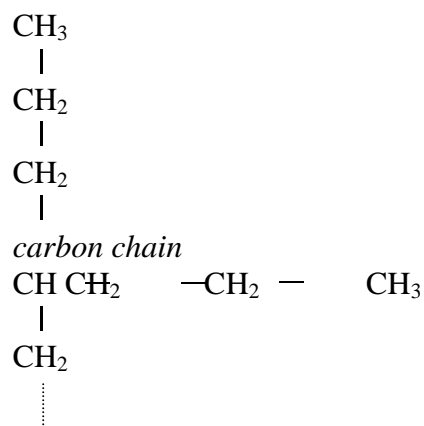
Mineral oils generally mean oils obtained from petroleum, although they can also be obtained from similar sources, such as oil shales and tar-stands. The mineral oils used for lubrication were originally just the fractions, obtained by distilling petroleum, which had a suitable viscosity for lubrication.

The chemical compounds, which comprise mineral oils, are mainly hydrocarbons, which contain only carbon and hydrogen. These are of three basic types. The majority in any lubricating oil is paraffin, in which the carbon atoms are in straight or

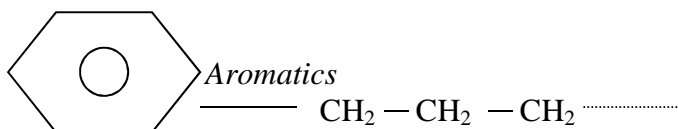
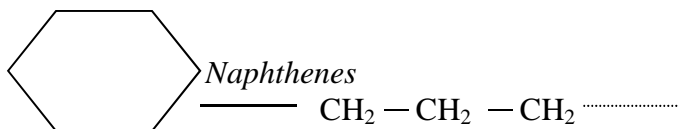
branched chains-but not rings. The second most common types are naphthenes, in which some of the carbon atoms form rings. Finally, there is usually a small proportion, perhaps two percent, of aromatics, in which carbon rings present, but the proportion of hydrogen is reduced.



*Paraffin with straight carbon chain*



*Paraffin with branched*



Apart from these four types of hydrocarbon, there may be small quantities of compounds present which also contain other elements, such as oxygen, sulphur, phosphorus and nitrogen. These compounds are sometimes referred to as asphaltenes.

Depending on the source of the crude oil and on the severity of the refining processes, mineral base oils are now available which range in character from the traditional paraffinic or naphthenic oils to the most severely refined types

## SYNTHETIC AND NATURAL OILS AND EMULSIONS

Many of the alternative types of oil are synthetic. They are manufactured from various feedstocks by chemical processes. There are different types of synthetic oil and are very different from each other in their performance and properties.

The widely-used synthetic oils include hydrocarbons, di-esters, polyol esters, phosphate ester, silicones, polyglycols, and- to a much smaller extent- polyphenyl ethers and perfluoroalkyl polyethers.

### ➤ Synthetic Hydrocarbons

There are several classes of synthetic hydrocarbon. The most important are branched-chain paraffins, which are known as polyalphaolefins (PAO). Their properties and performance are very similar to some of the most highly refined mineral oils. Polyalphaolefins are one of the most important classes of synthetic oil, yet they resemble mineral oils. Their inherent oxidation resistance is quite good and their boundary lubrication not very good, like those of the highly refined mineral oils.

### ➤ Di-esters and polyol esters

In terms of the total volume used, di-esters and polyol esters comprise the most important class of synthetic oils, as they are almost universally used for aircraft gas turbine engine lubrication.

Di-esters are a class of 'carboxylic esters', containing the carboxylic group  $-O-C=O$ . Poly esters are carboxylic esters with better thermal stability. Di-esters are used as base oils for high-temperature applications in industry, such as hot-rolling oils in steel rolling. They can be used at higher temperatures than mineral oils, have very good lubricating characteristics, and are readily available in a variety of viscosities.

Polyol esters are now extensively used in aircraft jet engines and are readily available in a few different viscosity grades. Apart from their good high-temperature properties, they also have very good lubricating characteristics.

### ➤ Phosphate esters

These oils are the esters, which are produced by reaction between alcohols and phosphoric acid. They are quite widely used for their outstanding fire resistance, especially in high fire-risk situations such as aircraft hydraulic systems, coal mines, and hot metal-processing. They are chemically similar to some of the best anti-wear additives, and consequently have excellent boundary lubricating behaviour. Their main disadvantages are poor thermal stability and their powerful solvent action on many paints, plastics, and rubbers.

### ➤ Silicones

Silicones are polymeric substances based on a chain skeleton containing alternate silicon and oxygen atoms. They are available in a very wide range of viscosity grades. They are generally used for their good high-temperature stability, which enables them to be used over 200°C. They are widely used as base oils for high-temperature greases. Their main disadvantage is that they are poor boundary lubricants, especially for steel against steel.

➤ Chlorinated biphenyls

The chlorinated biphenyls have very good fire resistance and chemical inertness, but are mediocre boundary lubricants.

➤ Polyglycols

Polyglycols are long-chain polymeric liquids. They are stable to about 200°C. When heated above this temperature, they decompose cleanly without producing any undesirable decomposition products.

➤ Fluorinated ethers and fluorocarbons

These oils have the highest thermal stability and chemical inertness of any oils, and can be used continuously at temperatures over 300°C. Like the silicones, however, they are poor boundary lubricants.

➤ Natural Oils

These include vegetable oils and animal fats. They are usually excellent boundary lubricants, but they are much less stable than mineral oils, and tend to break down to give sticky deposits. Rapeseed oil is still used by itself or as an additive to mineral oils to give improved boundary lubrication.

A recent development is an increase in use of castor oil and palm oil in manufacture of bio-degradable and food industry grade lubricants.

## (b) GREASES

Greases are not simply very viscous lubricating oils. They are in fact mixtures of lubricating oils and thickeners. The thickeners are dispersed in lubricating oils in order to produce a stable and colloidal structure or gel. Thus, a grease consists of oil constrained by minute thickener fibres.

The most widespread application of greases is as low-maintenance, semi-permanent lubricants in rolling contact bearings and some gears. The grease may be packed into a bearing or gear set and left for a period of several months or longer before being replaced. Inaccessible wearing contacts, such as are found on caterpillar track assemblies or in agricultural machinery, are conveniently lubricated by this means,

Grease is unable to remove heat by convection as oil does, so unlike oil, it is not effective as a cooling agent. It also cannot be used at speeds as high as oil because frictional drag would cause overheating. The lifetime of a grease in service is often determined by the eventual loss of the semi-solid consistency to become either a liquid or a hard deposit.

### • Composition

Greases always contain three basic active ingredients; a base mineral or synthetic oil, additives and thickener. For thickeners, metal soaps clays are used. In most cases the mineral oil plays the most important role in determining the grease performance, but in some instances the additives and the thickener can be critical. Very often additives, which are similar to those in lubricating oils, are used.

Mineral oils are most often used as the base stock in grease formulation. About 99% of greases are made with mineral oils. Naphthenic oils are the most popular despite their low viscosity index.

Synthetic oils are used for greases, which are expected to operate in extreme conditions. The most commonly used are synthetic esters, phosphate esters, silicones and

fluorocarbons. Their most common applications are in high performance aircraft, missiles and in space.

Vegetable oils are also used in making grease intended for the food and pharmaceutical industries, but even in this application their use is quite limited.

- **Thickener**

Soap type greases are the most commonly produced. According to the principles of chemistry, in order to obtain soap it is necessary to heat some fats or oils in the presence of an alkali, e.g. caustic soda (NaOH). Apart from sodium hydroxide (NaOH) other alkali can be used in the reaction, as for example, lithium, cadmium, aluminium, barium, etc. Fats and oils can be animal or vegetable, and are produced from cattle, fish, castor bean, coconut, cottonseed, etc. The reaction products are soap, glycerol and water. Soaps are very important in the production of greases. The most commonly used soap type greases are calcium, lithium, aluminium, and sodium.

In non-soap type greases inorganic, organic and synthetic materials are used as thickeners. Inorganic thickeners are in the form of very fine powders, which have enough porosity and surface area to absorb oil. The most commonly used are the silica and bentonite clays.

- **Additives**

The additives used in grease formulations are similar to those used in lubricating oils. Some of them modify the soap, others improve the oils characteristics. The most common additives include anti-oxidants, rust and corrosion inhibitors, tackiness, anti-wear and extreme pressure (EP) additives.

### (c) SOLID LUBRICANTS

Solid lubrication is simply the lubrication of two surfaces in moving contact by means of solid materials interposed between them.

Depending upon the nature of the two surfaces, a wide variety of solid materials can reduce the friction and prevent seizure. For example, dust, sand, or gravel on the surface of a road can cause vehicles to skid because they decrease friction between tyres and the road surface.

The vast majority of solid lubricant applications are met by only three materials: graphite, molybdenum disulphide, and PTFE (polytetrafluoroethylene).

- **Graphite**

Graphite was almost certainly the first solid lubricant to be used on a large scale. It is a grey-black crystalline form of carbon in which the carbon atoms are arranged hexagonally in regular layers.

In this hexagonal structure the bonds between the carbon atoms within a layer are strong chemical (covalent) bonds, so that the layers are strong and the crystals strongly resist bending or breaking of the layers. The bonds between the layers are weak (Vander Waals) forces, so that the crystals can be made to split easily between layers, and the layers will slide readily one over the other.

The layer-lattice structure of graphite would appear to give good natural low-friction properties. In fact, graphite only gives low friction when it is contaminated or 'intercalated' by water vapour or other condensable vapours.

High-quality graphite with water vapour present will give coefficients of friction varying from 0.05 at high contact pressures to 0.15 at low pressures; the friction is smooth and steady.

Graphite will adhere readily to surfaces either from a solid block or from dispersions in liquids. It can also be made to adhere more strongly by means of adhesive binders, usually epoxy, phenolic or alkyd, which may also be included in a dispersion.

#### ➤ Molybdenum disulphide

Molybdenum disulphide has been used for several centuries. It is found naturally as the ore molybdenite, the main source of molybdenum. This is a crude hexagonal molybdenum disulphide, and is found in large masses.

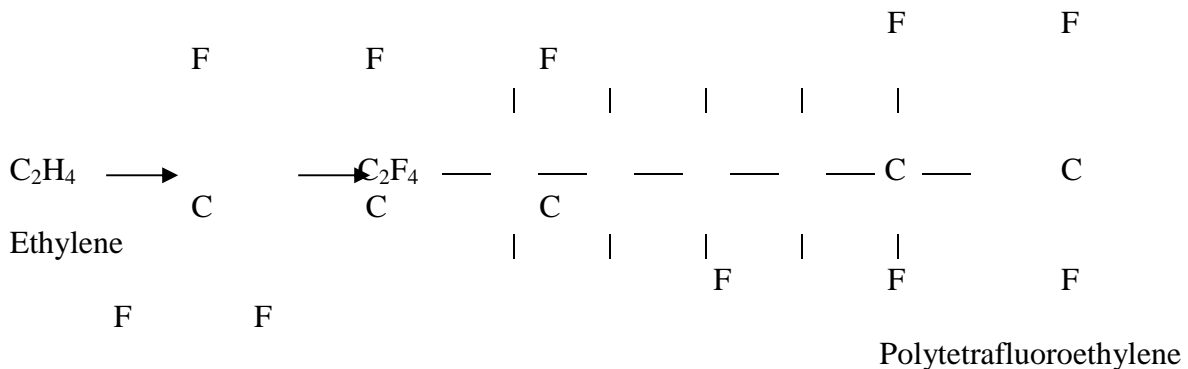
The chemical formula  $\text{MoS}_2$ , with one molybdenum atom joined to two sulphur atoms. Like graphite, it has a hexagonal layer-lattice structure, as well as other, non-lubricating, forms. The structure consists of alternate layers of molybdenum and sulphur atoms.

Molybdenum disulphide differs from graphite mainly in that its low friction is an inherent property and does not depend on the presence of absorbed vapours. Because of this, it can be used satisfactorily in high vacuum, and it has been used for many applications in spacecraft.

It adheres even more strongly than graphite to metal and other surfaces. A useful film can be obtained by simply rubbing or 'burnishing' molybdenum disulphide powder onto a metal surface with cotton wool or cloth.

#### ➤ PTFE and other similar polymers

PTFE (polytetrafluoroethylene) is a polymer of tetrafluoroethylene, which in turn is ethylene gas ( $\text{C}_2\text{H}_4$ ) in which all the hydrogen atoms have been replaced by fluorine.



It is often referred to as Teflon.

It is a white solid with a slightly waxy appearance, hard to the touch but easily cut and deformed. It is usually fabricated by sintering or hot compression moulding at above  $300^\circ\text{C}$ . It is difficult to form large components accurately, provided that the cutting speed and depth of cut are kept low to avoid thermal expansion. Bonding PTFE to metals has always been difficult, but it is said that treatment with hot alkali gives a surface, which can be bonded. Adhesives are commercially available which are claimed to be suitable. It should also be kept in mind that toxic and irritant vapours can be emitted from PTFE and other fluorinated polymers if the temperature rises during machining.

It is stable in use to almost  $300^\circ\text{C}$ , but it changes its state at  $325^\circ\text{C}$  and cannot be used above that temperature. It can also be very low temperatures, even down to  $-200^\circ\text{C}$  or lower

in liquefied gases. There is, however, some evidence that the wear rate increased at very low temperatures. It is also very resistant to oxidation, and can be used for lubrication or sealing in oxygen systems.

The attractive forces between the long straight-chain molecules are low, so that PTFE has fairly poor mechanical strength. For the same reason the long molecules slide easily over each other; it is with which gives it its low friction properties.

In view of this stability and low atomic forces, it is not clear why PTFE forms good, smooth, strongly adhering films to metal surfaces; but it does- probably more readily than graphite.

## LUBRICANT ADDITIVES

Lubricant additives are chemicals, nearly always-organic or organometallic, that are added to oils in quantities of a few weight percent to improve the lubricating capacity and durability of the oil. Specific purposes of lubricant additives are:

- improving the wear and friction characteristics by provision for adsorption and extreme pressure (E.P.) lubrication,
- improving the oxidation resistance,
- control of corrosion,
- control of contamination by reaction products, wear particles and other debris,
- reducing excessive decrease of lubricant viscosity at high temperatures,
- enhancing lubricant characteristics by reducing the pour point and inhibiting the generation of foam.

The most common package of additives used in oil formulations contains anti wear and extreme pressure lubrication additives, oxidation inhibitors, detergents, dispersants, viscosity improvers, pour point depressants and foam inhibitors.

## Wear and Friction Improvers

Additives, which improve wear and friction properties, are probably the most important of all the additives used in oil formulations. Strictly speaking these chemicals are adsorption and extreme pressure additives and they control the lubricating performance of the oil.

These additives can be divided into the following groups:

- adsorption or boundary additives,
- anti-wear additives,
- extreme pressure additives.

### • Adsorption or Boundary Additives:

The adsorption or boundary additives control the adsorption type lubrication, and are also known as 'Friction Modifiers' since they are often used to prevent the slips tick phenomena. The additives in current use are mostly the fatty acids and the esters and amines of the same fatty acids. They usually have the polar group (-OH) at one end of the molecule and react with the contacting surfaces through the mechanism of adsorption.

The surface film generated by this mechanism is effective only at relatively low temperatures and loads. The polar group to form a carpet of molecules, which reduces friction and wear, attaches the molecules to the surface.

- **Anti-Wear additives:**

In order to protect contacting surfaces at higher temperatures above the range of effectiveness of adsorption or boundary agents, anti-wear additives were designed and manufactured. There are several different types of anti-wear additives that are currently used in oil formulations. For example, in engine oils the most commonly used anti-wear additive is zinc dialkyldithiophosphate (ZnDDP), in gas turbine oils tricresylphosphate or other phosphate esters are used. Phosphorous additives are used where anti-wear protection at relatively low loads is required.

These additives react with the surfaces through the mechanism of chemisorption, and the protective surface layer produced is much more durable than that generated by adsorption or boundary agents.

Common examples of these additives are zinc dialkyldithiophosphate, tricresylphosphate, dilauryl phosphate, diethyl phosphate, dibutylphosphate, tributylphosphate and triparacresylphosphate. These additives are used in concentrations of 1% to 3% by weight.

Zinc Dialkyldithiophosphate:

It was originally developed as an anti oxidant and detergent, but it was found later that this compound also acted as an anti wear and mild extreme pressure additive. The term 'anti-wear' usually refers to wear reduction at moderate loads.

The surface protective films, which are formed as the result of action of ZnDDP, act as the lubricant, reducing wear and friction between two interacting surfaces. The lubricant mechanism of ZnDDP is quite complex as the additive has three interacting active elements, i.e. zinc, phosphorus and sulphur. All of these elements and compounds are involved in surface film formation, and our current understanding of the surface films produced is that they consist of a matrix of zinc polyphosphate with inclusions of iron oxide and iron sulphide. The problem of valve train wear and oil degradation in internal combustion engines was solved by applying ZnDDP.

Tricresylphosphate:

Like ZnDDP, it functions by chemisorption to the operating surfaces. It is very effective in reducing wear and friction at temperatures up to about 200c. Beyond this temperature there is sufficient energy input to the surface for the chemisorbed films to desorb and the compound will then form less effective, much weaker, thick phosphate films with limited load capacity.

Other anti-wear additives such as dilauryl phosphate, diethylphosphate, dibutylphosphate, tributylphosphate and triparacresylphosphate are also being used in lubricant formulation.

- **Extreme Pressure Additives**

These compounds are designed to react with metal surfaces under extreme conditions of load and velocity, i.e. slowly moving, heavily loaded gears. Under these conditions operating temperatures are high and the metal surfaces are hot. Extreme Pressure additives contain usually at least one aggressive non-metal such as sulphur, antimony, iodine or chlorine. They react with exposed metallic surfaces creating protective, low shear strength surface films, which reduce friction and wear. The reaction with the metallic surfaces is a form of mild corrosion, thus the additive concentration is critical.



There are several different types of Extreme Pressure additives currently added to oils. The most commonly used are dibenzyl disulphide, phosphosulphurized isobutene, trichloroacetane and chlorinated paraffin, sulphur chlorinated sperm oil, sulphurized derivatives of fatty acids and sulphurized sperm oil, cetyl chloride, mercaptobenzothiazole, chlorinated wax, lead naphthenates, chlorinated paraffinic oils and molybdenum disulphide.

Dibenzyl disulphide is a mild E.P. additive, which has sulphur, positioned in a chain between two organic radicals

Examples of this type of additive are butyl phenol disulphide and diphenyl disulphide. The specific type of hydrocarbon radical, e.g. diphenyl, provides a useful control of additive reactivity to minimize corrosion.

Trichloroacetane and chlorinated paraffin are powerful E.P. additives but they are also very corrosive, particularly when contaminated with water. They are applied in extreme situations of severe lubrication problems, e.g. screw cutting.

Paraffinic mineral oils and waxes can be chlorinated to produce E.P. additives. They are not very popular since the mineral oils are quite variable in their composition and usually a poorly characterized additive results from this procedure. Such additives may have very serious undesirable side effects, e.g. toxicity and corrosiveness.

Sulphur chlorinated sperm oil is an effective E.P. additive, but is becoming obsolete because of the increasing rarity of harvested sperm whale oil. It is still, however, used in heavy duty truck axles.

Molybdenum disulphide provides lubrication at high contact stresses. It functions by depositing a solid lubricant layer on the contacting surfaces. It is non-corrosive but is very sensitive to water contamination as water causes the additive to decompose.

## Anti-Oxidants

### Oil oxidation

Mineral oils inevitably oxidize during service and this causes significant increase in friction and wears which affects the performance of the machinery. The main effect of oxidation is a gradual rise in the viscosity and acidity of an oil. Oxidation is not the only cause of viscosity increase in lubricating oils. Another cause is diesel soot. Elevated oil acidity can cause concentrated corrosion of certain machinery components such as seals and bearings. For example, lead, copper and cadmium are used in the bearing of alloys of an internal combustion engine and they are particularly prone to corrosion.

### Oxidation Inhibitors

Most lubricating oils in present use contain anti-oxidant additives to delay the onset of severe oxidation of the oil. These are either natural anti-oxidants or artificially introduced additives that are able to suppress oxidation and any differences in the oxidation resistance of oils largely depend on the presence of these inhibitors. Natural sulphur or nitrogen containing compounds which are present in mineral oils act as oxidation inhibitors by scavenging the radicals produced by the oxidation process. Sulphur based E.P. and anti-wear additives are also quite effective as anti-oxidants.

Widely used anti-oxidant additives are zinc dialkyldithiophosphate, metal deactivators, simple hydrocarbons such as phenol derivatives, amines and organic phosphates. Sulphur and phosphorus in elemental form or incorporated into organic compounds are also effective as anti-oxidants and anti-wear additives. They are sometimes added to oils (a very old practice) but are likely to cause corrosion problems or may precipitate also lose

effectiveness as an additive. Anti-oxidants are usually added to the oil in very small quantities at a concentration of approximately 1% by weight.

### Corrosion Control Activities

In this category two groups of additives are distinguished in the literature: corrosion inhibitors and rust inhibitors.

Corrosion inhibitors are used to protect the non-ferrous surfaces of bearings, seals, etc. against corrosive attack by various additives, especially those containing reactive elements such as sulphur, phosphorus, iodine, chlorine and oxidation products. Some of the oxidation products are very acidic and must be neutralized before they cause any damage to the operating parts of the machinery. The combination of corrosive additives, oxidation products, high temperature, and very often wear, can make the corrosion attacks on non-ferrous metallic parts which are used in almost every machine very severe. The commonly used additives to control the corrosion of non-ferrous metals are benzotriazole, substituted azoles, zinc diethyldithiophosphate, zinc diethyldithiocarbamate, trialkyl phosphites.

Rust inhibitors are used to protect the ferrous components against corrosion. The main factors, which contribute to accelerated corrosion attack of ferrous parts, are oxygen dissolved in the oil and water. These can cause an electrolytic attack that may be even more accelerated with increased temperature. Rust inhibitors are usually long chain agents, which attach themselves to the surface, severely reducing the mobility of water. The commonly used additives, which control the corrosion of ferrous metals, are metal sulphonates (i.e. calcium, barium, etc.), amine succinates, or other polar organic acids.

### Contamination Control Additives

With the introduction of the internal combustion engine a whole new class of additives has been developed. Engine oils are regularly exposed to fuel and combustion products, which inevitably contribute to their contamination. When sulphur is present in the fuel, sulphurous or sulphuric acid is formed during combustion. If either of these compounds is dissolved by water then corrosion or corrosive wear of the engine will be accelerated. There can also be many other possible contaminants such as soot from inefficient fuel combustion, wear debris, unburned fuel, breakdown products of the base oil, corrosion products, dust from the atmosphere, organic debris from microbiological decomposition of the oil, etc. Without proper control of contamination, the oil will lose its lubricating capacity, become corrosive and will be unsuitable for service. Various additives have been developed to control the acidity of the products of sulphurous combustion of dirty fuel and to prevent agglomeration of soot from combustion and wear particles. The agglomeration of particles can be very destructive to engines since it blocks the oil supply pipe-lines or even the filters. Additives, which prevent the development of all these detrimental effects, are known in the literature as 'detergents' or 'dispersants'.

The primary functions of these additives are:

- to neutralize any acids formed during the burning of fuel,
- to prevent lacquer and varnish formation on the operating parts of the engine,
- to prevent the flocculation or agglomeration of particles and carbon deposits which may choke the oil ways.

There are two types of dispersant: a mild dispersant and an over-based or alkaline dispersant.

Mild dispersants are often composed of simple hydrocarbons or ash less compounds (i.e. when the compound is burnt to oxides are left, since organic compounds burn to CO<sub>2</sub> and water). Mild dispersants are typically low molecular weight polymers of methylacrylate esters, long chain alcohols, or polar vinyl compounds. The function of these additives is to disperse soot (carbon) and wear particles.

Over-based dispersants are calcium, barium or zinc salts of sulphonic, phenol or salicylic acids. Over-based means that an excess of alkali is used in the preparation of these additives. The additive is present in the mineral oil as a colloid. The alkaline prepared additive serves to neutralize any acid accumulated in the oil during service. Alkaline dispersants have a disadvantage in that they accelerate oil oxidation and therefore require the addition of an anti-oxidant to the oil.

### Viscosity Improvers

These are additives, which arrest the decline in oil viscosity with temperature, and they are commonly known as viscosity index improvers. Viscosity improving additives are usually high molecular weight polymers which are dissolved in the oil and can change shape from spheroidal to linear as the temperature is increased. This effect is caused by a greater solubility of the polymer in the oil at higher temperatures and partly offsets the decline in base oil viscosity with temperature. The linear or uncoiled molecules cause a larger rise in viscosity in comparison to spheroidal or coiled molecules.

The main problem associated with these additives is that they are easily degraded by excessive shear rates and oxidation. Under high shear rates viscosity improvers can suffer permanent or temporary viscosity loss.

Although specialized synthetic lubricants have been successfully replacing mineral oil on various applications for many years, general-purpose synthetic lubricants have only recently been introduced on a large scale. They are generally more expensive but have better oxidation and thermal resistance than mineral oils.

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