

**INTRODUCTION**

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The development of modern engine and transmission technologies would be impossible without lubricant additives. From its conception in the early 1900s, the lubricant additives industry has worked in partnership with the oil and the automotive industries to enhance durability and performance of engine and drive line systems through lubricant design [Hus, 2004; Havet et. al., 2001].

### **1.1. LUBRICATION**

Lubrication occurs when opposing surfaces are separated by a lubricant film. The applied load is carried by pressure generated within the fluid, and friction resistance to motion arises entirely from the shearing of the viscous fluid. The science of friction, lubrication and wear is called tribology.

Lubrication is classified into three major categories:

- 1- Hydrodynamic lubrication (HL) [the opposing surfaces are completely separated- like aquaplaning on a road].
- 2- Elastohydrodynamic lubrication (EHL or EHD) [the opposing surfaces are completely separated and the solid bodies deformed by a major load].
- 3- Boundary lubrication [the bodies are not entirely separated].

Lubrication is required for correct operation of engines and many other mechanical systems where parts must slide over each other without seizing. Lubrication theory is used to describe the flow of fluids (liquids or gasses) in a geometry in which one dimension is significantly smaller than the others [Skinder and Gur 'yanov, 2003].

Lubricants can often also assist in a cooling and in preventing corrosion of the lubricated parts [Lansdown, 1982]. Generally speaking the smoothness of movement is improved by reducing friction, but this is not 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 [Lansdown, 1982].

In addition to reducing or controlling friction, lubricants are usually expected to reduce wear and often to prevent over heating and corrosion, and these requirements will be considered later [Lansdown, 1982].

When one surface moves over another, there is always some resistance to movement, and the resisting force is called friction. If the friction is low and steady, there will be smooth, easy sliding. At the other extreme the friction may be so great, or so uneven, that movement becomes impossible and the surfaces can over heat or be seriously damaged [Lansdown, 1982].

## 1.2. LUBRICATING OIL

The term lubricating oil is generally used to include all those classes of lubricating materials that are applied as fluids [Geore, 1980]. Lubricating oils are made from the more viscous portion of the crude oil which remains after removal by distillation of the gas oil and lighter fraction [Dowson, 1998; Pirro and Wessol, 2001; Spikes, 2001; Stachowiak and Batchelor, 2001; Pawlak, 2003]. An idea of the complexity of the lubricating oil-refining problem can be obtained from a consideration of the variations that can exist in a single hydrocarbon molecule with a specific number of carbon atoms. For example, the paraffinic molecule containing 25 carbon atoms has 52 hydrogen atoms. This compound can have about 37,000,000 different molecular arrangements [Geore, 1980]. The hydrocarbons of the crude oils are:

### 1.2.1. Paraffinic Components

The paraffinic components, which determine the pour point, contain not only linear but also branched paraffins. The straight chain paraffins of high molecular weights raise the pour point of oils (waxy compounds) and should be removed by dewaxing processes.

The branched paraffins are chemically interesting hydrocarbons and they are found in large quantities in lubricating oil fractions from paraffinic crudes. Oil rich in paraffinic hydrocarbons have

relatively low density and viscosity for their molecular weight and boiling range. Also, they have good viscosity/ temperature characteristics. In general, paraffinic components are reasonably resistant to oxidation and have particularly good response to oxidation inhibitors [ Avilino, 1994; Mortier and Orszulik, 1993].

### **1.2.2. Naphthenic Components**

They have rather higher density and viscosity for their molecular weight compared to the paraffinic components. An advantage which naphthenic components have over the paraffinic ones is that they tend to have low pour point and so do not contribute to wax. However, one disadvantage is that they have inferior viscosity/ temperature characteristics. Single ring alicyclics with long paraffinic side chains, however, share many properties with branched paraffins and can in fact be highly desirable components for lubricant base oils. Naphthenic components tend to have better solvency power for additives than paraffinic components but their stability to oxidative processes is inferior [Avilino, 1994; Mortier and Orszulik, 1993].

### **1.2.3. Aromatic Components**

They have densities and viscosities which are still higher viscosity/ temperature characteristics are in general poor but pour point is low, although they have the best solvency power for additives, their stability to oxidation is poor. As for alicyclics,

single ring aromatics with long paraffinic side chain may be very desirable base oil components. The classifying of hydrocarbon as paraffinic, naphthenic and aromatic groups which are generally used for characterizing the base oil should not be taken as absolute but as an expression of the predominating chemical tendencies of the base stocks [ Avilino, 1994; Mortier and Orszulik, 1993; O'connar et. al., 1968].

#### **1.2.4. Non Hydrocarbon Components**

The non hydrocarbons in lubricating oil are analogous in many ways to the hydrocarbons. Sulfur and nitrogen compounds are found almost entirely in ring structures such as sulfides, thiophene, pyridine and pyrrol types. More complex molecules are also thought to exist in lubricating oil in which nitrogen and sulfur atoms are found in the same molecule. As in the case of hydrocarbons, these compounds will probably also have paraffinic side chains and possibly be condensed with naphthenic and aromatic ring structures [ Avilino, 1994; Mortier and Orszulik, 1993; O'connar et. al., 1968].

Although these non hydrocarbons may be present in only trace amounts, they often play a major role in controlling the properties of lubricating oils. In general they are chemically more active than the hydrocarbon, and hence they may markedly affect properties such as oxidation stability, thermal stability and deposit

forming tendencies. In refining the general tendency is to reduce the non hydrocarbons content to a minimum.

Naphthenic acid account for most of the oxygenated compounds found in petroleum. These are removed in the refining processes by neutralization and distillation. The naphthenates are retained in the residue from the distillation and can be removed by deasphalting process. Modern refining methods generally remove most of resins, asphaltenes, polycyclic aromatic, di aromatic and their analogous non hydrocarbons, so that the final lubricant consists chiefly of saturated and monocyclic aromatic fraction [Allyson et. al., 2001].

### **1.2.5. Properties of Lube Oils**

#### **1.2.5.1. Physical properties of lubricating oil**

##### **a. Viscosity**

Viscosity is the measure of the internal friction within a liquid; the way the molecules interact to resist motion. It is a vital property of a lubricant because it influences the ability of the oil to form a lubricating film or to minimize friction [Pawlak, 2003].

##### **b. Viscosity index**

The most frequently used method for comparing the variation of viscosity with temperature between different oils by calculation of dimensionless numbers, known as the viscosity index (VI). The kinematic viscosity of the sample is measured at two different

temperatures (40°C, 100°C) and the viscosity compared with an empirical reference scale. VI is used as a convenient measure of the degree of aromatics removal during the base oil manufacturing process, but comparison of VI of different oil samples is only realistic if they are derived from the same distillate feedstock [Pawlak, 2003].

### **c. Low temperature properties**

When a sample of oil is cooled, its viscosity increases in a predictable manner until wax crystals start to form. The matrix of wax crystals becomes sufficiently dense with further cooling to cause an apparent solidification of the oil. Although the solidified oil does not pour under the influence of gravity, it can move if sufficient force is applied. Further decrease in temperature cause more wax to form, increasing the complexity of the wax/oil matrix. Many lubricating oils have to be capable of flow at low temperatures and a number of properties should be measured.

- **cloud point**

It is the temperature at which the first sign of wax formation can be detected.

- **pour point**

It is the lowest temperature at which the sample of the sample of oil can make to flow by gravity alone.

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**d. High temperature properties**

The high temperature properties of oil are governed by distillation or boiling range characteristics of the oil.

- **volatility**

It is important because it is an indication of the tendency of oil to be lost in service by vaporization.

- **flash point**

It is important for oil from a safety point of view because it is the lowest temperature at which auto-ignition of the vapour occur above the heated oil sample.

**e. Other physical properties**

Various other physical properties may be measured, most of them relating to specialized lubricant applications. Some of the more important measurements are:

- **density**

Important, because oils may be formulated by weight, but measured by volume.

- **demulsification**

Ability of oil and water to separate.

- **foam characteristics**

Tendency to foam formation and stability of the foam that results.

- **pressure/viscosity characteristics**

- **thermal conductivity**

Important for heat transfer fluid.

- **electrical properties**

Resistivity, dielectric constant.

- **surface properties**

As surface tension, air separation.

### **1.2.5.2. Chemical properties of lubricating oil**

#### **a. Oxidation degradation**

Oxidation degradation of lubricants by oxidative mechanisms is potentially a very serious problem. Although the formulated lubricant may have many desirable properties when new, oxidation can lead to a loss performance in service by reaction such as corrosion due to formation of organic acids & formation of polymers leading to sludge and resins.

#### **b. Corrosion**

The lubricant base oil should not contain components, which promote corrosion of metal parts in an engine or machine.

#### **c. Carbon residue**

This test is to measure the tendency of base oil to form carbonaceous deposits at elevated temperatures.

#### **d. Seal compatibility**

Lubricants are often used in machines where they come into contact with rubber or plastic seal. The strength and degree of swell of these seals may be affected by interaction with the oil. Various tests have been devised to measure the effect of base oils on different seals and under different test conditions [Anon, 1996; Mortier and Orszulik, 1997; Pirro and Wessol, 2001; Pawlak, 2003].

### **1.3. LUBE OIL ADDITIVES**

Lubricating oils contain always different types of additives. These additives differ in quantity and in quality according to the purpose they are needed for [Nehal, 1992]. Additives are selected and properly blended to achieve a delicate balance in performance characteristics of the finished lubricant [Geore, 1980; Allyson et. al., 2001].

Additives are chemical compounds added to lubricating oils to impart specific properties to the finished oils. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in product during its service life [Geore, 1980; Waleska et. al., 2005].

Although additives of many diverse types have been developed to meet special lubrication needs, their principal functions are

relatively few in numbers. They are used to reduce the oxidative or thermal degradation of harmful deposits on lubricated parts, to minimize rust and corrosion, to control frictional properties, to reduce wear, and to prevent destructive metal-to-metal contact. They are also employed to alter purely physical properties of oil such as viscosity, viscosity-temperature relationship (viscosity index), and a tendency to form stable foams [Smalheer and Kennedy, 1967]. Over the years a host of terms has arisen to identify additives and briefly denote their intended functions. Thus, the trade readily recognizes designations such as antioxidant (oxidation inhibitor), corrosion inhibitor, rust inhibitor, extreme pressure agent, anti-stain agent, antifoam agent, antiwear agent, viscosity index improver, pour point depressant, detergent/dispersant [Smalheer and Kennedy, 1967].

Lubricant additives can be grouped into three main functional areas [Anon, 1996; Mortier and Orszulik, 1997; Pirro and Wessol, 2001; Pawlak, 2003].

- A- Surface protective additives (antiwear, extreme pressure, detergent/ dispersant, anticorrosion and rust inhibition).
- B- Performance additives (pour point and viscosity index).
- C- Lubricant protective additives (antioxidant, antifoamant and other additives).

#### 1.4. VISCOSITY INDEX IMPROVERS

Once a viscosity index had been defined in 1929 there was a desire to improve the viscosity index of base oils [Dean et. al., 1940; Davis and Blackwood, 1931]. A motor oil must be not too viscous at low temperatures, so as to avoid serious frictional losses, to facilitate cold starting and provide free oil circulation right from the start thus permitting too fluid at the working temperatures in order to prevent excessive wear and keep down oil consumption [Alphonse, 1968].

Viscosity index is an arbitrary number, which indicates the resistance of a lubricant to viscosity change with temperature. The higher viscosity index value, the greater the resistance of a lubricant to thicken at low temperatures and thin out at high temperatures [Dean et. al., 1940; Davis and Blackwood, 1931; Smalheer and Kennedy, 1967; Pawlak, 2003 ].

It is recalled that viscosity index is an empirical number indicating the effect of change of temperature on viscosity; a low viscosity index signifies relatively large change of viscosity with temperature [Alphonse, 1968]. The viscosity index of automotive engine oil has received considerable attention. Starting requires low viscosity at low temperature but normal operation requires maintaining an adequate fluid film near 149°C [Pawlak, 2003].

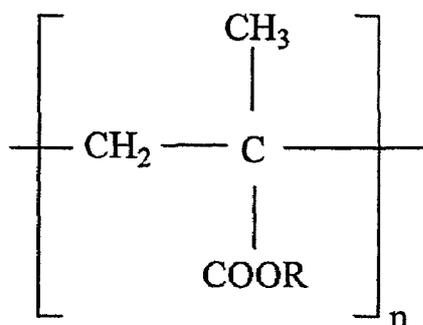
One of the earliest, and still widely used, ways in which high viscosity index oils were made, was to blend a thin base oil with a percentage of refined residual cylinder stock. This is not altogether satisfactory for high compression ratio spark ignition engines. Firstly, the cylinder stock leads to carbon deposits in the combustion chamber and secondly, the base oils, refined with modern techniques, can not economically be blended to produce a viscosity index better than 105. Even by careful selection of narrowly cut distillates, which is not an economic proposition, it is scarcely possible to exceed 110. In fact, only a very limited improvement of viscosity index can be expected from this method of blending very fluid oil with very viscous oil, or dilution of the latter with a thin one [Alphonse, 1968].

To overcome these difficulties and to meet the increasing demand for high viscosity index oils, the lubricating oil manufacturers incorporated polymeric additives called "viscosity index improvers" in the base oils and this led to the appearance of the present day multigrade oils. These additives, whose molecular weight is very high in comparison with that of the base oils (10,000 to 20,000 against about 300 for a SAE 30 oil and 600-1,000 for a bright stock), have the primary function of reducing viscosity variation with temperature [Alphonse, 1968].

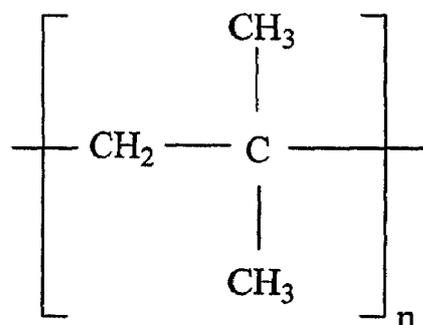
At low temperatures, these polymers are sparingly soluble in oil and exist as closely coiled chains with little influence on the viscosity of the oil. As the temperature increases, the polymer becomes more soluble and expands into loose, random coils. These expanded polymers restrict movement of the oil molecules and serve to reduce the rate at which oil thins out with increasing temperature [Arlie et. al., 1975; Neudoerfl, 1986; Pennewis et. al. , 1988; Akhmedov and Leushina , 1986; Akhemeov et. al. , 1985; Balliu et. al, 1987; Otani et. al. , 1988; Akhmedov and Isakov , 1989; Liu et. al. , 1989; Hart et. al. , 1989 ] .

The amount of thickening they provide depends on the size of the polymer molecule [ Pawlak, 2003 ]. A viscosity index improver is a product which, added in small concentrations to an oil, improves its rheological properties (flow characteristics) but does not affect other important properties such as thermal and chemical stability, no interfere with the action of other additives present in the oil. The modifications of the rheological properties are characterized by an increase of body at all temperatures [Alphonse, 1968].

Simplified chemical structure of major VI improver classes



Polyalkyl methacrylate

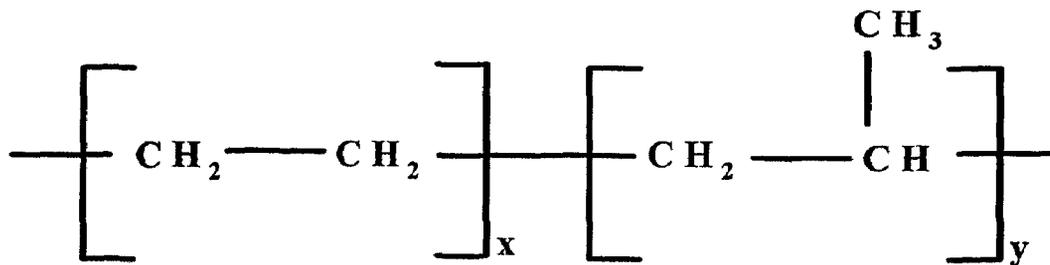


Poly isobutylenes

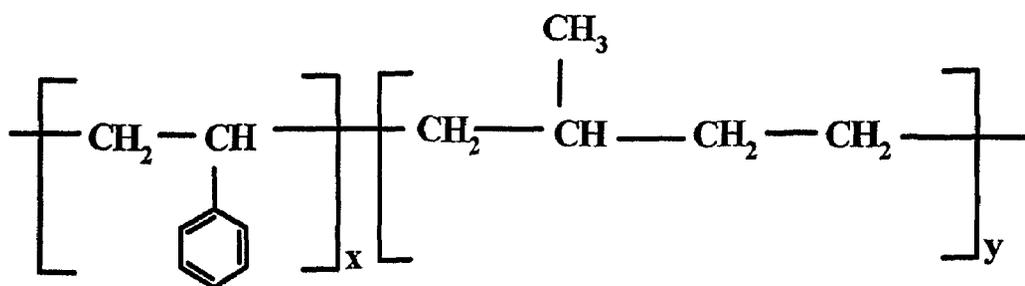
Five core technologies currently find important commercial usage. These include polymethacrylates (generally to as PMAs), poly(ethylene-co-propylene) and closely related modifications (so-called olefin copolymers or OCPs), hydrogenated poly (styrene-co-butadiene or-isoprene) and modifications (HSD or, in the case of isoprene, SIP, as well as several other abbreviations), esterified poly (styrene-co-maleic anhydride) normally referred to by the chemically incorrect description of styrene polyester, or SPE) and a combination of the first two, concentrate compatibilized PMA/OCP systems[Souza, 2000; Bair and Qureshi, 2003].

A larger or higher molecular weight polymer of the same type will generally contribute to more thickening. Shear stability is another important property of viscosity index improvers. Larger long chain polymers are more likely to be broken apart by shear forces between moving surfaces. Once this type of permanent

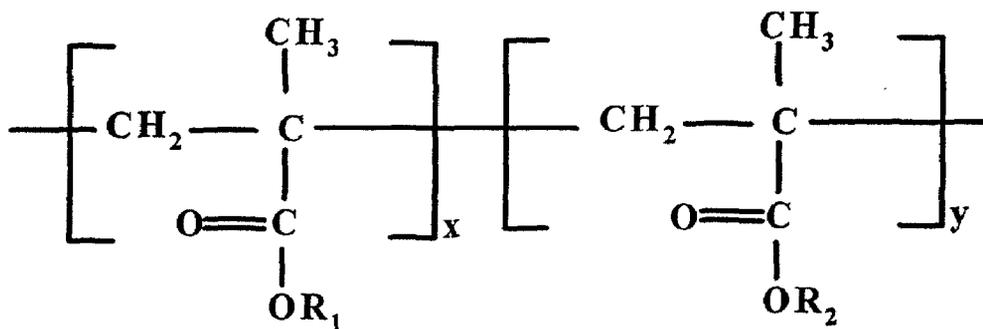
shearing takes place, the polymer contributes less to high temperature thickening. Therefore, formulation of high viscosity index oils using polymeric viscosity index improvers require selection of a polymer that will continue to provide adequate high temperature thickening in service [ Pawlak, 2003; Santos et. al., 2004; Pedersen and Ronningsen, 2003].



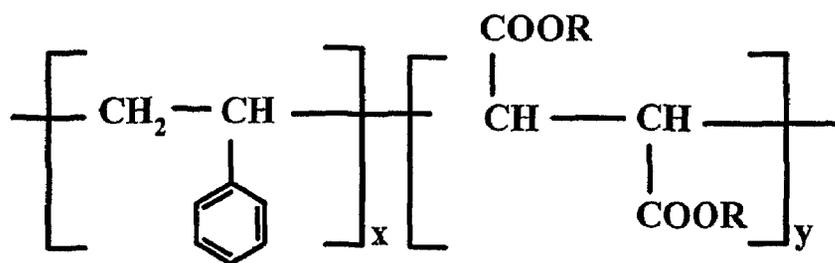
OCP



SIP



PMA



SPE

### **1.4.1. General Properties of Viscosity Index Improvers**

These additives are expected to satisfy the following general requirements:

- 1-Oxidation stability and absence of corrosive action;
- 2-Thermal stability;
- 3-Compatibility with other additives present in the oil.

#### **1.4.1.1. Oxidation stability and absence of corrosive action**

In general, the currently used viscosity index improvers possess good oxidation stability and do not give rise to any corrosive action. The results of several types of comparative tests on base oils with and without viscosity index improvers show no significant change in oxidation resistance. Further, the effective response of the commercial antioxidants in the straight or additive treated base oils appears to be the same. It is nevertheless advisable, when developing a formula, to check the possible action of the viscosity index improver on the oil to the same standard as that of the other additives, by high temperature engine tests [Alphonse, 1968].

#### **1.4.1.2. Thermal stability**

Field experience confirms that the commercial viscosity index improvers do not undergo appreciable thermal degradation at normal engine operating temperatures, provided that peroxides (polymerization catalysts) are completely eliminated. A trace of

catalyst is sufficient to cause serious thermal degradation even under relatively low temperature conditions.

The multigrade oils do not contribute to carbon formation in the combustion chambers of the spark ignition engines. They have low carbon residues and in this respect differ to their advantage, from the oils containing bright stock.

Considerable deposit formation is sometimes observed on certain engine components such as valve heads which reach temperatures of the order of 300-400°C. To overcome this, the viscosity index improver is always associated with a detergent additive in view of the increasingly severe thermal conditions due to development of modern high speed engines, the thermal stability of the viscosity improvers themselves will have to be carefully watched [Alphonse, 1968].

#### **1.4.1.3. Compatibility with other additives present in the oil**

Generally speaking the viscosity index improvers are compatible with other additives, such as antioxidants, anticorrosive additives, etc., and there is no mutual interference. However, it is advisable to check the compatibility of the different additives used. The detergency of some multigrade oils, for example, may be reduced by the presence of certain viscosity index improvers. This necessitates increasing the dosage of the detergent additive to compensate for the effect of the VI improver [Alphonse, 1968].

### **1.4.2. Factors that Limit the Action of Viscosity Index**

#### **Improvers:**

The effect produced by a viscosity index improver is limited by the following:

- 1- nature of the base oil;
- 2- concentration of the additive;
- 3- molecular weight of the additive;
- 4- polymer composition (effect of the substituted radical, R);
- 5- pressure.

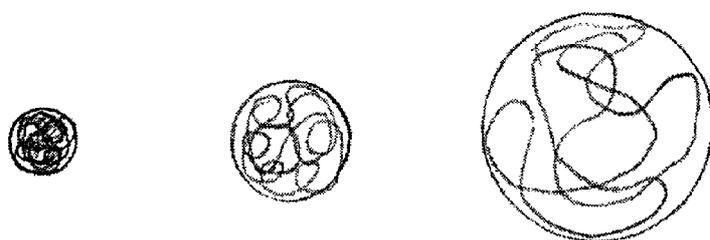
#### **1.4.2.1. Nature of the base oil**

The specific factor is the solubility of the additive in the oil; this solubility must be sufficiently high over the normal temperature range so that no separation occurs even after prolonged storage under different temperature conditions. This condition is generally fulfilled by the commercially available additives. Solubility problems encountered with some additives may appear with high paraffinic oils even without the inclusion of bright stock.

The solution of the additive in the oil must not be such as to produce a single phase system, one of which is finely dispersed in the other. The dispersed, colloidal particles are too small to be seen under an optical microscope but a strong beam of light passed through the oil is scattered and individual particles in such

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a colloidal solution are revealed as flashes of scattered light (Tyndall effect). The solubility of the additive is always limited but increases with temperature. The polymer can be present in the oil in two forms, contracted or expanded [Alphonse, 1968].



Low ← Solubility power → Good

Low ← Temperature → High

**Fig.(1.1): Expansion and contraction of a macromolecule**

The contracted form is observed in liquids of low solvent power. The molecules of the polymer are not separated but remain attached to each other. The combined intermolecular and intermicellar forces expel the solvent and the polymer takes the shape of a compact mass as shown in the wrapped-up form. Under these conditions there is little or no viscosity increase. The expanded or unrolled form is observed in liquid of high solvent power. Temperature augments the solvent power of the oil. The solvated effectively increases the volume and these enlarged

molecules increase the viscosity because they are more resistant to flow and obstruct the movement of the smaller oil molecules. In the second case, the expanded form, the solvated molecule already exists. The effect of temperature is that of a straight mineral oil, loss of viscosity and low thickening effect [Alphonse, 1968].

#### **1.4.2.2. Concentration of the additive**

With all the additives, there is therefore an optimum concentration below which the viscosity index increases with concentration but above which the viscosity index varies little or not at all, while the viscosity increase grows. These observations are of great practical importance and also show that the viscosity index improvers are relatively expensive and so any possible small gain of viscosity index for additive concentrations over the optimum may be very dearly bought. The most economic combination of additives and base oils should be based on laboratory experiment [Alphonse, 1968].

#### **1.4.2.3. Molecular weight of the additive**

At the same concentration, the polymer with the higher molecular weight produces the higher viscosity index. However, these polymers are more sensitive to shear compared with those of lower molecular weight [Alphonse, 1968].

#### 1.4.2.4. Polymer composition

This factor only concerns the polymethacrylates and polyacrylates. The thickening effect increases with the length of the chain R, and is more marked in the case of isoalkyls (branched chain) than in the case of normal alkyls (straight chained) having the same number of carbon atoms. Because of the lower polymer solubility of the short chained alkyls, they have a more marked effect on viscosity index than the long chained ones. To achieve satisfactory oil solubility, R must have a minimum four carbon chain length. The branched chains, which in general are more soluble than the straight chain radicals, give rise to relatively small increase in viscosity index. The advantage of this radical ``R`` effect is obtained by using a blend of different alcohols for the manufacture of the polymethacrylates [Alphonse, 1968].

#### 1.4.2.5. Pressure

All oils increase in viscosity under high pressure. Within the allotted limits of this quantity in lubrication, the logarithm of viscosity is proportional to the pressure. Further, the coefficient of proportionality varies inversely as the viscosity index the effect is therefore more pronounced with oils of naphthenic than paraffinic character [Alphonse, 1968].

### 1.4.3. Mechanism of Viscosity Index Improvement

The polymer molecule in solution exists as random coil, which is swollen by the lube oil solvent. Polymer solubility generally increases with increasing temperature as the polymer molecule change from tight coils to an open configuration, which has a greater volume. This increase in volume causes increases of the viscosity of the oil, which offsets the normal reduction in viscosity with increasing temperature. Increasing polymer molecular weight also increases the polymer volume in an oil solution. It is postulated that in cold oil, the molecules of the polymer adopted a coiled form and are held in colloidal suspension so that their effect on viscosity is minimized. In hot oil, the molecules are more soluble so tend to straighten out. Viscosity improvers react to temperature in a manner similar to springs. The molecules in the VI improver shrink when cold and expand or thicken when hot. These changes in the physical characteristics of the VI improver help compensate for what would otherwise be changes in the base oil stock.

The result is improved temperature stability of the oil over a wide temperature range. Chemical and thermal stability of the viscosity index improving polymers is dependent on their chemical structure. In the ring belt, particularly in diesel engines and heavy-duty gasoline engines, the polymer is subjected to strong

acids, oxygen, and temperatures up to 550°F. Under these conditions, cleavage, or oxidative degradation may occur and result in ring fouling [Abdel-Azim and Malcolm; 1983].

### **1.5. POUR POINT DEPRESSANTS**

The pour point is defined as the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under prescribed conditions [Nehal, 1992; Machado et. al., 2001]. Mineral oils thin out at high temperatures and thicken at low temperatures. These are natural properties of oil that are determined by the crude oil and the refinery processing it receives. Mineral oils selected for a particular lubricant should allow that the lubricant remains fluid over the entire temperature range it may encounter in service [Pawlak, 2003; Zhang et. al., 2004; Zhang et. al., 2005; Graulin et. al., 1953; Lawrence and Pohorilla, 1962; Sweeney, 1976; Corrossland and Clair, 1977; Song et. al., 2005].

There are three distinct phases during a cold start:

- 1- Freeing the engine. This is done by a static unsticking couple which is made up of individual couples of different engine components, i.e., piston, piston rings, crankshaft, etc. In this respect the scraper rings probably represents the most important resisting couple, because, when cold, the

piston clearance is at a maximum and they have no tendency to seize [Lawerenco and Pohorilla, 1962].

- 2- Cranking the engine at sufficient speed to start it; here the characteristics of the fuel have also to be taken into consideration [Neher and Hollander, 1931]
- 3- The rapidity of oil circulation, which mainly depends upon the pumpability of oil [Coutinho et. al., 2000].

The pour and cloud points of an oil have been considered for a long time as the principal properties affecting the cold starting of an engine. In reality, viscosity plays a more important role, of two given oils; the one which has a lower pour point may conceivably have a higher viscosity at low temperature than the other. In other words, the pour point must be considered in relation to the maximum allowable viscosity at the temperature at which the engine has to start [Zuo et. al., 2001].

During cold starting the oil is required to:

- (a) Offer the least possible resistance during cranking;
- (b) Provide rapid lubrication of the engine.

These considerations help in the study of the pour point depressants [Graulin et. al., 1953;]. The oils subjected to very low temperatures may undergo changes in their physical properties which are shown by:

- (1) Solidification without precipitation of a solid phase;

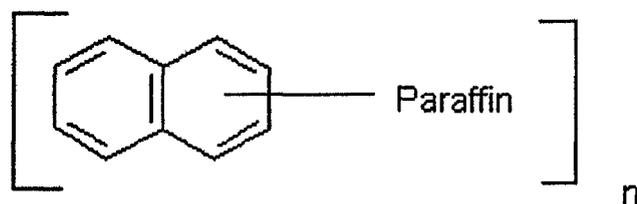
(2) Solidification with precipitation of a solid phase. This latter is due to the appearance of:

(a) Macrocrystals of paraffins which cause total solidification of oil, or

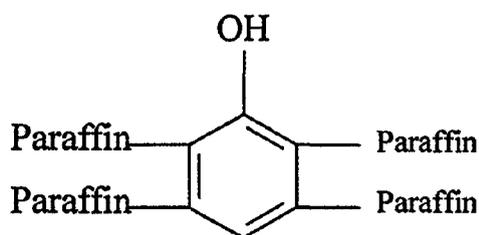
(b) Microcrystals of wax which swell, forming a crystalline structure trapping a significant volume of oil.

Paraffin wax present in most refined oils comes out of solution at low temperatures in the form of wax crystals. At these temperatures, the oil itself is still capable of flowing, but an interlocking network of wax crystals will not permit flow. Polymeric additives such as polymethacrylates at concentration of 0.1 to 0.5% [Hipeaux et. al., 2000; Machado et. al., 2001] or condensation products of chlorinated wax [Davis and Blackwood, 1931; Pawlak, 2003] and long chain alkyl phenols [Sanin, 1971; El-Gamal et. al., 1994] can be used to interfere with wax crystal growth and alter the formation of the interlocking network [Pawlak, 2003; Sweeney, 1976; Corrossland and Clair, 1977; Song et. al., 2005; Florea et. al., 1999; Anwar et. al., 1999; Denis, 1989; Xuhong et. al., 2004; Zhang et. al., 2003; Li and Zhang, 2003; Hoshimato et. al., 1988; Kostusky and Rizvi, 1987].

- Chlorinated paraffin wax with naphthalene



- Tetra paraffin phenol



The pour point of an oil varies with cooling rate and also with its previous thermal history, either in storage or in an engine [Jukic ' et. al., 2005]. To obtain low pour points, the refiner removes constituents which solidify at relatively high temperatures, a procedure known as dewaxing, already described. To dewax completely would reduce the yield to an uneconomic level and also detract to some extent from the oil's lubricating power. Thus the process is completed in effect by the use of additives .

A pour point depressant is a chemical product, with a concentration generally below 1%, restricts the growth and interlocking of the first crystals formed, and in so doing, ensures the free flow of oil at temperatures lower than the normal pour

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point. So the pour point depressant does not modify the cloud point (the appearance of crystals) but lowers the pour point .

In the case of oils having a naturally high viscosity index, an appreciable difference between the pour point and cloud point indicates the presence of a pour point depressant. A pour point depressant should have no deleterious effect on any other essential property of the oil [Zhang et. al., 2005].

There are a number of products which can be used as pour point depressants. Amongst the bodies which naturally exist in the crude oil, asphalt has a good effect, but cannot be used because of its chemical instability and its dark color. Synthetic products include very different types such as metal soaps, esters, nitrogen compounds [Alphonse, 1968].

### **1.5.1. Mechanism of the Action of Pour Point Depressants**

The generally accepted theory of the action of pour point depressants is one of surface adsorption. Adsorption on the surface of the wax particles inhibits their growth and, at the same time, their capacity to absorb oil and form gels depending on crystal type. In the absence of long interlocking crystals and / or swollen particles, the oil moves freely even though solid wax particles are suspended in it. The theory has received support from X-ray studies and measurements of the heat of solidification [Queimada et. al., 2001].

The theory explains: the negative effect in the absence of crystal formation, i.e., with naphthenic oils; the limited effects with oil of high pour point, i.e., with large proportions of wax; the maximum effect observed in the case of low pour point, particularly where such oils contain wax of fine crystalline structure, (known as microcrystalline wax or sometimes petroleum ceresin). The depression of the pour point may be as much as 30° C to 40°C. The effect of these additives is limited in general by two factors; the nature of the oil and the nature and concentration of the additive itself [Alphonse, 1968]:

### **1.5.2. The Influence of The Oil**

The effect produced by a given depressant may vary within wide limits depending on the composition of the oil. Natural inhibitors (asphalts, resins, etc.) may inhibit the action of synthetic ones. Therefore, it is necessary to eliminate them before adding any pour point depressant. Pour point depressants have no effect in the case of oils having high pour points and containing aromatic compounds. The effect of a pour point depressant is more marked in case of the more fluid oils (SAE 10, 20) than with viscous ones (SAE 50).

As a rule, pour point depressants are not used in oils with a viscosity greater than, say SAE 30, as their behavior at low

temperatures is affected by the large increase in viscosity, on which the depressant has no effect whatever [Alphonse, 1968].

### **1.5.3. The Effect of Concentration and Type of Depressant**

Different types of pour point depressants used in the same concentration in particular oil do not necessarily produce the same effect. The final choice of additive should be made on the basis of laboratory tests. With all depressants, an optimum effect is observed at some critical concentration. Any increase of concentration may result in reduction in the lowering of the pour point [Alphonse, 1968].

### **1.5.4. Polymer Type Depressant**

In case of polymer type depressants the effectiveness depends on both molecular weight and the polymer structure.

#### **(a) Molecular weight**

Such bodies should consist of polymers of as near as possible the same molecular weight, and their manufacture should be directed to the elimination of those of too high or too low a value. Polymers in general use have a molecular weight under 8000. Their effectiveness varies to some extent with molecular weight but far more with other features [Mirante Fa'tima and Coutinho, 2001].

**(b) Structure of the polymer**

The nature of the radical substituting R in the ester (COOR) plays a very important role in the effectiveness of the product. These substituting radicals are generally the normal paraffinic chains which should be sufficiently long, have at least 12 carbon atoms to ensure satisfactory oil solubility. The length of the chain also influences the effectiveness of the depressant [Alphonse, 1968].

**1.6. DETERGENTS / DISPERSANTS**

Detergent additives act to prevent an accumulation of sludge in the crankcase and on the cylinder walls. A main source of deposits is the oxidation of oil in high temperature gasoline or diesel engines; this can be reduced by using antioxidants. Dispersants, on the other hand, are additives, which disperse sludge formed in engines operated at relatively low temperatures. [Alemán et. al., 2001; Morey et. al., 2006].

The major use of detergent/ dispersant additives is in crankcase oils for gasoline and diesel engines. Their main function is to keep particulate matter dispersed, and maintain engine cleanliness. The "dirt" in an engine arises mainly from the "blow-by" (past the piston rings) products of incomplete combustion of the fuel and to a lesser extent from oil oxidation. These phenomena lead to deposits on engine parts, e.g. pistons, known

as varnish, and deposits in the engine sump, known as sludge [Ford, 1968].

The engine deposits depend on both fuel and lubricant degradation products. The dominant feature in any particular case will depend on the type of engine and fuel and the operating conditions; in all cases temperature plays an important role. The formation of all types of deposits in an engine can be controlled by the use of detergent/ dispersant additives. These additives can be ash containing or ashless ones. The neutral and basic sulphonates, alkylphenates and salicylates belong to the first type, while the ashless ones are represented by succinimides, thiophosphonates, esters, amides of high molecular weight, and Mannich bases [Drummond, 1964].

### **1.6.1. Metallic Detergent/ Dispersant Additives**

Practically all detergent/ dispersant additives contain the following components:

- 1- Polar / hydrophilic group (e.g. sulphonate, hydroxyl, mercapto, carboxyl and carbonamide groups).
- 2- Oleophilic group (e.g. aliphatic, alkyl aromatic, cycloaliphatic hydrocarbon radical, which gives the oil solubility).
- 3- Generally one or more metal-ion or amino groups. [Klamann, 1983; Wilderotter, 1972].

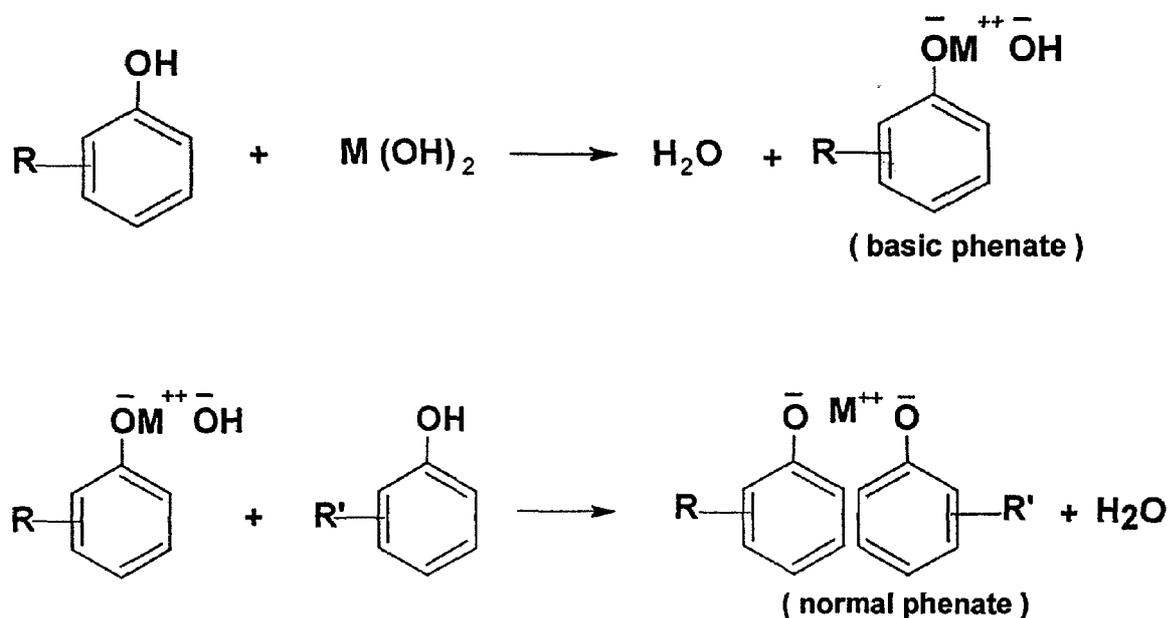
Detergent oils prevent an engine from becoming dirty by holding in suspension the solid and semi-solid by-products of combustion and oxidation. Mainly, detergents have a large non-polar hydrocarbon end that is oil soluble and a polar end that is water soluble.

The detergents / dispersants include: basic and over-basic alkaline earth metal additives, Mannich bases, polyacid- polyamines condensation products, and polyacid-alcohol condensation products. The most widely used types of metallic detergents are the phenates, sulphoates, and salts of phosphorus acids.

#### **1.6.1.1. Phenates**

The phenates include the normal and basic metal salts of alkyl phenols [Gardiner and Denison,1941], alkyl phenol sulphides [Winnings, 1944] and alkyl phenol-aldehyde condensation products [Griffin and Van Ess,1945; Wilson,1941] . Solubility in oils is achieved by using alkylated phenols, prepared by alkylation of phenols with olefins [Orudzheva and Gasanov,1966; Loppin et.al.,1968] or with chlorinated paraffin wax . Phenates and phenate sulphides have played an important role as detergent additives for crankcase oil. All phenates used commercially in crankcase oils are barium, calcium, and lead phenates.They are manufactured by reacting the substituted phenols with the metal carbides [Denison and Ettlign , 1941] , oxides, or hydroxides

dispersed in a hydrocarbon or a polar solvent such as alcohol or glycol [Stewart,1954;Walker and Shiells,1954]. By use an excess of metal oxide or hydroxide over the theoretical amounts required to form the normal phenate, the so called basic or superbasic phenates which have greater neutralization power than the normal phenates could be prepared. It has been reported [Chafatez, 1974] that basic alkaline-earth phenates, containing two or three times of the stoichiometric amount of the metal required for the normal phenates, have been prepared. Structure postulated for the normal and basic phenates are



Where:

M: Ca or Ba

R: is an oil solubilizing group

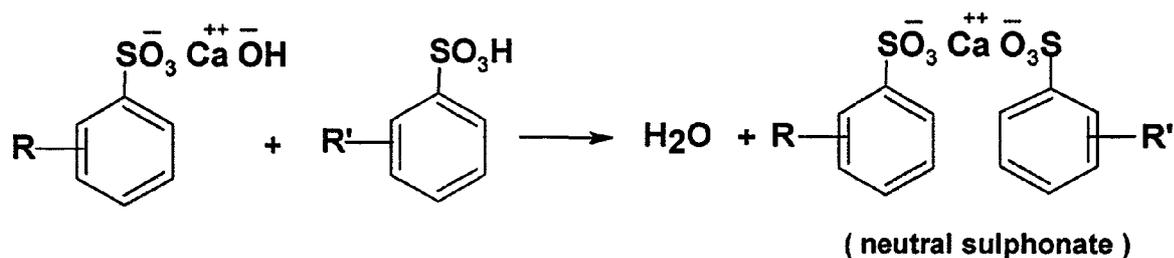
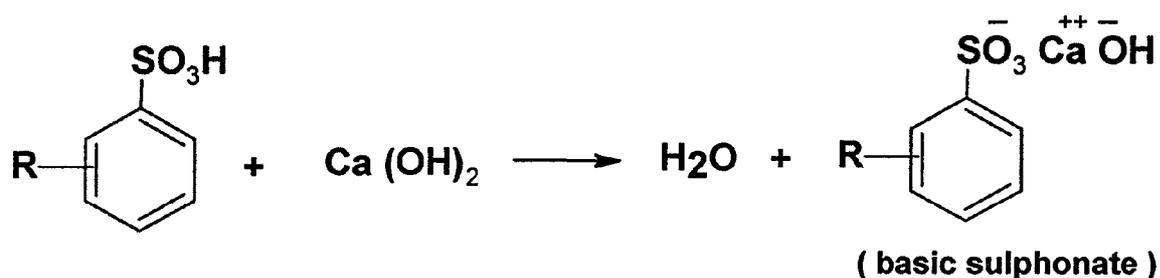
Conversion of the substituted phenols to their barium salts in the presence of carbon dioxide is reported to facilitate the neutralization and interoduction of excess metal [Le Suer, 1973; Miliotis et. al., 1969].

#### **1.6.1.2. Sulphonates**

These include the normal and basic metal salts of petroleum sulphonic and long chain alkyl substituted benzene sulphonic acids. The normal metal salt of an acid is one which contains the stoichiometric amount of metal required for the neutralization of the acidic group, but a basic salt is one which contains more metal than is required for the indicated neutralization reaction [De Vault,1970; Gragson and David, 1972; Hilton,1969; Duck Worth and Tattum,1973; Baker et. al., 1954; Sabol, 1976; Asseff et. al.,1954].

Sulphonates have the general formula  $(RSO_3)_x M_y$ . They are produced from the oil-soluble mahogany sulphonic acids which must be have 245 or higher molecular weight in order to obtain oil solubility (the mahogany acids were first employed as detergent additives in commercial crankcase oils. The metal present in such sulphonates is mainly calcium or barium [Pritzger, 1945].

As in case of phenates, neutral, basic and over basic sulphonates can be prepared depending on the percentage of metal introduced in their molecules.



Phenols and alkyl phenols are also employed to promote incorporation of basic compounds in sulphonate additives. Heating the sulphonate with an excess of metallic base and water at an elevated temperature, gives products containing up to twice as much metal as the corresponding normal sulphonates [Harold et. al., 1944; John and Ejnar, 1949; Richard, 1950; William et. al., 1946]. Fully oil-soluble sulphonate containing from 3 to 10 or 15 times as much metal as the corresponding normal sulphonates have been prepared. Such highly basic sulphonates as "over based", "super basic" and "hyper basic", were found to possess unusually high detergent power and great capacity to neutralize

Fujihana and Terauchi, 1977; Kempter and Gulbins, 1978; Thompson et al., 1978].

### 1.6.1.3. Salts of phosphorus acid

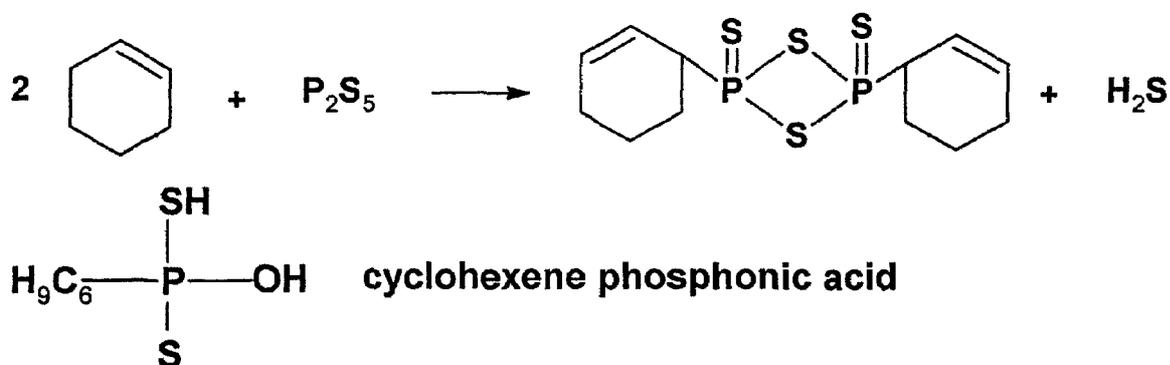
These constitute a variety of phosphorus compounds, include metal organic phosphates, thiophosphates, phosphonates and salt derived from reaction products of various sulphides of phosphorus with hydrocarbons, chiefly olefins [Farrington and Clayton, 1941; Rutherford and Miller, 1941; Farrington et al., 1945; Loane and Gaynor, 1943; Mel'Kin et al., 1970].

The commercially important detergents based on phosphorus have been the calcium alkyl phosphates, potassium, barium salts derived from olefin - phosphorus pentasulphide reaction products. Although zinc, barium alkyl and dithosphates have moderate detergent activity, they are primarily as oxidation, corrosion and wear inhibitors [Avico and Tcherkezoff, 1954; Gharieb, 1972].

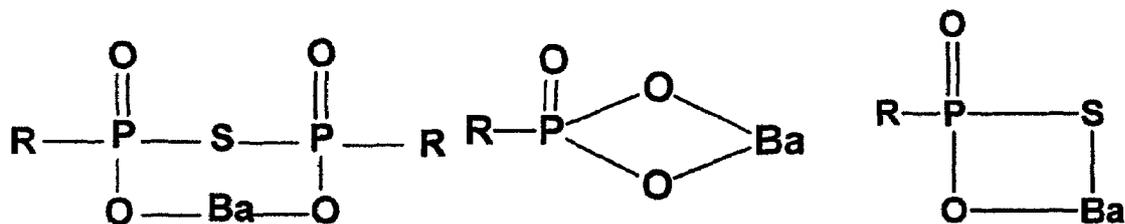
Polybutenes in the molecular weight range of 500-1000 are employed in the commercial manufacture of the olefin-phosphorus pentasulphide detergents. The reaction of the polybutenes with phosphorus pentasulphides detergents can be catalysed by sulphur or phenates. Conversion to the salts can be accomplished by neutralizing the reaction products with metal hydroxides or oxides either dry or in presence of water or

catalysed by sulphur or phenates. Conversion to the salts can be accomplished by neutralizing the reaction products with metal hydroxides or oxides either dry or in presence of water or alcohols [Mixon and Loane, 1954; Brown, 1959; Sabol and Karel, 1958].

Fay and Lenkelma established that hydrolysis of the reaction product of cyclohexene with phosphorus pentasulphide yields cyclohexene phosphonic acid, the reaction product before hydrolysis is the thioanhydride which is the anhydride of  $\Delta^2$ -cyclohexene dithiophosphoric acid [Fay and Lankelma, 1952; Hellmuth and William, 1976].



Acids obtained by acidification of commercial detergent additives and by hydrolysis of polybutene-phosphorus pentasulphide reaction products. They concluded that the organic salts present were principally thiopyrophosphate, accompanied in some cases by 10-25 mole % of thiophosphonates and phosphonates [Hu et. al., 2000; Hitzlerotts et. al., 1968; Coupland, 1972; William et. al., 1963].



(Thiopyrophosphate) ( Phosphonate ) ( Thiophosphonate )

Although the metal salts of phosphorus pentasulphide-treated polyolefins have dominated the phosphonate – thiophosphonate detergent additives, phosphors containing reagents other than phosphorus pentasulphide have also found limited commercial acceptance for the preparation of the detergent additives. Among such reagents are phosphorus trichloride or phosphorus trichloride-sulphur chloride mixture, phosphates and phosphate chlorides [William et. al., 1962; William et. al., 1961].

### 1.6.2. Ashless Detergent / Dispersant Additives

The ashless detergent additives are of two types, high molecular weight polymeric detergents for the formulation of multigrade oils (poly polar polymers), and low molecular weight additives for use where viscosity index improvement is not required. These additives are much more effective than the conventional metal salt detergents in controlling the sludge and varnish deposits [Gubbin, 1980; Englin et.al.,1976; Gureev and Chertkova,1977; Englin et. al., 1972; Astafev and Malyshev,1972] . An additional important advantage of these additives is the avoidance of the ash

formed by the metal salt detergents on decomposition. Polycarboxylic acids and polymers of acrylic acid and derivatives are ashless polymeric [Plonsker and Malec, 1977; Najman et. al., 2006].

Ashless dispersant, bis succinimides, Mannich bases and derivatives of these materials are used as motor oil additives. The additives have high level of thermal stability, so that they can be used to reduce the formation of both low-temperature and high-temperature deposits in engines operating on high detergency oils [Plonsker and Malec, 1977]. The ashless dispersant can be divided into the following groups:

a- Copolymers which contain a carboxylate ester function and one or more additional polar functions such as amine, amide, hydroxyl , ether, epoxide, carboxyl or anhydride. Most of the products in this group are prepared by the copolymerization of long chain alkyl acrylates or methacrylates with monomers containing the indicated polar functions [Charles and Swarthmore, 1962].

b- Hydrocarbon polymers which have been treated with various reagents to introduce polar functions. This group includes principally products prepared by treating polyolefins such as polyisobutene first with a phosphorus sulphide or chloride and

then with reagents such as urea, ethylene oxide, or amines [Donald and Barrington, 1963].

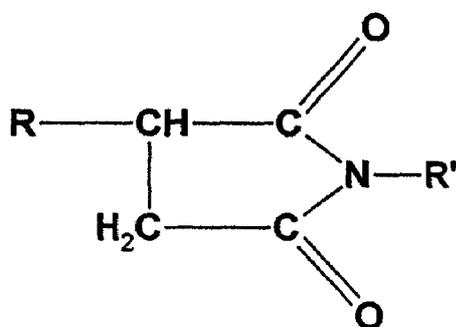
c- N-substituted long chain- alkenyl succinimides: in most of these products, the alkenyl radical is derived from liquid polyisobutenes containing from 50 to 200 or more carbon atoms.

d- High molecular weight amides and polyamides: typical products in this group are prepared by the reaction of higher fatty acids or their esters with polyamines such as tetraethylene pentamines [Hendrickson et. al., 1970; Horodysky et. al., 1988].

e- High molecular weight esters and polyesters: included in this group are polyethylene glycol dibenzoate, dialkyl nonyl boronate [Korcek et. al., 1981 ;Malec,1976; Nabel, 2005].

f- Amine salts of high molecular weight organic acids such as petroleum sulphonic acids, organo phosphorous acids and mixtures of such acids [He et. al., 2002].

Ashless detergents are based on polyamine derivatives polybutenyl succinic acid e.g. polyisobutylene succinimides.



Where:

R: is a polyisobutylene group.

R: is a polyamine which has a terminal-NH<sub>2</sub> group [Piasek and Karll, 1976; Fenoglio et. al., 1990]

### **1.6.3. Mechanism of Detergency**

These mechanisms have been established to explain the action of the detergent additives to keep engines clean

-Neutralization of acidic materials.

-Peptization of solid particles in the oil.

-Solubilization of oil insoluble materials [Adriaan, 1966; Edmund and Robert, 1972; Edmund and Robert, 1972; Trofirmov et.al.,1977;Lyashenko and Nazarova,1973; Blagovidov and Shar,1973;Mokhova and Fialko,1971; Zaslavskii and Morozova,1970; Morozova and Zaslavskii,1973].

#### **1.6.3.1. Neutralization of acidic materials**

Denison and Clayton concluded that metal carboxylates and phenates function by reaction with acidic deposit precursors. They showed that piston ring groove deposits from diesel and gasoline engines, operated at high temperatures, were highly acidic and postulated that the deposits were derived by condensation of oxyacids formed by oxidation of the lubricating oil. Their evidence indicated that the condensation involved, in part, polymerization of hydroxyacids. It was established that the oxyacids would react with various salts of weaker acids, e. g.

aluminium and magnesium naphthenates, to yield oxyacid salts that did not interact to form engine deposits [ Denison and Clayton, 1945]

The basic additives, the phenates, the basic sulphonates, and the basic phosphonates, function in part by neutralization of the acidic deposit precursors [Malec, 1974; Smiechowski and Lvovich, 2005].

#### **1.6.3.2. Peptization of solid particles in the oil**

The action of detergent additive is to maintain the carbon particles in the oil in a finely dispersed state, so that they are not deposited within the engine. Detergent additives were assumed to operate in two ways [Bray et. al., 1939]:

**A-** To coat metal surface with an absorbed layer and prevent adherence of soot and resins [Crawford,1978].

**B-** To coat particles of soot and other oil insoluble particles with an absorbed layer to prevent their agglomeration into larger particles and deposition on metal surface , due to electrokinetic phenomena [Briant and Bernelin , 1959; Briant ,1961 ] between polar group in additive molecule and carbon particles. For example [Alphonse, 1968], if two electrode are immersed in a used detergent oil, one of them becomes covered by carbon particles while the other remains clean. In case of succinimide [Sanin et. al., 1971], pronounced solubilizing ability has been

reported by some investigators [Ford, 1968; Wood , 1969; Vipper et. al., 1967], while other, focused their attention on effective stabilization of suspended carbonaceous matter in oil in the presence of succinimides [Blagovidov et. al., 1968].

### **1.6.3.3. Solubilization of oil insoluble materials**

Solubilizing ability is believed to be one of the factors permitting to retain the oil insoluble products in colloid solutions [Vipper et.al., 1968; Vipper et. al., 1968]. It has been assumed that [Nicholase, 1967] dispersant additives form hydrogen bonds with hydroxylic compounds found in engine crankcase [Fontana and Thomas, 1961; Kaufma, 1962]. This action contributes to engine cleanliness by preventing the reaction of such sludge and rust precursors (alcohols,acide and hydroxyacids) and by minimizing the agglomeration and deposition of sludge particles.

In respect of solubilizing , the ashless detergent / dispersant additives are the most effective, while the polymer detergent / dispersant effect is the adsorption on the metal surface ; the produced film hinders the deposition of undersired materials, because the surface activity of the detergents is more intensive than that of resins oxyacides and asphalthenes [Piasek and Karll,1976].

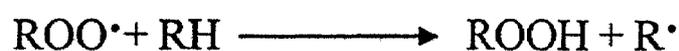
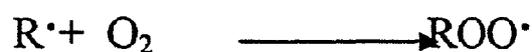
## 1.7. ANTIOXIDANTS

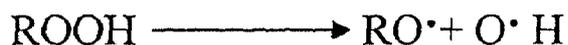
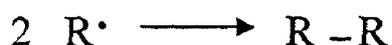
Additives that reduce oil oxidation are called antioxidants, e.g. , aromatic amines, hindered phenols, sulfurized phenols, and zinc dithiophosphates (ZDDPs) . Antioxidants act to retard oxidation of the lubricating oils, thus preventing the formation of corrosive products. Much research has been done on the nature of oxidation, but it is not fully understood in all of its aspects [Allyson et. al. , 2001; Cerny et. al., 2001; Gilks, 1964; Mahoney, 1968; Stadtmiller and Smith, 1986; Walling, 1957]. Antioxidants act in two different ways, by inhibition of peroxides or by radical scavenging. ZDDPs exhibit both types of antioxidant behavior. In oxidation, it is generally postulated that organic peroxy radicals (ROO·) are formed by the removal of a hydrogen atom from the hydrocarbon chain (RH) with the resultant formation of a "free radical" (R·) which reacts with oxygen to form a peroxy radical [Gamlina et. al. , 2002].

### Initiation



### Chain propagation



**Chain branching****Termination**

These peroxy radicals act as the precursors for further oxidation. They may remove a hydrogen atom from another hydrocarbon molecule to form a hydroperoxide (ROOH) and another free radical in chain reaction. The process is further complicated by decomposition reactions which result in a variety of organic compounds such as alcohols, ketones, aldehydes, and acids which may further oxidize and react with one another to form high molecular mass polymers. Some of these polymers may be oil soluble, resulting in a viscosity increase of the lubricant; others may be oil insoluble and drop out as sludge, carbon or varnish [Brajendra et. al., 2004; Huang et. al., 2004].

Both the initiation and propagation of the oxidation are materially affected by temperature (oxidation rates are doubled for each 10°C rise in temperature), but may also be catalyzed by the presence of various metals or by light. The termination of the oxidation reaction may result from the exhaustion of the oxygen supply in lubrication systems or from the formation of stable products in the oxidation chain reaction. Antioxidant or oxidation

inhibitors may function as chain terminating agents by reacting with free radicals to form stable products or by acting as peroxide decomposers, or they may act as metal passivators to prevent catalytic effects [Castro Dantas et. al. , 2003; Huang et. al. , 2000] The chain terminating additives are usually aromatic amines, phenols, or sulfides. Those that inhibit the catalytic effect of metallic ions such as Cu, Fe, Pb, Mn, and Co are generally organic sulfides, phosphites, or thiophosphates [Zhang et. al., 2001].

Although oxidation or corrosion inhibitors are frequently referred to separately, many of the phosphorous and sulfur containing compounds are effective in both applications. The entire matter of oxidation is affected by many things, including the temperature of the lubricant and the material of construction of the equipment in which the lubricant is used. It is also materially affected by inherent resistance of the base oil to oxidation [Shen et. al., 2000 ; Hassan et. al., 2000; Pawlak, 2003].

Metal compounds reach the lubricating oil by surface abrasion or the corrosive action of acidic oxidation products. The combustion fuel products with metal ions can be combined in a complex form and thus "masked" by so-called deactivators. Materials previously referred to as corrosion and rust inhibitors also function as metal

ion deactivators, due to their ability to form a coating on the metal surface [Jose' Carlos et. al., 2004; Mohamed, 2002].

The degradation of ZDDP is very complex and much work has been done to understand the mechanism of its degradation and its interactions with other additives. Some workers have tried to follow the reactions by oxidizing ZDDP in the laboratory [Burn et. al. , 1971 ; Burn et. al. , 1990 ; Burn et. al. ,1990; Harrison and Kikabhai, 1987; Paddy et. al. , 1989; Paddy et. al. , 1990] and others follow the reaction of ZDDP in engine environment [Korcek et. al. ,1981; Peng et. al.,1994]. In the decomposition of cumene hydroperoxide(CHP) in the presence of ZDDP, the disulfide was identified as an initial degradation product, and zinc sulfate was identified as a final product. In organic solvents, the basic form of ZDDP dissociates to form zinc oxide which inhibits hydrolysis of ZDDP. The degradation process of ZDDP in a fully formulated engine oil was seen to be temperature dependent, formed a complex with succinimide dispersant, and the process was complicated [Pawlak, 2003; Smith, 2000].

As a rule, however, the final formulation of products must be subjected to time- consuming practical tests. This is particularly true for motor oils, where only the practical test in the engine can assess, for instance, high temperature efficiency of dithiophosphates and the frequently antagonistic effects of

dispersants and oxidation inhibitors in a given additive combination [Klamann, 1984; Mortier and Orszulik, 1997; Pawlak, 2003; Zeng et. al., 2005].

### **1.8. CORROSION INHIBITORS**

A number of kinds of corrosion can occur in systems served by lubricating oils. Propably the two most important types are corrosion by organic acids that develop in the oil itself, and corrosion by contaminants, that are picked up and carried by the oil. One of the areas where corrosion by organic acids can occur is the high strength bearing inserts used in internal combustion engines. Some of the metals used in these inserts, such as the lead in copper-lead or lead- bronze, are readily attacked by organic acids in oil. The corrosion inhibitors form a protective film on the bearing surfaces that prevents the corrosive materials from reaching or attacking the metal. The film may be either adsorbed on the metal or chemically bounded to it. The additive used for this purpose is primarily zinc dithiophosphate, but other sulfur and phosphorus containing materials is also used [He et. al., 2004].

During combustion in gasoline or diesel engines, certain materials in the fuel, such as sulfur and antiknock scavengers, can burn to form strong acids. These acids can then condense on the cylinder walls and be carried to other parts of the engine by the oil.

Corrosive wear of rings and cylinder walls, and corrosion of crankshafts, rocker arms, and other engine components can then occur. It has been found that the inclusion of highly alkaline materials in the oil will help to neutralize these strong acids as they are formed, greatly reducing this corrosion and corrosive wear. These alkaline materials are also used to provide detergency [Geore, 1980]. Example metal dithiophosphate and metal dithiocarbonate [McQueen et. al., 2005].

### **1.9. ANTIWEAR (AW) / EXTREME PRESSURE (EP) ADDITIVES**

The distinction between antiwear and extreme pressure is related to two types of chemistry being involved. Antiwear is based on the prevention of damage caused by moderate or sporadic loading. Extreme pressure chemistry is based on the protection from shock loading and continually applied heavy or sliding loads [So and Hu, 2005]. One of the primary functions of lubricants is to reduce wear, examples, zinc dithiophosphates, organic phosphates, chlorine and sulfur compounds, sulfides and disulfides [Pawlak, 2003; Xiangqiong et.al., 2005].

### **1.10. ANTIFOAMANT**

All automotive lubricants which are subject to sufficient agitation will entrain air and produce foam. This is undesirable because it

increases exposure of the lubricants to oxygen and thereby increases the rate of oxidative decomposition [Hu et. al., 2002]. Entrained air and foam also reduce lubricant efficiency as a coolant and hydraulic fluid. Polymers of silicone and organic copolymers are commonly used to control foam. These additives have lower surface tension than the lubricant and low solubility in the lubricant. This permits them to spread over the surface of the foam bubbles at a concentration high enough to weaken the oil film, causing it to collapse [Ross, 1967]. Liquid silicones (in particular, polydimethylsiloxanes) are the most efficient antifoam agents at concentration of 0.0001% to maximum 0.001% [Pawlak , 2003].

### **1.11. MULTIFUNCTIONAL LUBE OIL ADDITIVES**

Today multifunctional additives play a major role in the technology of engine oils. Thus, research throughout the world is increasingly directed towards producing additives with more than one purpose, i.e. multifunctional additives [Mohamed et.al.,1994]. Use multipurpose lubricants and other general purpose oils can be applied to a wide range of equipment and help reduce the number of lubricants required. Although some lubricants are not listed as multipurpose they may be used in this capacity.

One of the problems associated with a multifunctional additive is the difficulty in achieving a proper balance of its various

characteristics, so that each desirable property can fully manifest itself under actual service conditions and yet complement other desirable properties [Lester, 1972].

### 1.12. RADICAL COPOLYMERIZATION

Benzoyl peroxide (BPO), due to its higher radical reactivity as compared to azo bisisobutyro nitrile (AIBN), is known to promote grafting onto cis-polybutadiene. Switching from AIBN to BPO initiator made a dramatic difference in the extent of grafting for styrene and methacrylate monomers, but only a modest difference for acrylate monomer. For styrene and methacrylate monomers, graft site formation is due to BPO initiator radical attack onto the backbone via allylic hydrogen abstraction. Significant levels of grafting are achieved and depend upon the relative concentrations of monomer and backbone polymer but not upon the level of initiator. For acrylic monomer, graft site formation was found to be due to polymer radical attack at the double bond in the backbone. Abstraction of allylic hydrogen also occurs but results in retardation of the overall reaction rate. Graft level was dependent upon initiator and backbone polymer concentrations but not upon monomer concentration. The effective role of the initiator is only to produce polymer radicals; the BPO has no direct role in the formation of effective graft sites.

Styrene-maleic anhydride copolymer and octadecene-maleic anhydride copolymer are two examples for alternating copolymers. Styrene, maleic anhydride and octadecene are monomers prefer to make copolymer with other monomers than homopolymerization.

Copolymerization may closely follow the kinetics of homopolymerization of the component monomers when the monomers are very similar to each other. Such molecules are called copolymers, while the original idea was to combine the useful properties of both homopolymers, sometimes new materials have been developed with very valuable properties that are not just a plain combination of properties of the corresponding homopolymers. Copolymers have been used with lubricating oils to improve their pour points, dispersant efficiency, viscosity and viscosity index.