

## CHAPTER II

### THEORETICAL CONSIDERATION

#### 2.1 Lubrication [1]

The principal functions of a lubricant are containment of contaminants, removal of heat and reduction of frictional effects. In order to meet all of these requirements, it is necessary to supplement the base fluid with additives of the following general nature

##### Containment of contaminants

- Dispersant
- Anti-wear additives
- Anti-rust additives
- Anti-oxidant
- Bearing corrosion inhibitors

##### Removal of heat

- Anti-oxidants
- Viscosity improvers

### Reduction of frictional effects

- Antiwear additives
- Viscosity improvers and pour point depressants
- Anti-foam agents
- Friction modifiers

## 2.2 Synthetic Base Oils [2,3]

Modern engines are frequently working under extreme conditions, thus creating lubrication problems which cannot be solved by the use of hydrocarbon components alone. The shortage of mineral oils or motor oils with low pour point plus increasing demand with respect to oil quality, for instance for aircraft engines, have both contributed to the development of synthetic lubricating fluids.

Combined requirements, such as low viscosity variations and good lubricating property over a wide range, chemical stability, aging and oxidation resistance, as well as resistance to radioactive radiation, can be satisfied in most cases only by special synthetic products.

Synthetic lubricants frequently satisfy special requirements such as non-flammability, thermal stability, resistance to oxidation and radiation much better than mineral oil products. They can be modified with respect to viscosity grade, viscosity-temperature characteristics, high-pressure stability, low

temperature behavior, corrosion and foaming characteristics, thus making possible the production of specialized lubricants. Commercial synthetic fluids are not confined to a single chemical type.

Among those of current commercial interest are the following classed:

1. Alkylated Aromatics
2. Olefin Oligomers
3. Ester of Dibasic Acids
4. Neopentyl Poly Esters
5. Polyglycols
6. Phosphate Esters
7. Silicones
8. Silicate Esters
9. Polyphenyl Ethers

### 2.3 Additives [2]

The stability is affected by the environment in which it operates. Such factors as temperature, oxidation potential and contamination with water, unburned fuel fragments and corrosives acids limit the useful life of a lubricant. It is in this that additives have made a major contribution in the improvement of the performance characteristics and the extension of the useful life of lubricants.

Today, the substances added to lubricants represent synthetic compounds or mixtures which are known under the collective name of additives. Some of the additives affect the physical properties of the base oils, other have a chemical effect. They can assist each other resulting in a synergistic effect, or they can lead to antagonistic effects. Many modern additives have several functions (multipurpose additives) and thus reduce the possibility of additives interfering with each other.

### 2.3.1 Oxidation and Bearing Corrosion Inhibitor [4-7]

The function of an oxidation inhibitor is the prevention of deterioration associated with oxygen attack on the lubricant base fluid. These inhibitors function either to destroy free radicals (chain breaking) or to interact with peroxides which are involved in the oxidation mechanism.

Among the widely used anti-oxidants are the phenolic types, aromatic amines, organocopper antioxidants, organosulfur compounds, organophosphorus compounds, zinc dialkyl dithiocarbamates and zinc dithiophosphates (ZnDTPS).

Phenolic types, aromatic amines and organocopper antioxidants are considered to be of the chain-breaking variety, whereas organosulfur compounds, zinc dialkyl dithiocarbamates, organophosphorous compounds and zinc dithiophosphates are believed to be peroxide destroyers.

The corrosion of bearing metals is generally considered to be due largely to acid reaction with the oxide bearing metal. In engine operation, these acids originate either from products of incomplete combustion of the fuel which find their way into the lubricant as blow-by gases, or are produced from oxidation of the lubricant.

Oxidation inhibitors can significantly reduce this tendency. Basic dispersants can reduce bearing corrosion by neutralization of the corrosive acids.

Other inhibitors such as the zinc dithiophosphate and the phosphorized olefins not only inhibit oxidation, but are also capable of forming a protective film on the bearing surface making it impervious to acid attack.

### The Phenolic Inhibitors

The inhibitor efficiency of phenol is markedly increased by substitution of alkyl groups in the two ortho and para positions. It is particularly enhanced when the ortho substituents are bulky groups such as tert-butyl and the para substituent is a primary alkyl group.

A variety of hindered phenols are produced commercially and employed as inhibitors in transformer turbines and engine oils.

The major structural types which are commercially available are shown in Table 2.3.1

Table 2.3.1 Major commercial phenolic antioxidants and their application

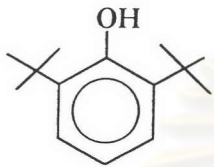
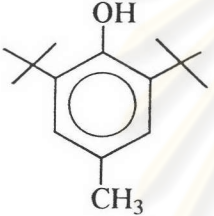
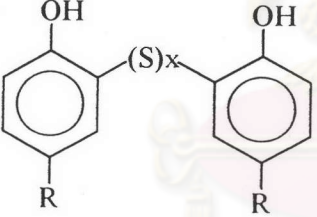
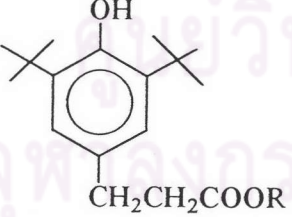
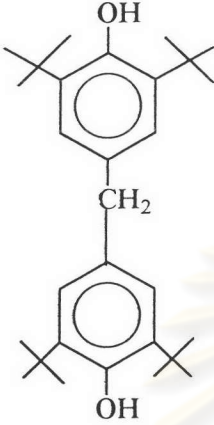
Structure	Application
	Industrial Oil
	Industrial Oil , grease
	Engine Oils
	Industrial Oils, engine Oils

Table 2.3.1 (Continued)

Structure	Application
	Industrail Oils, Engine Oils

#### Aromatic amines [8]

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

The reaction mechanism of diphenylamines is dependent on the temperature. Under low-temperature conditions ( $<120^{\circ}\text{C}$ ) the interaction with peroxy radicals predominates. Under high-temperature conditions ( $>120^{\circ}\text{C}$ ), e.g. engine oil, an extended stabilization mechanism in the form of a catalytic cycle has been suggested.

The major structural types which are commercially available are shown in Table 2.3.2

Table 2.3.2 Major commercial aromatic amines antioxidants and their application

Structure	Application
	Industrial Lubricants, Engines Oils, Automatic Transmission Fluids, Greases
	Industrial Lubricants, Greases
	Greases
	Industrial Lubricants, Engine Oils, Greases

### Organocopper antioxidants

A breakthrough in terms of controlling the oxidation of automotive oils has been achieved with the introduction of organocopper salts.



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, organo copper salts control the oxidation of engine oils.

#### Organosulfur compounds [9,10]

These compounds convert hydroperoxides into non-radical products thus preventing the chain propagation reaction.

#### Zinc diakyl dithiocarbamate

These compounds are mainly used as antioxidants although, like the ZnDTPs, they also have extreme pressure activity.

#### Organophosphorus compound

Phosphites are the main organo phosphorus 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 polyalphaolefin, hydrocracked or severely hydrotrated based stocks and white oils.

### Zinc Dithiophosphate [11]

Of greatest commercial importance in engine lubricants are the zinc dithiophosphates which not only serve as anti-oxidants but also provide both anti-wear and bearing corrosion protection. Both the alkyl and aryl derivatives are employed commercial. The alkyl derivatives are generally more effective as anti-wear additives. The aryl derivatives have a higher degree of thermal stability but are poorer in hydraulic stability. Both the anti wear and thermal stability characteristic of the alkyl compounds can be varied using different alcohols, i.e., primary vs. secondary and high vs. low molecular weights. The principal alkyls are propyl, butyl, hexyl, octyl and mixtures of these. The effect of the alkyl radical on the thermal decomposition temperature of zinc dialkyldithiophosphate (ZnDTPs) were shown in Table 2.3.3

Table 2.3.3 Effect of Alkyl Radical on Thermal Decomposition Of ZnDTPs

Alkyl Radical	Decomposition Temp. <sup>o</sup> C
Iso-propyl	196
4 methyl pentyl 2	197
n-Amyl	212

Table 2.3.3 (Continued)

Alkyl Radical	Decomposition Temp. °C
n-Octyl	>251

The stability increases with the length of the alkyl chain and is lower for branched chains than for straight chain of the same number of carbon atoms. It should be pointed out, however, that the overall performance characteristic of the ZnDTPs are not necessarily proportional to the decomposition temperature. The major structural types which are commercially available are shown in Fig. 2.1

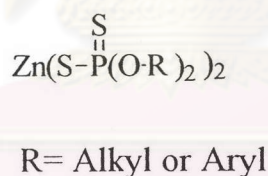


Figure 2.1 The major structural types of Zinc Dithiophosphates

### 2.3.2 Viscosity Index Improvers [1]

Viscosity Index (VI) improvers are additives which improve the viscosity temperature characteristics of oils, i.e. which reduce the decrease of viscosity with temperature. Oils containing these additives combine

the good starting and friction properties of thin oil at low temperature with the good lubricant properties of a more viscous oil at high temperature.

These viscosity improvers are generally oil soluble organic polymers with molecular weights ranging from approximately 10,000 to 1,000,000. The polymer molecule in solution is swollen by the lubricant. The volume of this swollen entity determines the degree to which the polymer increases viscosity. The higher the temperature, the larger the volume and the greater the “thickening” effect of the polymer and, hence, the less the “thinning” tendency of the oil due to increased temperature. In addition to viscosity improvement characteristics, the performance of these polymers is also dependent on the shear stability or resistance to mechanical shear and on their chemical and thermal stability.

With a given polymer system, the shear stability decreases with an increase in molecular weight. The loss due to shear is reflected in a loss in viscosity of the lubricant. On the other hand, the “thickening power” of the viscosity improver increases with an increase in molecular weight for a given polymer system. An economical balance must then be established taking into consideration the shear stability needs as well as the thermal and oxidative stability in actual engine operations.

### Polymethacrylates [12,13]

Polymethacrylate VI improvers are free-radically initiated solution copolymers. The VI improvers for engine oils have a molecular weight ( $M_w$ ) of between 250,000 and distribution ( $M_w/M_n$ ) of between 3 and 4. The products are sold commercially as concentrate which range from about 35-55% polymer. Because free radical solution chemistry can be used to produce a broad range of molecular weights and compositions, polymethacrylates find utility in virtually all lubricant areas where viscosity temperature modification is desirable. This includes both mineral oil-based applications and a range of synthetic fluids

### Olefin copolymers [14-16]

Olefin copolymer VI improvers are produced by solution polymerization of the ethylene and propylene catalyzed by soluble Ziegler-Natta catalysts. The molecular weight ( $M_w$ ) of OCP VI improvers is in the range of 50,000 to 200,000 with molecular weight distribution ( $M_w/M_n$ ) of about 2.0-2.5. The newer tapered compositions tend to be slightly higher in molecular weight with narrower molecular weight distributions (less than 2.0). OCP VI improvers are sold both as solids (typically bales of about 20-35 kg. wrapped in polyethylene) or more commonly as concentrated solution in mineral oil.

These polymers are excellent thickeners in the bulk phase and polymer content is limited by handling considerations to about 6-15%. OCP VI improver are not themselves pour point depressants, but pour-depressed versions are often sold. These are merely physical mixtures of OCP VI improver with 2-3% of a conventional pour point depressant included in the concentrate.

The excellent thickening ability of OCPs has led to extensive use in engine oils, both diesel and gasoline. However, the relatively poor low shear, low temperature viscosity behavior of OCPs together with difficulty of achieving the necessary lower molecular weights (better shear stability) have precluded significant use in most other specialty lubricants.

#### Hydrogenated styrene-diene copolymer [17]

The products in this general class include several subclasses covering either butadiene or isoprene as the diene, and either random, block or star-shaped polymers. The basic member is a random copolymer of styrene and butadiene. These contain about 50-60% styrene and 40-50 wt% butadiene. For optimum thickening, it would be desirable for the butadiene to be polymerized with a high content of 1,4-configuration.

The final products are obtained by hydrogenation using a technique which gives very high conversion on the butadiene-derived unsaturation while

hydrogenating little or none of the styrene. Molecular weight ( $M_w$ ) can be in the range of 75,000 to 200,000 with distributions ( $M_w/M_n$ ) of less than 1.5. Block copolymers of styrene and isoprene have also found commercial use. Both diblock (A-B) and triblock (A-B-A) polymers, where A represents polyisoprene and B represents polystyrene. Hydrogenated styrene-diene VI improvers have found their widest utility in gasoline and diesel engine oils. They may also be used in other applications which have only moderate requirements for shear stability, such as tractor transmission fluids and aircraft piston engine oils. However, the shear stability demands of many of the specialty application precludes the use of products which are currently available.

#### Styrene polyester [18]

This family of VI improvers are styrene-fumarate copolymers derived from esterification of approximately 1:1 styrene-maleic anhydride copolymer. Only dispersant version are available. The dispersancy is provided by either an amide or, probably more likely, the imide derived from *N*-(3-aminopropyl)morpholine. Molecular weight ( $M_w$ ) is in the range of 350,000 to 700,000 with a ( $M_w/M_n$ ) of about 3-4. The final product is sold as a 35-45% polymer concentrate.

These products are used almost exclusively in automatic transmission fluids and multipurpose tractor fluids. Minor usage may remain in engine oils, but this application is largely obsolete.

#### Concentrate-compatible PMA/OCP blends [19,20]

These products are blends of conventional PMA and OCP VI improvers. These two polymers, which are normally incompatible in concentrated form, have been made compatible by incorporation of a small amount of polymethacrylate-OCP graft copolymer. The final product is normally about 65-75% PMA and 25-35% OCP on a polymer solids basis. Molecular weight and molecular weight distributions of the two components are in the conventional range for their classes. These products are used commercially only in gasoline and diesel engine oils

#### 2.3.3 Pour point Depressants [21]

Pour point depressants prevent the congelation of the oil at low temperature. This phenomenon is associated with the crystallization of the paraffin wax which is most often present in the mineral oil fraction.

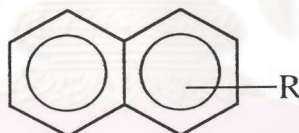
In order to obtain lower pour points, the refiner removes wax constituents which solidify at relatively high temperature by a process known as de-waxing. To de-wax completely would reduce the yield of lube oil to an



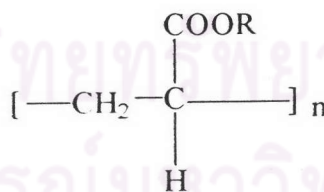
uneconomic level and also detract to an extent from the oil's lubricant characteristics. The de-waxing process is therefore supplemented by the use of additives which lower the pour point of the oil.

The pour point depressants do not prevent wax from crystallizing from the oil, but are absorbed on the wax crystals and thus reduce the amount of oil occluded on the crystal. The reduction in volume of the crystal permits flow of the lubricant. There are a range of pour point depressant additives of different chemical species.

The major structural types which are commercially available are shown in Fig 2.2

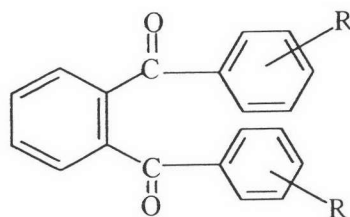


Condensation Products of a Chlorinated Paraffin Wax with naphthalene

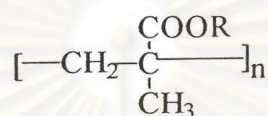


Polyacrylates

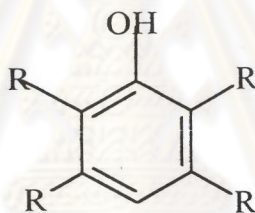
**Figure 2.2** The major structural types of pour point depressants which are commercially available



Di(tetra paraffin phenol)phthalate



Polymethacrylates



Condensation Products of Tetra Paraffin Phenol

Figure 2.2 (Continued)

### Polymethacrylates

These are the most widely used pour point depressants. R in the ester has a major effect on the product, and is usually represented by a normal paraffin 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 10000 number average molecular weight. Commercial materials normally contain mixed alkyl chains which can be branched.

#### 2.3.4 Detergent [22,23]

These compounds have been described in the literature as “detergents”. Since their function appears to be one of effecting a dispersion of particulate matter rather than one of “cleaning up” any existing dirt and debris, it is more appropriate to categorize them as dispersants.

Materials of this type are generally molecules having a large hydrocarbon “tail” and a polar group head. The tail section, oleophilic group, serves as a solubilizer in the base fluid while the polar group serves as the element which is attracted particulate contaminants in the lubricant. 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 need, 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.

Commercial detergents are generally available diluted about 50% in mineral oil and are used in engine oils in amounts ranging from 0.5% to 30%.

### Petroleum Sulfonates [22-26,28]

The petroleum sulfonates were formerly by products of the sulfuric acid treatment of oil fractions in the manufacture of the white oils. Currently, with high demand for detergent oils, sulfonate production has become the principal product.

The structure of the organic portion of the petroleum sulfonates is not completely known, and depending on the source of the crude oil, the structures include varying proportions of aliphatic, naphthenic and aromatic hydrocarbons. The majority of sulfonate detergents are in the form of barium, calcium and magnesium salts. The alkaline earth sulfonates can be prepared by direct reaction of the sulfonic acid with the metal oxide or hydroxide or by reaction of the metal chloride. Oil soluble sulfonates can be prepared which contain metal highly in excess of the stoichiometric amount required by normal sulfonate. Among the advantages of the basic sulfonates is the greater ability to

neutralize acidic bodies in addition to serving as dispersant for particulate contaminants.

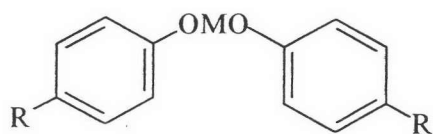
The choice of sulfonate type is usually dictated by cost versus performance. Alkylbenzene-bottoms-derived sulfonates are generally the least costly (The term “bottom” refers to the residue resulting from the distillation of alkylbenzene primary product. Bottoms are a complex chemical mixture.). They provide excellent performance as overbased metal derivatives in light-duty engine service. The more expensive mono and/or dialkylbenzene primary alkylate sulfonic acid derivatives are used to advantage in more severe engine service.

#### Phenates/salicylates/phosphonates

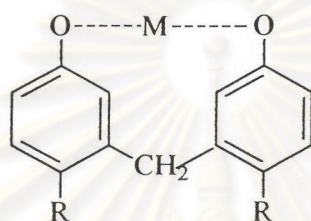
The structures of the other three important detergent polar substrates namely phenates, salicylates, and phosphonates are shown in Fig 2.3-

2.4.

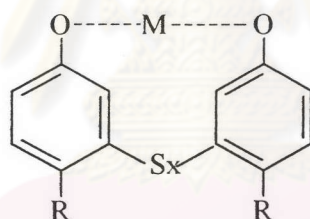
ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



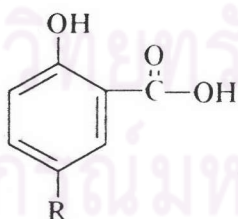
Normal phenate



Methylene coupled phenate



Phenate sulfide



Alkyl salicylic acid

**Figure 2.3** The structure of Normal phenate, Methylene coupled phenate, Phenate sulfide, Alkyl salicylic acid

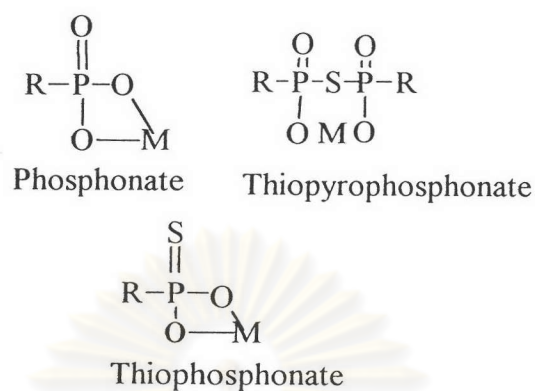


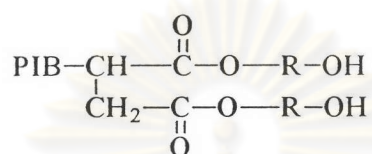
Figure 2.4 The structure of Phosphonate, Thiopyrophosphonate and Thiophosphonate

The principal functions performed by metallic phosphates in lubricating oil formulation are acid neutralization, high temperature detergency and oxidation inhibition.

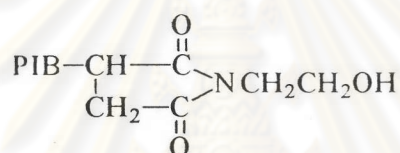
### 2.3.5 Polymeric Dispersants [27]

These ashless dispersants may serve a dual function. They can be both a viscosity index improver and consist of two general types of molecular configuration, i.e., those whose structure is similar to the ones employed as viscosity index improvers to ensure oil solubility and those containing “polar” compounds to impart the dispersancy characteristic. There

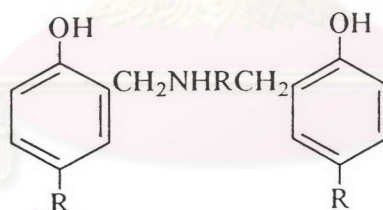
are four different types of ashless dispersants: succinimides, succinate esters, Mannich types and phosphorus types. The general formula of ashless dispersants are shown in Fig 2.5



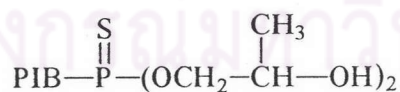
Succinate Ester



Hydroxyethyl imide structure



Mannich Base



Phosphorus dispersant

Figure 2.5 The general formula of ashless dispersants



### 2.3.6 Anti-Wear Additives [1,4]

Wear is loss of metal subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in engine malfunction. Among the principal factors causing wear are metal-to-metal contact. Presence of abrasive particulate matter, and attack by corrosive acids. Metal to metal contact can be prevented by the addition of film-forming compounds which protect the surface either by physical absorption or by chemical reactions. The zinc dithiophosphate are widely used for this purpose and are particularly effective in the reduction of wear involve train mechanisms. These compound were described under anti-oxidant and anti-bearing corrosion additives. Other effective additives contain phosphorous, sulfur, or a combinations of these elements. Abrasive wear can be prevented by effective removal of particulate matter by filtration of both air entering the engine and the lubricant during operation of the engine. Corrosive wear is largely the result of acidic blow-by products formed during combustion of the flue. This type of wear can be controlled by use of alkaline additives such as basic phenates and sulfonates.

### 2.3.7 Miscellaneous Additives [28]

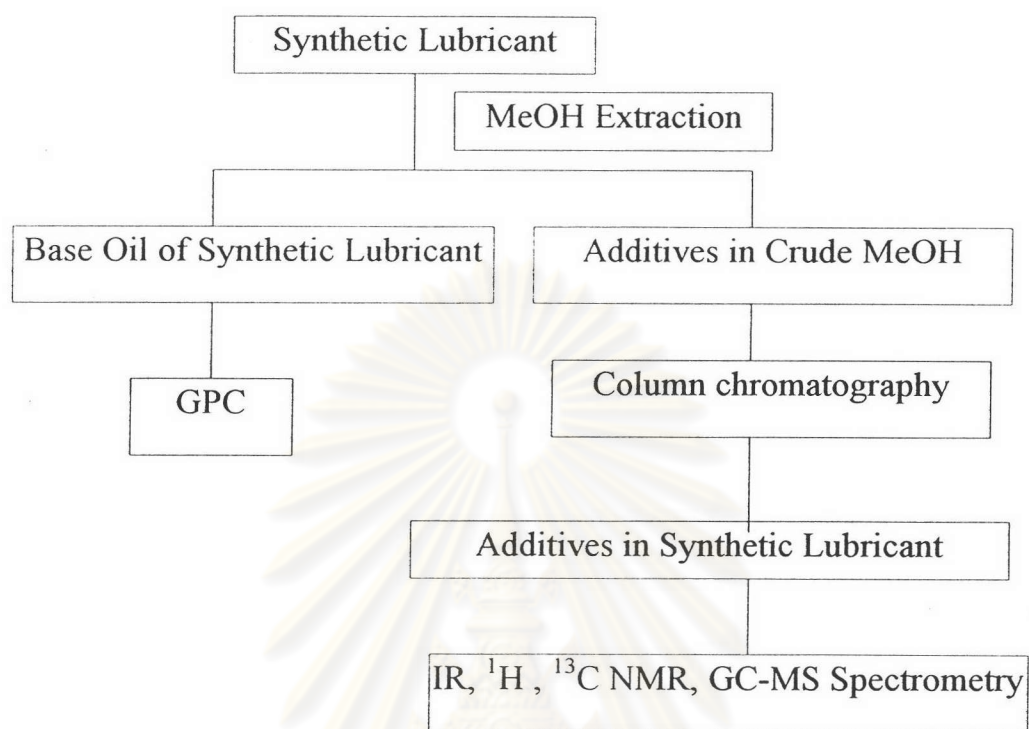
Under the category of the miscellaneous additive types are included the anti-rust compounds and foam inhibitors. Chemicals employed

as rust inhibitors include sulfonates, alkenyl succinic acids, substituted imidazolines, amines, and amine phosphate. The anti-foam agents include the silicones and miscellaneous organic copolymers.

#### 2.4 Development of a method for analyzing additives in synthetic lubricant by mass spectrometry.

Additives in synthetic lubricants were extracted with methanol. After separation and evaporation of the solvent under reduced pressure, crude MeOH of methanolic extract was obtained. Column chromatography technique was used for separating additives in the crude MeOH extract. Chemical constituents of additives in the crude MeOH extract of synthetic lubricants were analyzed by Infrared Spectrometry,  $^1\text{H}$ ,  $^{13}\text{NMR}$  Spectrometry and GLC-MS Spectroscopy to identify the chemical constituents. The molecular weight of the base oil in synthetic lubricants were analyzed by GPC-Evaporative Mass Detector (EMD).

The procedure for analyzing additives in synthetic lubricants by mass spectrometry is shown in Scheme 2.1.



Scheme 2.1

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย