

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 Lubricating Oils

2.1.1. Manufacturing methods

Lubricating oils of high quality can readily be made from paraffin-base oils, but most oils are mixed or naphthene base, and solvent refining is required to produce quality lubes. The Society of Automotive Engineers (SAE) has classified lube oils by means of a number system based on viscosity, change of viscosity with temperature.

Very early lubricants were made by simple distillation of petroleum to recover the lower boiling gasoline and kerosine fractions and leave a residue which was useable as a lubricant. It was found that lubricant quality could be improved by additional very simple processing to remove some of the less desirable components, such as asphalt, wax and aromatics. In this era lubricants relied on the inherent properties of the base oil because virtually no additives were used.

Distillation under vacuum allowed the separation of lube distillates from the crude oil, leaving the asphalt behind in the distillation residue. Wax was removed by chilling the lube distillate and filtering in plate and frame presses. Aromatics were reduced by treating the oil with sulfuric acid and separating the acid tar phase. Finally, finishing treatments such as adsorption of acid residues and impurities by activated clays gave further improvement in product quality.

These processes were mainly batch operations, labor intensive and characterized by their hazardous nature. They were not suitable for the great expansion in production capacity which the industry was being called upon to supply. New technology was developed which allowed continuous operation so that plants became much larger

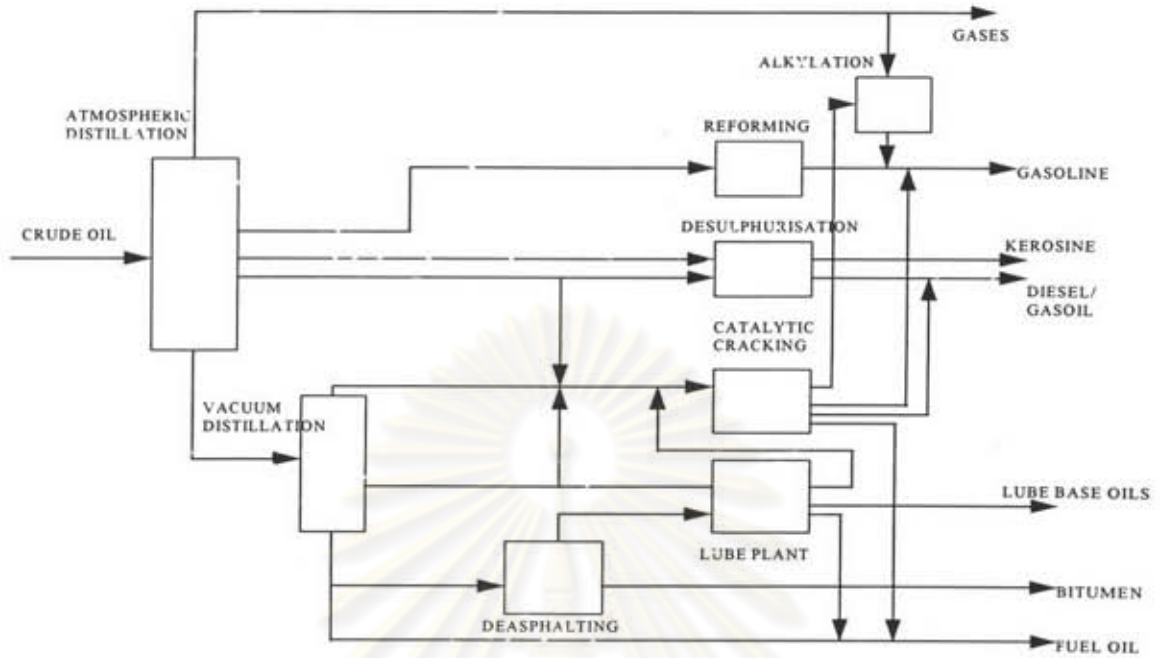
and could make more consistent quality products at lower cost. These new process methods were based on the use of solvents: continuous selective solvent extraction for aromatics removal was the process which replaced acid treatment and continuous solvent dewaxing replaced the very labor-intensive cold-pressing technique.

In a modern refinery, most base oil plants are integrated with mainstream oil refineries which produce a range of transportation and heating fuel products. Overall production capacity for lubricant base oils is a very small part of total refinery throughputs, in America amounting to less than 1.5%.

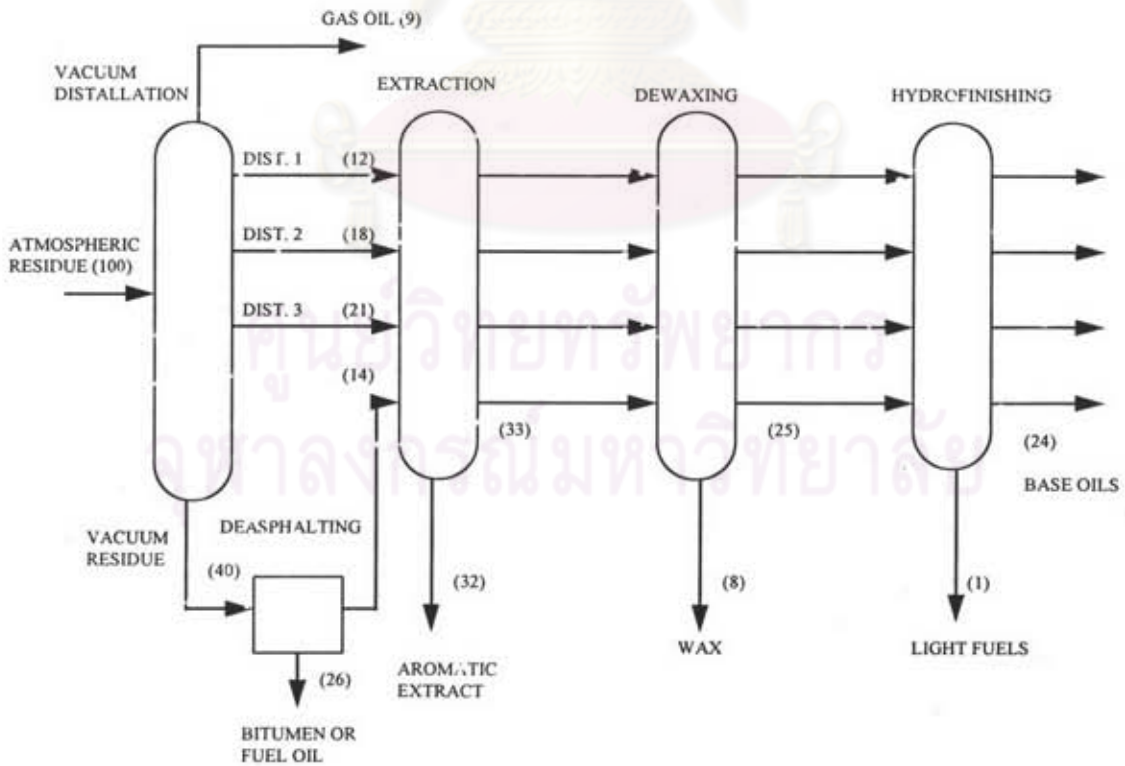
Scheme 1 indicates where a lubricant base oil plant fits into the process flow-scheme of a typical refinery-if there is such a thing. Although the scheme is simplified, the inter-relationship between the base oil plant and other process units and product stream is evident. In a sense, the base oil plant and fuels upgrading plant, such as the catalytic cracker, compete for feedstock from vacuum distillation. By-products from base oil manufacture are largely incorporated into production streams. These interactions are very important to the logistics and production economics of making base oils.

Base oil manufacture produces large quantities of by-products, the unwanted components of the crude oil. Scheme 2 is a typical base oil production flow-scheme in which the numbers indicate the relative amounts of intermediate and final products throughout the manufacturing process. The basis for the scheme is the processing of the residue from atmospheric distillation of a good quality Middle East crude. Starting with 100 parts of residue (which itself represents only about 50% of the original crude oil), even when the maximum possible amount of each base oil grade is produced, only 24 parts of base oil result.

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Scheme 2.1 Simplified refineries flow-scheme



Scheme 2.2 Base oil production flow-scheme

Distillation : This is the primary process for separating the useful fractions for making lubricant base oils from crude oil. Crude oil is distilled at atmospheric pressure into components essentially boiling below 350°C. (gases, naphtha, kerosine and gas oil) and a residue containing lube boiling range components. Thermal decomposition is increasingly likely to occur at higher temperatures and so further separation of the atmospheric residue into lube distillates is carried out at reduced pressure in a vacuum distillation unit.

De-asphalting: The residue from vacuum distillation is black and very viscous material because it contains large amounts of asphaltic and resinous components. When these are removed, a useful high viscosity base oil fraction, known as brightstock, is available. Low molecular weight hydrocarbons are effective for dissolving the more desirable components while leaving the asphaltic material as a separate phase. Liquefied propane is by far the most frequently used solvent for de-asphalting of residues to make lubricant bright stock, whereas butane or pentane produce lower grade de-asphalted oils which are more suitable for feeding to fuels upgrading units.

Solvent extraction: Solvent extraction replaced acid treatment as the method for improving oxidative stability and viscosity/temperature characteristics of base oils. The solvent selectively dissolves the undesired aromatic components (the extract), leaving the desirable saturated components, especially alkanes, as a separate phase (the raffinate). Solvent in commercial use include sulphur dioxide (historically important, but rare nowadays), phenol (use is in decline), furfural (the most widely used) and N-methylpyrrolidone (increasing in importance). N-methylpyrrolidone is gaining in popularity for new units and conversions because it has the lowest toxicity and can be used at lower solvent/oil ratios which save energy.

Solvent de-waxing: The material which crystallises out of solution from lube distillates or raffinates is known as wax. Wax content is a function of temperature, because as the temperature is reduced, more wax appears, Sufficient wax must be removed from each base oil fraction to give the required low-temperature properties for each base oil fraction to give the required low-temperature properties for each base oil grade. Naphthenic feedstocks, of course, are relatively free of wax and do not normally

require de-waxing. Commercial solvents used for de-waxing include propane, methyl isobutylketone, and mixed solvents such as methylethylketone/toluene or methylene chloride/dichloromethane. The use of paired solvents helps to control the oil solubility and wax crystallisation properties better than use of a single solvent.

Hydrofinishing: Hydrofinishing differs from all the process steps used so far because it is not a physical separation procedure. It depends on the selective, catalysed hydrogenation of the impurities to form harmless products and is carried out under relatively mild conditions. Yields of finished base oil are high (at least 95%) organonitrogen molecules because they are largely responsible for poor colour and stability of base oils, while organosulphur molecules should be retained because they tend to impart natural oxidation stability to the base oil.

In recent years, some of the solvent-based separation processes have acquired competition from new processes based on catalytic hydrogenation as an alternative means of removing unwanted components from the base oil. Hydrogenation may offer economic advantages over solvent processes and gives products that are clearly differentiated from conventional solvent-refined base oils. In fact, some of the processes can go a stage further and actually create new and highly desirable components, so that the resulting base oils have characteristics which are superior to anything that could be made by conventional solvent-refining technology relying on physical separation processes.

2.1.2. Inherent Properties

Physical Properties

Viscosity: Viscosity is a measurement 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 minimise friction and reduce wear. Another method of defining viscosity is to measure

the rate of flow of the liquid through a capillary under the influence of the constant force of gravity. This is the kinematic viscosity and is defined as follows:

$$\text{Kinematic viscosity} = \frac{\text{Absolute viscosity}}{\text{Liquid density}}$$

Viscosity/temperature relationship-viscosity index The most frequently used method for comparing the variation of viscosity with temperature between different oils is by calculation of a dimensionless number, 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 change is compared with an empirical reference scale. The original reference scale devised by Dean and Davis (1929) was based on two sets of lubricant oils derived from separate crude oil.

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, but it has not undergone a true phase change in the way a pure compound, such as water, freezes. Many lubricating oils have to be capable of flow at low temperatures and a number of properties should be measured. Examples of these properties are :- cloud point, pour point etc.

High-temperature properties The high-temperature properties of an oil are governed by the distillation or boiling range characteristics of the oil, such as:- volatility, flash point.

Other physical properties These properties may be measured for the specialized lubricant applications, such as :- density, demulsification, foam characteristics, pressure/viscosity characteristics, thermal conductivity, etc.

Chemical properties

Oxidation Degradation of lubricants by oxidative mechanisms is potentially a very serious problem. Although the formulated lubricant may have many

desirable properties, oxidation can lead to a dramatic loss of performance in service by reactions such as:

- corrosion due to formation of organic acids
- formation of polymers leading to sludge and resins
- viscosity changes
- loss of electrical resistivity

Corrosion The lubricant base oil should not contain components which promote corrosion of metal parts in an engine or machine. The problems of oxidation products leading to corrosion have been mentioned above.

Carbon residue This test is used to measure the tendency of a base oil to form carbonaceous deposits at elevated temperatures. Tests such as the Conradson carbon residue test (ASTM D189) determine the residue which remains after pyrolytic removal of volatile compounds in the absence of air.

Seal compatibility Lubricants are often used in machines where they come into contact with rubber or plastic seals. 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 effects of base oils on different seals and under different test conditions.

2.2. Common Additives

Additives are used to enhance the performance of a petroleum lubricant. In most case, the enhanced performance in one area may be slightly offset by a decrease in performance in some other areas; e.g., adding an extreme-pressure additive to a gear oil will increase the extreme-pressure capabilities but slightly decrease the oxidation life of the product. The addition of some additives may also reduce the demulsibility, which would be undesirable in an application where water contamination is normal and water separation is important. Should this be a potential problem in a circulating oil system, it should be well noted by the oil supplier and equipment manufacturer.

Some of the most common additives for lubricants follow.

2.2.1. Oxidation Inhibitors

These types of additives decrease the rate of oil oxidation by reducing the tendency of the hydrocarbons to combine with oxygen molecules, and as a secondary effect, they can reduce the tendency to corrode certain types of sensitive bearing materials. Oxidation increases a lubricant's viscosity and causes a chemical change which results in the formation of peroxides and organic acids. These chemical changes produce elements which cause corrosive action. High temperatures, catalytic metals, and exposure to air increases the oil's rate of oxidation. After the oxidation inhibitors are depleted, the rate of oxidation depends on the natural oxidation resistance of the base oil. A quality base oil will then oxidize more slowly than will a poorer-quality base oil. The self-accelerating oxidation of hydrocarbons is called autoxidation which can be classified into 3 categories.

2.2.1.1 Oxidation of hydrocarbons at low temperature (30-120°C.)

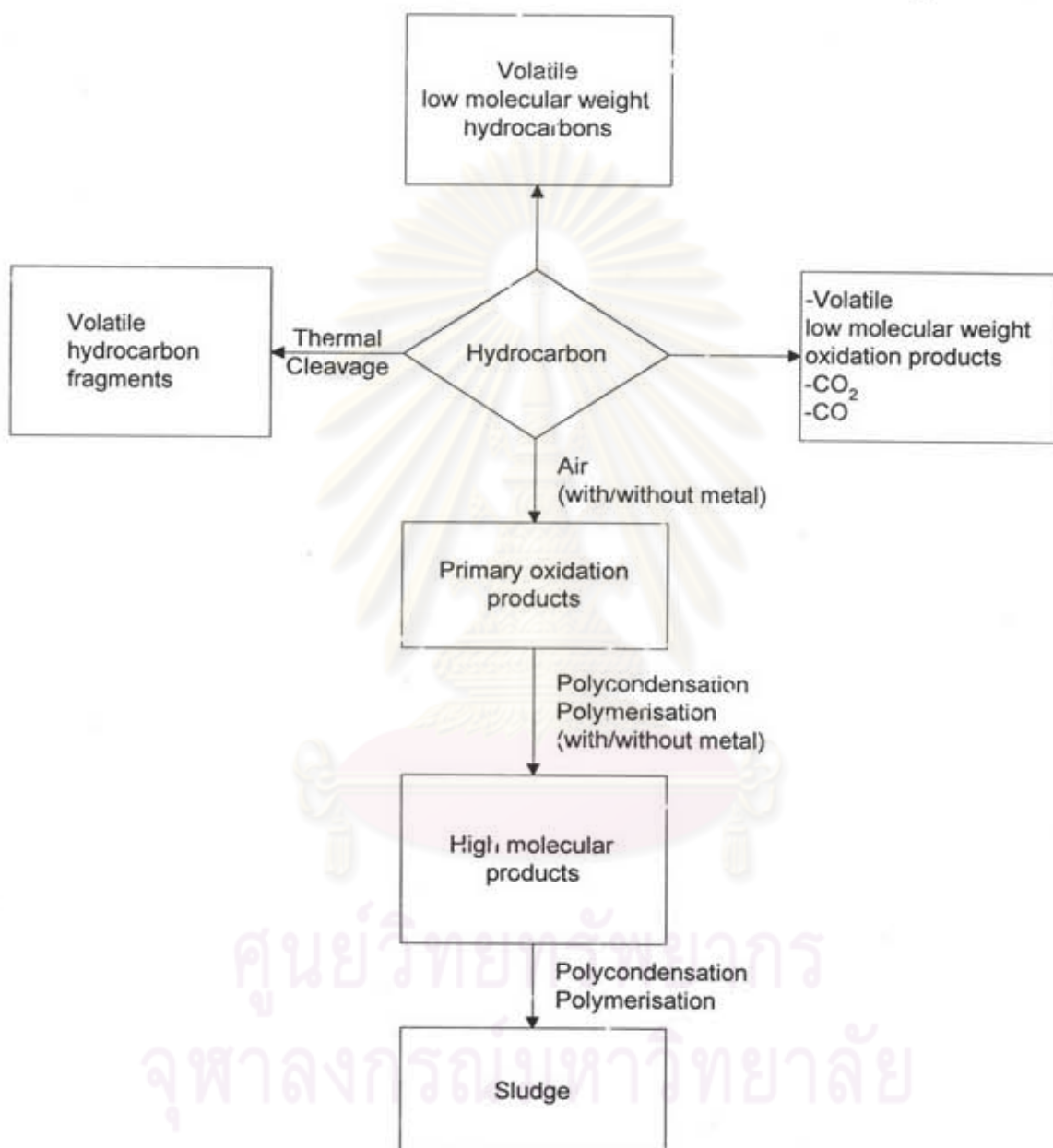
The degradation is driven by an autocatalytic reaction which can be described by the well-established free radical mechanism. It consists of four stages:

- initiation of the radical chain reaction
- propagation of the radical chain reaction
- chain branching
- termination of the radical chain reaction

The reactions of hydrocarbons at low temperatures leads to alkylhydroperoxides, dialkylperoxides, alcohols, aldehydes, and ketones. In addition, cleavage of a dihydroperoxide leads to diketones, keto-aldehydes, hydroxyketones and so forth.

2.2.1.2 Oxidation of hydrocarbons at high temperature (>120°C.)

The model for high temperature oxidation can be described by Scheme 2.3



Scheme. 2.3 Model of lubricant degradation under high temperature condition.

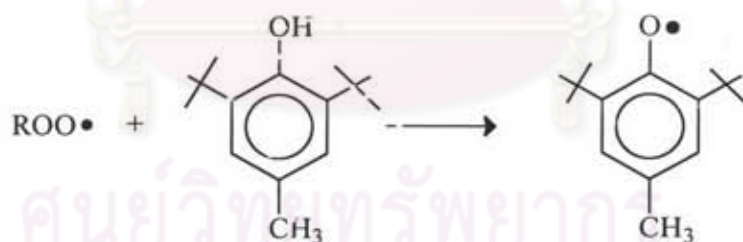
2.2.1.3 Metal catalysed autoxidation of hydrocarbons

The decomposition of an alkyl hydroperoxide molecule occurs at temperatures of about 150°C. Transition metal ions having two ionic valence states, such as $\text{Fe}^{2+/3+}$, $\text{Pb}^{2+/4+}$ and $\text{Cu}^{1+/2+}$, reduce the activation energy of this decomposition process. These ions must be present as metal soaps otherwise they are not catalytically active.

The most widely used types of radical scavengers are phenolic and aminic antioxidants. Recently, organo-copper salts have been introduced to control the oxidative degradation of engine oils.

- **Sterically hindered phenols.** Phenols which are substituted in the 2 and 6 positions with tertiary alkyl groups are called sterically hindered phenols. The most common substituent is the tertiary butyl group.

Reaction mechanism Sterically hindered phenols like (VII) compete successfully with the rate-determining steps of the propagation reaction



The resonance-stabilised phenoxyl radical (VIII) preferentially scavenges an additional peroxy radical to form a cyclohexadienone peroxide (IX).

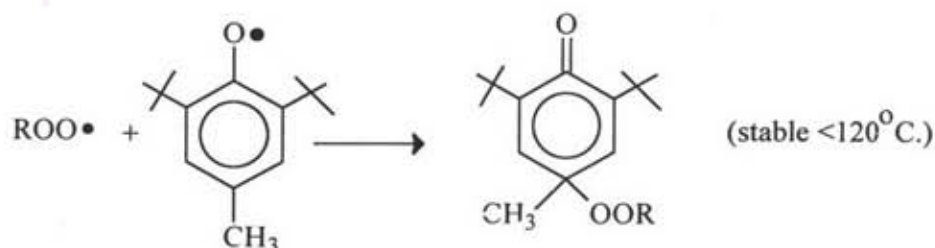
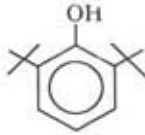
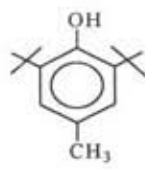
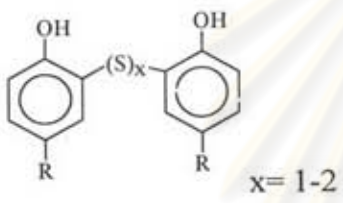
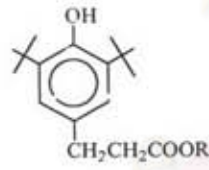
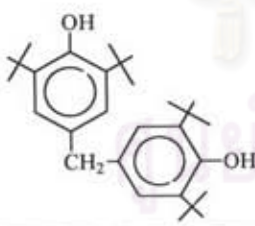


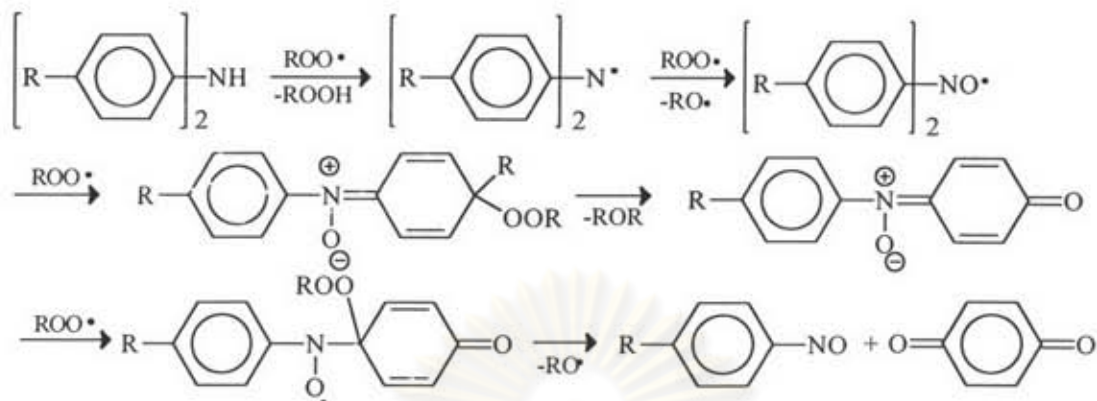
Table 2.1. Major commercial phenolic antioxidants and their applications

Structure	Major use
	Industrial oils
	Industrial oils, greases
	Engine oils
	Industrial oils, Engine oils
	Industrial oils, Engine oils

- **Aromatic amines.** Secondary aromatic amines are another important class of antioxidants used in lubricants. The principal substituents of the nitrogen atom are either two aryl or one aryl and a naphthyl group.

Reaction mechanism The reaction mechanism of diphenylamines is dependent on the temperature. Under low-temperature conditions (<120°C) the interaction with peroxy radical

predominates.



According to the above reaction sequence, one diphenylamine molecule eliminates four peroxy radicals. By definition, the stoichiometric factor is four. In the case of a sterically hindered monophenol, this factor is two. Hence diphenylamines perform better as peroxy radical scavengers than monophenols at temperatures of $< 120^{\circ}\text{C}$. Under high-temperature conditions ($>120^{\circ}\text{C}$), e.g. engine oils, an extended stabilisation mechanism in the form of a catalytic cycle has been suggested.

Table 2.2 Major commercial aminic antioxidants and their applications

Structure	Major use
	Industrial lubricants, engine oils, aviation oils, automatic transmission fluids, greases
	Greases
	Industrial lubricants, greases
	Industrial lubricants, engine oils,

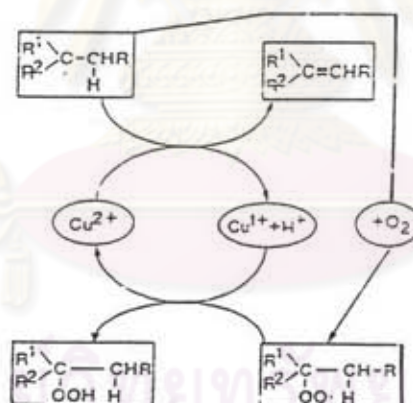
- **Organocopper antioxidants** A breakthrough in terms of controlling the oxidation of automotive oils has been achieved with the introduction of organocopper salts. They can also act as pro-oxidants, and several bench oxidation tests use copper or copper salts as a catalyst in order to make test conditions more severe and so shorten test duration. The catalytic activity of copper ions dominates up to 40 ppm of copper but in the range of 100-200 ppm in combination with ZnDTP or dithio-thiadiazoles organocopper salts control the oxidation of engine oils.

Reaction mechanism The way in which copper controls oxidation may be outlined as follows.

- Reduction in Fe^{2+} concentration results in a stabilisation step because Fe^{2+} is more active than Fe^{3+} in catalysing oxidation:



- Copper ions eliminate catalytically active alkyl and peroxy radicals.



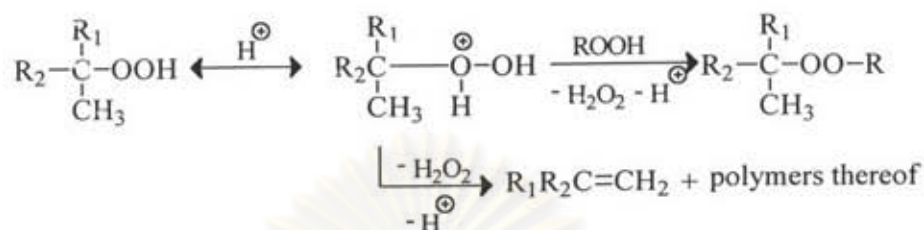
- **Hydroperoxide decomposers**

These compounds convert hydroperoxides into non-radical products thus preventing the chain propagation reaction. Traditionally organosulfur and organophosphorus additives have been used for this purpose.

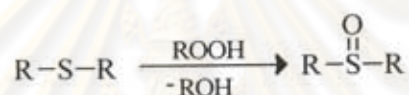
Reaction mechanism of organosulfur compounds The most important reaction mechanism to eliminate hydroperoxides is the acid-catalysed decomposition. The catalysts are protic (RSO_2H) or Lewis (SO_2) acids:



$R_1 = H$ or alkyl group

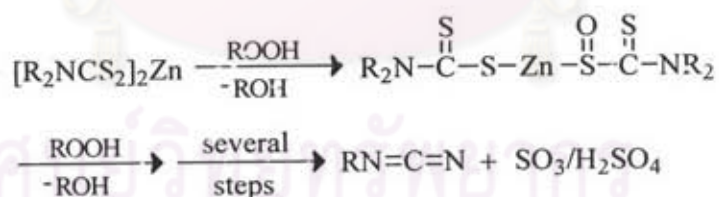


Organosulfur compounds are the main source for the formation of the acid catalyst. Compounds such as R-S-R react with hydroperoxides to yield sulfoxides as key intermediates for the stabilisation of the lubricant:



- **Zinc dialkyl dithiocarbamates** These compounds are mainly used as antioxidants although, like the ZnDTPs, they also have extreme pressure activity.

Reaction mechanism The formation of sulfur acids, which serve as the catalyst for ionic hydroperoxide decomposition, arises through the oxidation of zinc dithiocarbamates by hydroperoxides.



In addition, zinc dithiocarbamates also act as radical scavengers, whereas in the literature the main emphasis is generally put on their capability to destroy hydroperoxides. Areas of application comprise grease and engine oils.

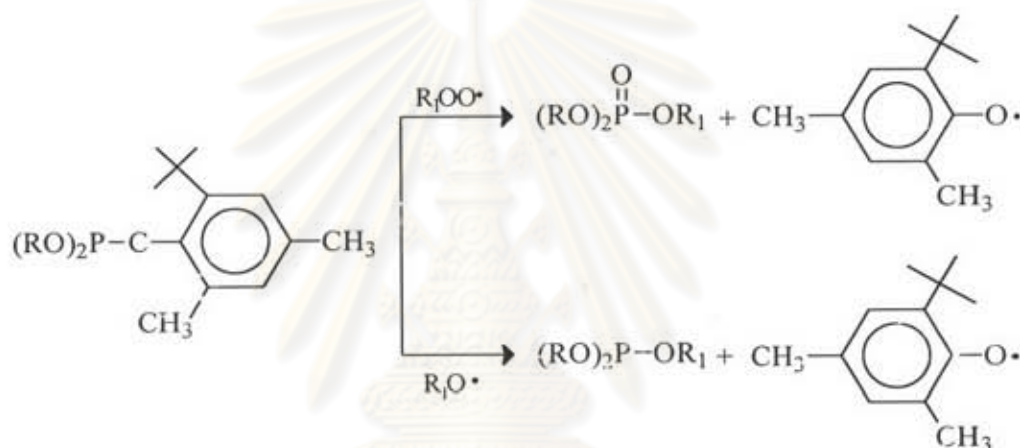
- **Organophosphorus compounds** Phosphites are the main organophosphorus compounds used to control oxidative degradation of lubricants. They eliminate hydroperoxides, peroxy and alkoxy radicals, retard the darkening of lubricants over time,

and also limit photodegradation. These performance characteristics may be of importance for polyalphaolefins, hydrocracked or severely hydrotreated base stocks and white oils.

Reaction mechanism The major non-radical mode of action is the reduction of hydroperoxides, especially under high-temperature conditions:



Phosphites with substituted phenoxy groups also behave as peroxy and alkoxy radical scavengers forming relatively stable phenoxy radicals, which again eliminate peroxy radicals.



- Multifunctional additives

- **Zinc dithiophosphates** The dominating position of ZnDTPs as additives for lubricating oils is due to their multifunctional performance. Not only do they act as antioxidants, but they also improve the wear inhibition of the lubricant, and protect metals against corrosion. ZnDTPs are mainly used to formulate anti-wear hydraulic fluids and engine oils.

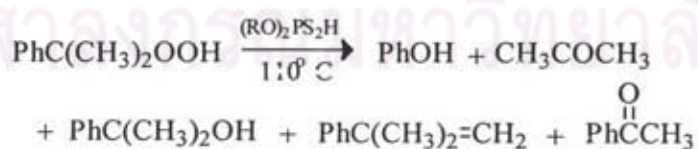
Reaction mechanism The performance of ZnDTPs is strongly influenced by the type of alcohols used for their synthesis. Table 2.3 gives an overview of the variance of performance with type of alcohol.

The way ZnDTP performs as an antioxidant is a complex interaction pattern involving hydroperoxides and peroxy radicals. The performance matrix is additionally influenced by other additives which are present in industrial or engine oil formulation.

Table 2.3 Structure activity dependency of ZnDTPs

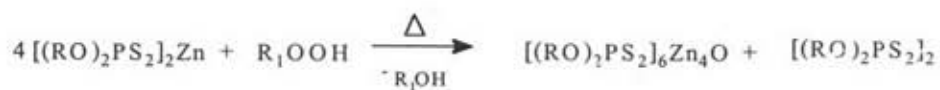
Structure	Function		Property	
	Oxidative Inhibition	Water Protection	Thermal stability	Hydrolytic stability
Primary ZnDTP				
$Zn \left[S-\overset{\overset{S}{\parallel}}{P}(OCH_2R)_2 \right]_2$	satisfactory	satisfactory	good	satisfactory
Secondary ZnDTP				
$Zn \left[S-\overset{\overset{S}{\parallel}}{P}(OCHR_1R_2)_2 \right]_2$	good	good	moderate	good
Aryl ZnDTP				
$Zn \left[S-\overset{\overset{S}{\parallel}}{P}(O-\text{C}_6\text{H}_4-R)_2 \right]_2$	moderate	bad	very good	bad

In a model system comprising cumene hydroperoxide and diverse ZnDTPs, it was demonstrated that the antioxidant mechanism proceeds by an acid-catalysed ionic decomposition of the hydroperoxide. The catalyst species is O,O'-dialkylhydrogendithiophosphate, $(RO)_2PS_2H$, derived from the ZnDTP.



Whilst the first four products are the result of an acid-catalysed cationic chain reaction, the acetophenone is formed by free radical mechanism.

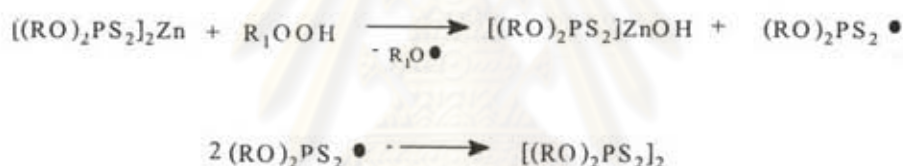
There are two inter-related mechanisms for the formation of the acid catalyst. In the first, a rapid, initial reaction of ZnDTP and hydroperoxide forms a basic ZnDTP and a disulfide.



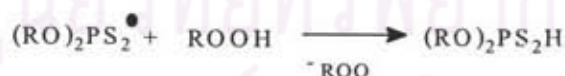
An induction period follows where the rate of decomposition of the hydroperoxide is slow. In this reaction phase the basic ZnDTP dissociates to form ZnDTP and ZnO



The ZnDTP then reacts with hydroperoxide to form additional disulfide via the dithiophosphoryl radical:



The kinetics of the reaction result in a final rapid decomposition of the hydroperoxide provided the concentration of the basic ZnDTP is low. Under these conditions the sulfur radical is unable to dimerise. Instead it reacts with hydroperoxide leading to the catalytically active acid:



Nowadays aryl ZnDTPs are less important than alkyl ZnDTPs. Very often mixtures of low (<C₅) and high molecular weight alcohols (>C₅) are used for the synthesis. If only one type of alcohol is used, R should contain at least five carbon atoms.

Organomolybdenum compounds Recent patent literature shows that these compounds are of general interest in the engine oil area. They are anti-oxidants and in addition improve the frictional and anti-wear characteristics of the lubricants. Reaction below outlines the synthesis of a typical representative of this chemistry.

Overbased phenates and salicylates Both phenates and salicylates of magnesium or calcium behave as antioxidants at high temperatures. The anti-oxidant activity may be related to hydroperoxide decomposition by the sulfur in structure, and peroxy radical scavenging by the OH group in structure.

Addition of MCO_3 to phenates and salicylates leads to the corresponding overbased products, which also act as acid scavengers.

Sulfur/nitrogen and sulfur/phosphorus compounds Other multifunctional sulfur/nitrogen, sulfur/phosphorus based additives have antioxidant and anti-wear properties.

These additives interact with peroxy radicals and hydroxides thus stabilising industrial lubricants and engine oils.

2.2.2 Pour-Point Depressants

Oils containing paraffinic hydrocarbons tend to form wax crystals at moderately low temperatures. These wax crystals prevent the oil from flowing. This is undesirable in applications where start-up may be at temperatures lower than the pour point of the oil. Although many of the paraffin elements are removed by dewaxing in the refining process, some remain in the oil. Wax, as a by-product, has become a salable and profitable by-product for the oil companies. Pour-point depressants are high-molecular-weight polymers which inhibit the formation of the wax crystals and therefore allow the oil to flow at a lower temperature. They will not entirely prevent the formation but will lower the temperature at which the wax structures start forming. They act through surface adsorption on to the wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. In the absence of long interlocking crystals or swollen particles, oil can move freely through any solid wax particles that are present.

Pour point depressant additives There is a range of pour point depressant additives of different chemical species.

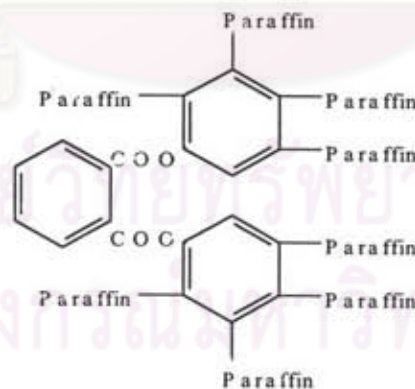
(i) Polymethacrylates

These are the most widely used pour point depressants. R in the ester has major effect on the product, and is usually represented by a normal paraffinic chain of at least 12 carbon atoms. This ensures oil solubility. The molecular weight of the polymer is also very important. Typically these materials are between 7000 and 10,000 number average molecular weight. Commercial materials normally contain mixed alkyl chains which can be branched.

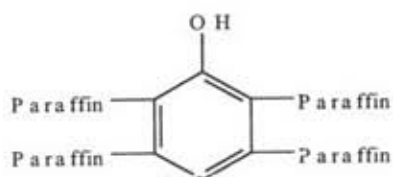
(ii) Polyacrylates

These are very similar in behavior to the polymethacrylates.

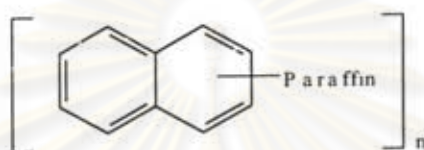
(iii) Di (tetra paraffin phenol) phthalate



(iv) Condensation products of tetra paraffin phenol



(v) Condensation product of a chlorinated paraffin wax with naphthalene



2.2.3 Corrosion Inhibitors

These additives are used in very small amounts, and the type used varies with the finished product's application. Some corrosion inhibitors improve the oil's ability to adhere tenaciously to steel surfaces and therefore prevent moisture from penetrating the protective oil film. The conditions that influence the onset of corrosion are the entrainment of atmospheric oxygen, moisture from the combustion of fuel, and stop-start running coupled with temperature cycling. In the marine diesel engine, the problem is exacerbated by contamination with fortuitous saline. Corrosion inhibitors are added specifically to cope with this electrochemical process. These additives operate by creating a physical barrier, in the form of a dense hydrophobic monolayer of chemisorbed surfactant molecules, which prevent access of the water and oxygen to the metal surface.

Corrosion inhibitors additives In the selection of an appropriate corrosion inhibitor, an important consideration is the problem of adverse competition with other additives designed to adsorb on the liquid-metal interface. Extreme pressure and/or anti-wear agents compete for the same sites as the corrosion inhibitor. Fatty amines are good corrosion inhibitors in this type of environment. However, their adverse effect on the performance of ZDDP additives often prohibits their use. Half esters or amides of dodecylsuccinic acid and phosphate esters or thiophosphates are frequently employed. A combination of inhibitors is sometimes used, for example fatty carboxylic acids or the

dimer/trimer analogues of the unsaturated acids used in conjunction with an amine or an amide and sarcosines. Shorter chain carboxylic acids and amines are used as volatile corrosion inhibitors.

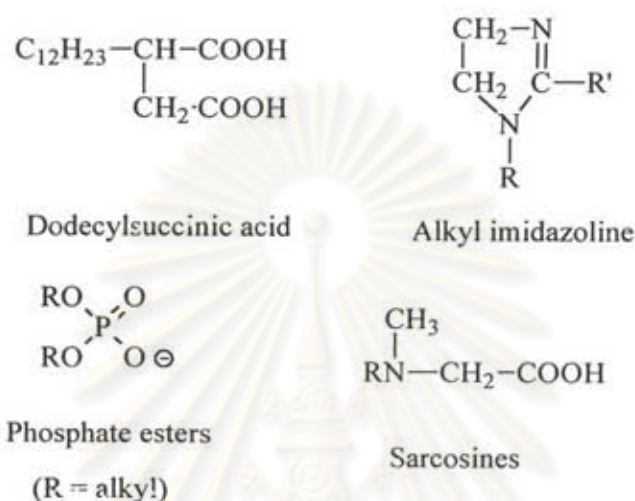


Fig 2.1 Some types of corrosion inhibitors

2.2.4 Antiwear Additives

When machine components operate under boundary lubrication (where metal-to-metal contact can and normally does occur) antiwear additives are necessary. Good examples are high-pressure hydraulic systems and engines. Zinc dithiophosphates or zinc dialkyldithiophosphates are commonly used antiwear or antiscaff additives which combine the effect of an antioxidant and corrosion inhibitor with antiwear protection. They are classified as a mild extreme-pressure or friction-reducing additive. Tricresyl phosphate has also been used in some hydraulic and circulating systems. Most of the common synthetic anti-wear additives are compounds containing phosphorus, such as zinc dialkyl(or diaryl) dithiophosphate (ZDDP), tricresyl phosphate (TCP), trixylyl phosphate (TXP) and dilauryl phosphate. One of the most widely used of all additives is ZDDP, which has anti-wear, antioxidant and corrosion-preventing properties. Like stearic acid, ZDDP initially adsorbs on the metal surface and, in this state, has mild anti-wear properties. Under the influence of heat, electron transfer can take place to produce a

chemisorbed film; the heat itself is generated by sliding. Similar mechanisms occur with the other phosphorus compounds such as tricresyl and trixylyl phosphate.

Apart from ZDDP itself, there is also a variety of the dialkyl dithiophosphates. The intermediate acid is neutralised with zinc oxide. If the intermediate acid is neutralised with a different metal oxide, a different range of dialkyl dithiophosphates are formed. The exact range of properties of the product depends on the metal atom and the alkyl group.

2.2.5 Extreme-Pressure Additives

Where film strength and extreme-pressure characteristics are needed to combat high or shock loading of components, sulfur-, phosphorus-, and /or chlorine-based additives are used. A sulfur-phosphorus combination is the most commonly used extreme-pressure additive especially in automotive and industrial gear oils. Extreme-pressure additives are activated by heat rather than pressure. They chemically react with metal surfaces to form a film, or surface compound, which gently wears or polishes off rather than allowing the mating surfaces to weld and tear loose, causing destruction. It takes time for this compound to develop in service.

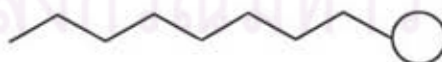
Table 2.4 Some successful extreme-pressure additives

Dilauryl phosphate	Sulphurised sperm oil
Didodecyl phosphite	Sulphurised mineral oil
Tricresyl phosphate (TCP)	Sulphur chloride treated fatty oils
Zinc dialkyl (or diaryl) dithiophosphates(ZDDPs)	Chloronaphtha xanthate
Phospho-sulphurised fatty oils	Cetyl chloride
Zinc dialkyldithiocarbamate	Chlorinated paraffinic oils
Mercaptobenzothiazole	Chlorinated paraffin wax sulphides
Sulphurised fatty oils	Chlorinated paraffin wax
Sulphurised terpenes	Sulphurised oleic acid
	Alkyl and aryl polysulphides

2.2.6 Detergents and Dispersants

These are the additives commonly used in engine oils to disperse the particles of contamination created by combustion and help prevent the formation of harmful deposits, such as sludge and varnish. Regular drain intervals and filter changes are essential to the prevention of the particles depositing in the engine. The filter removes many of these particles and products of oxidation which would tend to accelerate the rate of oxidation. Over-extended drain intervals or excessive by-products of combustion can cause the depletion of these additives and allow the contaminants to deposit themselves throughout the engine. Detergent-dispersant additives are used more to keep an engine clean than to clean up deposits already in the engine.

Calcium, magnesium, or barium soaps of petroleum sulfonic acids or synthetic sulfonic acids are some of the materials which may be used. Various compounds of barium, sulfur, and phosphorus-containing polymeric and ashless detergents are also used. They are commonly found in motor oils and, to a lesser degree, some hydraulic oils. The detergent polar substrate is made up basically of two parts as illustrated in Fig. 2.2. The hydrocarbon tail or the oleophilic group is the portion of the detergent polar substrate that acts as the solubilizer to enable the detergent to be fully compatible and soluble in base oil. The other part of the detergent polar substrate is the polar head containing a metal cation. Many metals have been incorporated into detergents but currently, based on cost/performance, the three most commonly used metals are calcium, magnesium, and sodium. These metals have largely replaced the less cost/performance effective barium materials. In addition, barium compounds may have toxic properties. Some countries limit the amount of barium allowed in consumer goods like motor oils.

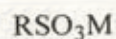


Hydrocarbon Tail
Oleophilic Group
Solubilizer

Polar Head
Metal Attachment
Point

Fig. 2.2 Detergent polar substrate.

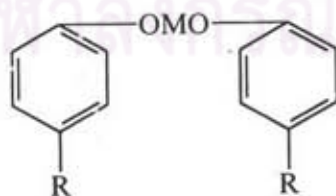
The addition of ash-type detergent additives will increase the ash residue and can be detrimental in applications where increased ash can cause increased maintenance. In engine application, where acidic conditions can easily occur, ash-type additives provide a higher and more stable TBN (total base number) to more effectively combat corrosive wear of the engine components. Detergent polar substrate types consist of four major classes: sulfonates, phenates, salicylates, and phosphonates. Sulfonates are the most widely-used detergent additives followed by phenates, salicylates, and phosphonates. Detergents have varying capacity to provide engine rust protection. Rust protection is needed, not only in low-temperature engine operation, but also for protection when the engine is not in use. Sulfonates in particular provide excellent engine anti-rust properties. Phenates, in addition to detergency characteristics, provide oxidation inhibition properties and a somewhat lower sulfated ash content at equal alkalinity when compared with sulfonates. Some diesel engine builders include a maximum sulfated ash level in their engine oil specifications. The use of salicylates is limited while phosphonate use is minimal. These additives structures are shown in Fig. 2.3.



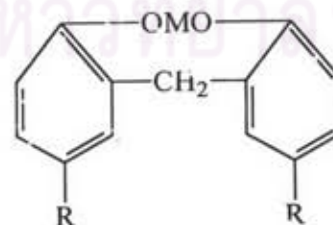
R = alkyl, aryl

Fig 2.3 Neutral sulfonate

Overbased sulfonates are formed by a complex reaction between a neutral metal sulfonate and a metal hydroxide. This complex reaction takes place using carbon.



Normal phenate



Methylene coupled phenate

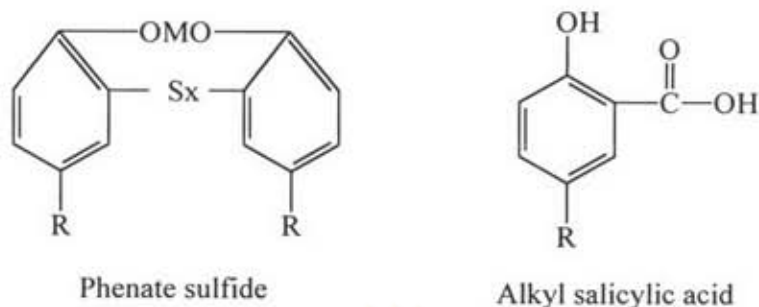


Fig 2.4 Some types of detergents

dioxide in the presence of a promoter, which is generally an alcoholic-type material. The promoter dissolves a small amount of metal hydroxide, which is subsequently reacted with carbon dioxide to form a metal carbonate. The advantage of the basic sulfonates is their greater ability to neutralize acidic bodies.

Dispersants are very effective and are used in many modern engine oils today. Dispersants are non-metallic or ashless cleaning agents. Fig 2.5 shows the stylized structure of an ashless dispersant. The structure of an ashless dispersant is similar to the structure of a detergent in that the dispersant has a hydrocarbon tail or oleophilic group which enables the dispersant to be fully soluble in the base oil used. The dispersant also has a polar head. The polarity of a dispersant is derived from the inclusion of oxygen, phosphorus, or nitrogen atoms into the molecule.

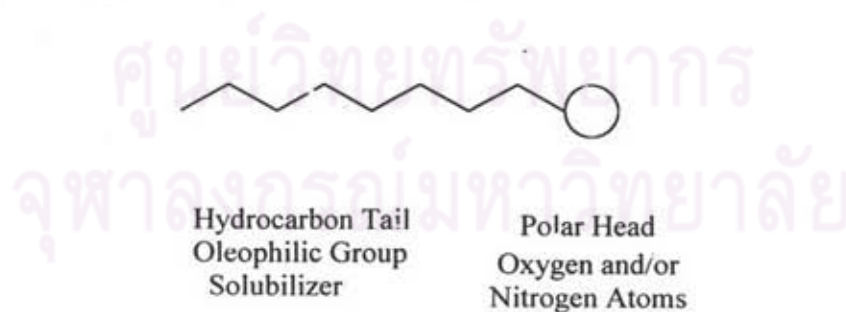


Fig 2.5 Stylized dispersant

The sludge and varnish-forming precursors, resulting as a by-product of engine fuel combustion, contaminate the engine oil as they blow by the piston rings into the

engine crankcase. Prior to the introduction of dispersants, these contaminants would settle out on critical parts of the engine hampering operation and eventually requiring engine overhaul. Ashless dispersants are designed to have their polar chemical heads attached to rather large hydrocarbon groups. As shown in Fig 2.5 these polar heads interact with sludge. The hydrocarbon groups provide the solubilizing action which maintains the potentially harmful debris in suspension in the oil. Most dispersants currently in use are prepared from polyisobutylenes of 1000 to 10000 molecular weight. There are four different types of ashless dispersants: (1) succinimides, (2) succinate esters, (3) Mannich types, and (4) phosphorus types. Their structures are shown in Fig 2.6

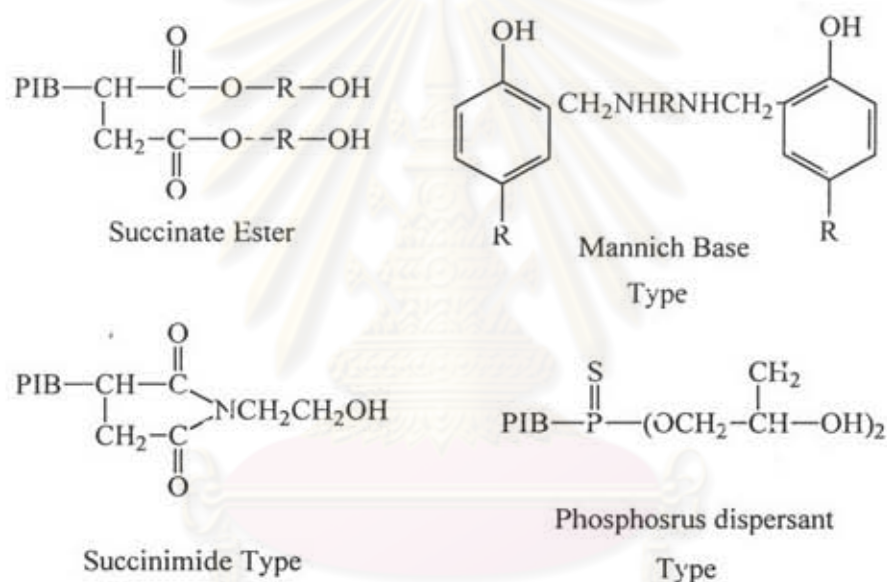


Fig 2.6 Structures of some dispersants

2.2.7 Viscosity Index Improvers

An oil thins when it is heated and thickens when cooled. The resistance of an oil's viscosity to change with temperature is called the "viscosity index." The higher the viscosity index, the more resistant an oil is to thinning with increased temperature. A viscosity index improver will increase the oil's resistance to thinning with increasing temperature. Thus, a high VI oil will resist thinning better than a low VI oil. It has resisted thinning with heat and therefore now has a high viscosity index. VI improvers are

used in some hydraulic oils, transmission fluids, motor oils, gear oils, and many other applications.

2.2.8 Defoamants

An oil's tendency to foam will depend on the type of crude, refining, viscosity, and application. A defoamant will reduce the surface tension of the oil, allowing the small air bubbles to combine into large bubbles and then dissipate into the air. Only the proper amount of defoamant should be added to an oil system.

2.3 Analytical Procedures

As described above, the commercial lubricants can be contained many additives, depend on their functions, climate of region, the types of vehicles, or any special purposes in which products can be archived.

Many analytical techniques, such as chromatography or spectroscopy, were employed to analyze the chemical additives contained in the lubricants. Most of the additives were added in the lubricating base oil in a little amount so that they can hardly be observed by the common analytical techniques. The additives should be isolated before being characterized by spectroscopic techniques. The specific isolation procedures were taken by the typical additives contained in the lubricating oil.

The successful identification of an unknown lubricant by spectroscopic methods depends, in the first instance, on the successful isolation of fractions sufficiently pure to enable their spectra to be interpreted. The separation procedures used fall into two categories: first, the preparative but low-efficiency techniques of dialysis and classical liquid chromatography using adsorbents or ion exchange resins and second, the analytical scale but more efficient techniques of thin layer (TLC), high-performance column (HPLC), and gel permeation chromatography (GPC). HPLC and GPC can be expected to be increasingly used for routine quantitative analysis in process and quality control, while TLC in particular is a useful aid to spectroscopic identification.

Description and discussed applications of the various separation techniques.

2.3.1 Dialysis

Dialysis is a very useful initial separation procedure since it provides a very clean separation between high-molecular-weight polymers (e.g., molecular weight greater than 10,000) and low-molecular-weight additives (e.g., metal sulfonates, phenates, carboxylates of molecular weight less than 1000). Other additives, such as some ashless dispersants, in the molecular weight range 2000 to 10,000 dialyze slowly and, under the test conditions which will shortly be described, portions will appear in both fractions, i.e., the dialysate and the residue. In addition to achieving this separation, the process of dialysis destroys the colloidal structure of the additive package and yields two fractions which, in contrast to the colloidal mixtures, are amenable to chromatographic analysis.

The apparatus used is shown in Fig 2.7. About 5 to 10 g oil is weighed into a surgeon's rubber fingercot, which has previously been washed with isopropanol to remove excess talc and allowed to dry in a stream of nitrogen. The open end of the fingercot was tied with glass tape over the flared end of the fingercot holder. The stuff is placed in the Soxhlet extractor as shown and supported with a glass stopper to prevent the fingercot from blocking the entrance of the sidearm. The sample in the fingercot was then extracted with boiling pure n-heptane which allows low-molecular-weight materials to diffuse through the rubber membrane and find their way into the boiler. Meanwhile, polymers and colloids were retained within the fingercot.

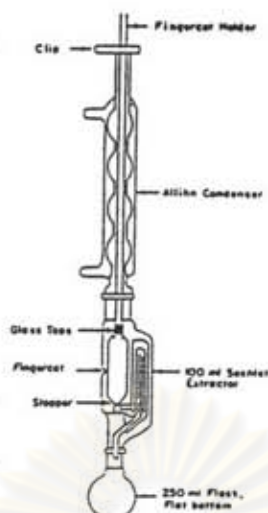


Fig. 2.7 Equipments of dialysis

2.3.2 Column Adsorption Chromatography.

Separation by displacement chromatography in a column packed with silica or Florisil using a series of eluents of gradually increasing polarity is a useful way of separating polar additives from nonpolar hydrocarbon oil in macro quantities, i.e., on a scale such that further substantial analytical work can be carried out on the fractions. It is more usual to carry out this technique on the sample, provided carbonate is absent, or on the dialysate. It can also be applied to the hydrolyzed dialysis residue, but the stronger acids, i.e., carboxylic or sulfonic may be esterified or saponified, so it is preferable to separate the hydrolyzed dialysis residue in columns packed with ion-exchange resins.

2.3.3 Methanol Extraction

Since some additives used in lubricating oil can dissolved in the polar solvents, so the extraction by the polar solvents was employed to isolate the polar additives from the lubricating oil. In this research, the polar solvent used is methanol by shaking methanol with the formulated oil about 5 minutes in the separatory funnel. Wait until the mixture separates into two phases. Separate the methanol fraction out, evaporate this fraction then take the residue to analyze furthermore.

2.3.4 Solvent Precipitation

The solvent used in this method is MEK (Methyl Ethyl Ketone). This procedure can be carried out by pour MEK into formulated oil gradually until the white precipitate formed fully. Separate the precipitate out, evaporate solvent out and then take the precipitate to analyzed furthermore. The precipitate occurred in this procedure is the polymeric additives or copolymers which perform as the viscosity index improver in the lubricating oils.

2.3.5 Hydrolysis

Dispersants or detergents usually have the hydrocarbon tails attached with polar ends. Such these additives can be extracted by means of hydrolysis reaction with acid or base to convert the additives into the salt form which dissolves in water then neutralize the solution and re-extract the additives with the proper solvent.

2.4 Literature Reviews

Many analytical methods had been used for analyzing the additives in petroleum products.

In 1960, Braithwaite isolated 2-Methyl-6-tert-butyl-p-cresol which used as an antioxidant in gasoline by column chromatography and calorimetry [23].

In 1961, Schafer and Delves examined alkyl lead compounds and antioxidants in petroleum products by paper chromatographic technique [24].

In 1965, Geldern detects zinc dithiophosphates directly in oil by TLC method, after converted to the corresponding ammonium salt [25].

Webster et al. [26] have studied the behavior of metal deactivators found in aviation lubricants and found that they produce colored complexes with the metal form of Amberlyst 15.

In 1992, S. Ashraf analyzed lubricating oil additives by supercritical fluid chromatography on open tubular and packed capillary columns. Carbon dioxide and modified carbon dioxide were used as mobile phases and detection was accomplished by flame ionization and micro UV [27].

J. Garciaacton [28] determined zinc in lubricating oils by polarography of emulsified samples and bubbling nitrogen through the emulsion.

M. Tsuchiya [29] analyzed organometallic compounds used as lubricating oil such as dialkyldithiocarbamate and dialkyldithiophosphate complexes by liquid ionization mass spectrometry.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย