CHAPTER 2

THEORETICAL CONSIDERATIONS

Soybean [1-4]

Soybeans are now the principle oilseed crop in the United States.They are believed to have been domesticated in the eastern half of northern China around the 11 th. century BC or earlier. They were later introduced and established in Japan and other parts of Asia, brought to Europe, and were introduced in the United States in the late 18 th. century or early 19 th. century. Soybeans became established as an oilseed crop in the United States in the late 1920s and attained major commercial importance during World War II.

Soybeans are the most important oilseed in international trade ; the United States, Brazil, and Argentina are the main suppliers to the export markets. The USA , Brazil, China and Argentina produce 87% of the world's soybeans. China has been a major producer for a long time, but the USA reached that status only in the 1940s and Brazil and Argentina only since the 1970s.

Soybeans are the predominant oilseed in the world. About half of the world oilseed production comes from soybeans, and this is more than the combined production of the next four oilseeds : cottonseed, peanut, sunflower, and rapeseed (canola).

Table 2-1: Soybean production (x 10^6 t) by major countries during the past 50 years .

	1940	1950	1960	1970	1980	1990
USA	2.1	7.8	16.3	30.7	48.7	52.4
Brazil	-	-	-	2.1	15.5	20.0
China	9.7	4.9	7.0	9.7	7.9	10.8
Argentina	-	-	-	-	3.4	10.5
World	11.9	17.8	28.1	45.2	81.2	107.1

Table 2-2: World vegetable oil production (x 10^6 t)

	1980	1982	1984	1986	1988
Soybean	12.8	13.8	13.4	14.8	15.0
Palm	5.2	5.6	6.9	7.9	9.0
Sunflower	4.7	5.8	6.1	6.6	7.0
Rapeseed	4.1	5.3	5.3	6.6	7.3
Cottonseed	3.2	3.4	4.2	3.2	3.6
Peanut	2.7	3.0	3.4	3.1	3.8
coconut	2.9	2.7	2.8	2.8	2.6

1. The Composition of Soybean Oil

Soybean oil consists mainly of unsaturated fatty acid more than 80%, the other is saturated fatty acid about 15%. The main unsaturated fatty acids are linoleic acid and oleic acid about 50% and 20%, respectively. The compositions of fatty acid in soybean oil show in the table 2-3.

Table 2-3 : Show Fatty Acid Composition of Soybean Oil

Unsaturated fatty acid	
Linoleic acid	55-61 %
Oleic acid	20-25 %
Lenolenic acid	6-9 %
Total	**80-85 %**
Saturated fatty acid	
Palmitic acid	10-11 %
Stearic acid	3-4 %
Total	**13-15 %**

Besides fatty acid compositions, soybean oil also consists minor components of the phospholipids about 400-700 ppm in crude oil. Soybean phospholipids contain phosphatidic acid(5%), phosphatidylinositol(20%), phosphatidylethanolamine(23%), phosphatidylcholine(39%) and unidentified components(13%).

Furthermore, some other minor components in soybean oil are given in the table 2-4.

Furthermore, some other minor components in soybean oil are given in the table 2-4.

Table 2-4 : Some Minor Components in Soybean Oil

Tocopherols(total)	530-1500 approx. mg/kg
α-Tocopherol	90-120 mg/kg
γ-Tocopherol	740-1020 mg/kg
δ-Tocopherol	240-300 mg/kg
Chlorophyll	1500 μg/kg
Hydrocarbons	300 mg/kg (squalene 150 mg/kg)
Sterols	1000-3500 mg/kg
Triterpene alcohol	600 mg/kg

The characteristics of soybean oil show in the below table.

Table 2-5 : The Characteristics of Soybean Oil

	Draft Codex (Codex,1979)
Relative density(20 °C/water at 20° C)	0.919-0.925
Refractive index (n_D^{40})	1.466-1.470
Saponification value	189-195
Iodine value	120-143
Unsaponifiable matter (g/kg)	Not more than 15

2. Uses

Soybean oil is widely used in the chemicals industry. Firstly, in the drying oil industry it is used mainly in alkyd resins. The skipped methylene unsaturated acids can be conjugated by the action of catalysts, e.g. nickel, sulphur dioxide or iodine, to produce faster-drying coatings.

Second, the epoxidation of soybean oil is carried out with performic acid , peracetic acid or hydrogen peroxide in the presence of a strong acid or ion-exchange resin. The epoxidized oil is used both as a stabilizer and plasticizer.

Moreover, the dimerized fatty acids of soybean oil are used in adhesives, coating, lubricants, printing inks and iron corrosion inhibitors. They are produced by condensing two unsaturated fatty acids in the presence of a catalyst, clay. They are further converted to polyamides for applications in adhesives, coating and inks.

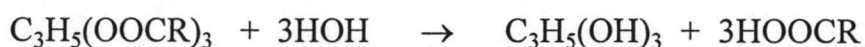## 3. The Reaction of the Fats [5]

3.1 Oxidation

Unsaturated fats are commonly oxidized at the double bonds and the oxidation products, the first of which are hydroperoxides, lead to rancidity with the loss of palatability due to obnoxious flavors and odors, and may effect the blenchability of the oil, In oil production the substances most likely to promote oxidation (pre-oxidants) are free atmospheric oxygen and traces of metals ; the process is accelerated by light. Oxidation and consequent rancidity does not, however, proceed so fast in vegetable as in animal fats

owing to the present of naturally occurring protective materials or anti-oxidants. Oxidation to hydroperoxides is measured as the "peroxide value" of the fat; this represent the reactive oxygen content, and is estimates though the liberation of iodine from potassium iodine in glacial acid and recorded in terms of milliequivalents of peroxide-oxygen per 100 grams of fats.

### 3.2 Hydrolysis

Under the proper condition of fat/water miscibility, the triglycerides of fats and oils are hydrolyzed to free fatty acids and glycol:

$$C_3H_5(OOCR)_3 \ + \ 3HOH \quad \rightarrow \quad C_3H_5(OH)_3 \ + \ 3HOOCR$$

The reaction is not a simple one; it proceeds in stages, and it is reversible. If reactants and product are not removed from the sphere of the reaction, an equilibrium depending on the concentration of the former eventually is reached. In the several methods of industrial fat splitting, a high degree of hydrolysis is ensured by using a large excess of water and repeatedly withdrawing the aqueous glycerorich phase and replacing it with water.

High temperature and high pressure accelerate aqueous hydrolysis. The temperature selected is determined by the content of polyunsaturated and particularly, conjugated polyunsaturated fatty acids in the fat because if polymerization is permitted to interfere with the hydrolysis as a competing reaction, splitting is troublesome. Hydrolysis can be autocatalytic in the presence of water, be catalyzed by metals, or be brought about by the action of the enzyme lipase. Hydrolysis is alkaline is distinguished as "saponification" and give rise to soaps and glycerol as equation:

$$C_3H_5(OOCR)_3 \ + \ 3NaOH \quad \rightarrow \quad C_3H_5(OH)_3 \ + \ 3NaOOCR$$
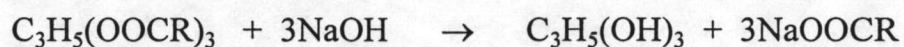
3.3 Hydrogenation

It is generally acknowledged that hydrogenation or " harding" of fats has contributed more to the interchangeability of fats and fatty oils than any other process and therefore is a factor in the maintenance of stable economic conditions in the production of all fats. Broadly, hydrogenation process add hydrogenation atom at the double bonds of unsaturated fats converting these into the higher melting point saturated fats. Additional information hydrogenation will be found later.

3.4 Halogenation

The reaction which is used as a measure of the proportion of unsaturated constituents present in a fat. This is halogenation to the double bonds of the unsaturated fatty acids and the quantity of halogen taken up is expressed in terms of iodine as the " iodine value ", which is the number of grams of iodine absorbed per 100 grams of fat.

Purposes of Lubrication [6-8]

Purposes of lubricantion are:

- To reduce friction

- To curb power losses

- To preclude movable machine components from the wear or the
  seizure

- To eliminate or lessen heat generated during operation

- To ensure smooth operation and a longer service life for
  machines

- To improve productivity

Above purposes are accomplished by supplying a suitable lubricant in the friction surfaces of machines in a proper manner. Lubrication plays a vitally important role in satisfactorily operating the engines and other machines of a manufacturing plant as it provides various functions, including friction reduction, sealing, cooling, stress dispersion, anticorrosive and rust-preventive action, and dustproofing.

In addition to ensuring satisfactory operation of bearings and gears, lubrication helps improve finishing accuracy and working efficiency in cutting, rolling, drawing, pressing, and various other metal working processes. The following table shows the specific purposes of lubrication for different uses.

Table 2-6 : Purposes of Lubricants

Purposes / Uses	Reduction of friction	Cooling	Sealing	Stress dispersion	Anti-corrosion	Dust-proofing
Bearings;						
- Miscellaneous bearings	x				x	x
- High-quality high-speed bearing	x	x				x
- Ball and roller bearings	x	x		x	x	x
Slide way	x				x	x
Cylinder	x	x	x		x	x
Gears;						
- Simple, small, and open gears	x			x		
- High-quality gears	x	x		x	x	
Cutting	x	x			x	
Rolling	x	x			x	
Wire,rod,tube drawing	x	x			x	
Press drawing	x	x			x	

The Basic Function of Lubricant

1. The Reduction of Friction

Simple stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, there by preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of a lubricating oil is it viscosity. It is factor in the formation of lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effect of oils and the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equilibrium satisfactory results are obtained only with the use of an oil of proper viscosity under the operated condition.

The basic concept of viscosity is shown in Figure 2-1 where a plate is being drawn at uniform speed over a film of oil. The oil adheres to both the moving surface at the stationary surface. Oil in contact with the moving surface travels at the same velocity (U) as that on surface, while oil at contact with the stationary surface is at zero velocity.
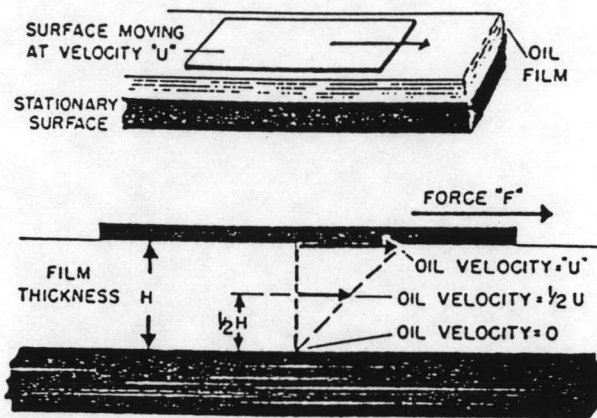
Figure 2-1 : Concept of dynamic viscosity

In between, the oil film may be visualized as made up of much longer, each being drawn by the layer above it is a friction of velocity "U" that is proportional to its distance above the stationary plate (Figure 2-1: lower view). A force (F) must be applied to the moving plate to over come the friction between the fluid layers. Since the friction is the results of viscosity, the force is proportional to viscosity.

2. Heat Removal

Another important function of a lubricants is to act as a coolant, removing heat generated eighter by friction or other sources such as via combustion process or transfer by contacting with substances at a higher temperatures. In performing this function, it is important that the lubricant remains in a relatively unchanged condition. Changes in thermal and oxidation

stability which affect its ability to reach the areas involved will materially decreases its efficiency in this respect.

3. Containment of Contaminants

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic combustion products, particular matters which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

The Principle Properties and Tests

1. Color, ASTM D1500

The color of lubricating oil is measured in a standardized glass container by comparing the color of the transmitted light with that transmitted by a series of numbered glass standard. Color varies from partically clear or transparent to opaque or black. This test is used for manufacturing control purposes and is important since the color is readily observed by the customer.

2. Specific Gravity , ASTM D1298

Specific gravity is the ratio of the mass of a volume of the substance at the standard temperature to the mass of the same volume of water at the same temperature. The standard temperature for specific gravity are 15.6/15.6°C (60/60°F). In the petroleum industry the API gravity scale is

almost universally used as the measure of the density of a petroleum product . API gravity is an arbitrary scale, calibrated in degree and related to specific gravity by

$$\text{API gravity} = \frac{141.5 \ - \ 131.5}{\text{sp.gr. } 15.6/15.6°C}$$

The API gravity value increases as the specific gravity decreases. Since both density and gravity change with temperature, determinations are made at a controlled temperature and then corrected to a standard temperature by using special table.

3. Viscosity , ASTM D445

Viscosity is the most significant property of a lubricating oil. To meet a particular application, viscosity is generally the most important controlled property for manufacture and selection.

The viscosity of a fluid is a measure of its internal resistance to flow by reason of the forces of cohesion between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extent of the viscosity change depends on the crude source of the oil and molecular weight of the constituent components.

The instrument used to determine the viscosity of an oil is called the viscometer. In generally, two types are used: the saybolt and kinemetic viscometers. Kinematic viscosity is the more common and measured by timing the flow of a fixed amount of oil through a capillary tube under gravitational

force at a standard temperature. Test temperatures are usually at 40 and 100 °C for centistokes units.

4. Viscosity Index , ASTM D2270

The viscosity index is an empirical number which indicates the effect of temperature changing on the viscosity of the oil . When the temperature increased, all lubricating oils film thin out or have lower viscosity. Likewise, oils become thicker or more viscous as the temperature reduces. The higher the VI, the smaller its change in viscosity for a given change in temperature. The VI of an oil is calculated from viscosity determined at two temperatures by means of tables polished by ASTM . Table on viscosity determined at both 100 and 212 ° F , and 40 and 100 °C are suitable.

5. Pour Point , ASTM D97

Most oil contains some dissolved wax. As an oil is chilled, this wax begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets in the structure. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test.

The pour point is the lowest temperature at which the oil will just flow under specified test condition and is roughly equivalent to the tendency of an oil to cease flowing from a gravity-fed system or container. Since the size and shape of the containers, the head of oil, and the physical structure of the solidified oil all influence the tendency of the oil to flow, the pour point of the oil is, and not an exact measure of , the temperature at which flow ceases under

the service conditions of a specific system. The importance of the pour point is limited to applications where low temperature are likely to influence oil flow.

6. Flash Point , ASTM D 92/93

The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire. This test of lubricating oil is determined by the open-cup method, usually called Cleveland Open Cup, and abbreviated COC.

7. Oxidation stability

The most important chemical aspect of lubricant is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and insoluble resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impair the efficiency of the lubricant.

Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps, the nature of the hydrocarbons in the lubricants having a considerable influence on the nature of the oxidation process.

Viewed chemically the reaction mechanism is known to be limited by peroxide or hydroperoxide formation . The thermogravimetric balance (TG) is the one of the recent technique developed to evaluate thermal behavior of different chemical compounds. It is useful in evaluating the effect

of temperature on the weight loss of the compounds. Applying the procedure to the different chemical structure base oils has been taken into consideration.

Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300°C. Higher than 300°C, the sample weight begins a rapid and continuous loss. Such a weight loss is typical to what occurs in tested samples in the absence of oxygen , i.e. due to thermal decomposition only. But , in the presence of oxygen is observed at temperature around 350°C or higher which leads to retard decreasing in weight loss. These temperatures can be named oxidation points. At higher temperatures than these oxidation points, weight loss was rapid and continuous again until the complete decomposition and oxygenated resins remains nearly constant with further increase in temperature. The oxidation points can be used as an indication for base oil thermooxidation stability.

Property and Structure and Relationship [9]

The most important characteristics of oil are therefore their viscosity and viscosity index, the pour point which must be compatible with climate conditions, the resistant to oxidation, and the ability to protect against corrosion. The base oil does not usually have all these properties and must be improved with appropriate additives.

In the table 2-7, show quantitatively that the most interesting structure for hydrocarbons containing 20 - 40 carbon atoms are the highly branched isoparaffin and monocyclic hydrocarbons, saturate or not, with long aliphatic chains and preferably five carbon atoms in the ring.

The straight, long-chain paraffin are wax-like and therefore their concentration must be minimized, especially in those oils for application at low

temperature. On the other hand, branched-chain paraffin can be very desired constituents in a lubricant because of their good stability and viscosity temperature characteristics. The longer the side chains in the molecule, the more marked do does attractive fraction become.

The disable properties still exist in those napthenes in which the number of ring per molecule is low, but the side chains and connecting links are linked and parafinic. With increasing ring condensation and shortening of parafinic chain, the viscosity and temperature characteristics of hydrocarbons progressively worsen in respect of their stability of lubricants.

Table 2-7: Lubricating Oil Properties of Some Typical Hydrocarbon Structures

Structures	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin	Very high	High	Good	Nil
Isoparaffin with linear chain	High	Medium	Good	Medium
Isoparaffin with isomerized chains	High	Low	Good	High
Highly substituted isoparaffin	Medium	Low	Good	Medium
Single ring with long aliphatic chain	High	Low	Good	High
Polycondensed naphthenes	Low	Low	Medium	Nil
Polycondensed aromatics	Very low (< 1)	Low	Week	Nil

Synthetic Lubricant

Synthetic lubricants have been used for many years. In the rarely 1930s, synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and the US. In the US, the development of a process for the catalytic polymerization of olefins led to the formulation of automotive crankcase lubricants with improved low temperature performance. These products were not commercialized due to the inherent cost of the new synthetic base fluids and to improve in the performance was one of the driving forces behide the development of similar products by Zorn although the main objective was to overcome the general shortage of petroleum base stocks.

With the exception of the special circumstances of World War II, synthetic lubricants did not become commercially significant until after the war. In general, the improved properties of lubricants achieved with the early synthetic base stocks could be obtained more cost effectively by improved formulations based on mineral oils. However, the requirements for lubricants, particularly military and aero-engine lubricants, to perform over increasing temperature ranges, has stimulated the continuing development of synthetic lubricant technology. Synthetic lubricants are now found in all areas of lubrication such as automobiles, trucks, marine diesels, transmissions and industrial lubricants, as well as aviation and aerospace lubricants.

Many compounds have been investigated as possible base stocks for synthetic lubricants. Gunderson and Hart (1962) identified over 25, of which seven types are of major importance.

1. Polyalphaolefins

2. Alkylated aromatics

3. Polybutenes

4. Aliphatic diesters

5. Polyolesters

6. Polyalkyleneglycols

7. Phosphate esters

Other materials such as silicones, borate esters, perfluorcethers and polyphenylene ethers are also of importance, but their applications are restricted due eighter to high cost or to performance limitations.

Some of primary applications for synthetic lubricants are listed in Table 2-8.

Table 2-8 : Primary Applications for Synthetic Lubricants

Field of service	Synthetic fluids used
Industrial:	
Circulating oils	Polyglycol, SHF, Synthetic ester
Gear lubricants	Polyglycol, SHF
Hydraulic fluids (fire resistant)	Phosphate ester, Polyglycol
Compressor oils	Polyglycol, Synthetic ester, SHF
Gas turbine oils	SHF, Synthetic ester
Greases	SHF
Automotive:	
Passenger car engine oils	SHF, Synthetic ester
Commercial engine oils	SHF, Synthetic ester
Gear lubricant	SHF
Brake fluids	Polyglycol
Aviation:	
Gas turbine oils	Synthetic ester
Hydraulic fluids	Phosphate ester, Silicones, SHF
Greases	Silicones, Synthetic ester, SHF

SHF: Synthesized Hydrocarbon Fluids such as polyalphaolefins, alkylated aromatics and polybutenes.

Synthetic Ester Lubricant [1,10,11]

Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and greases formulations. The inherent biodegradability of ester molecules offers added benefits to those of performance.

The direct effect of the ester group on the physical properties of a lubricant is to lower the volatility and raise the flash point. This is due to strong dipole moments, called the London forces, binding the lubricant together. The major type of esters and their feedstocks are reviewed in Figure 2-2. The presence of the ester group also other properties such as:

1. Thermal stability

2. hydrolytic stability

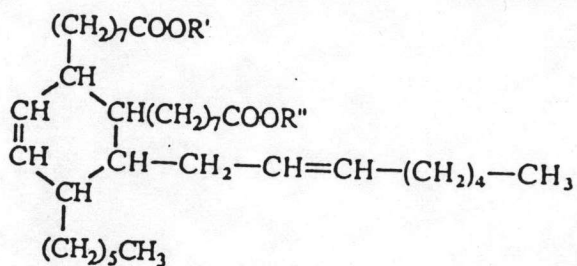3. Solvency

4. Lubricity

5. Biodegradability

Diester (dioates)

R'OOC(CH$_2$)$_n$COOR''
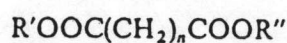
$n = 4$ = adipates
$n = 7$ = azelates
$n = 8$ = sebacates
$n = 10$ = dodecanedioates
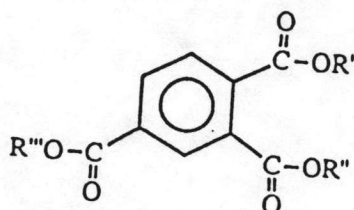
R',R'' = linear, branched or mixed alkyl chain

C36 dimer acid esters

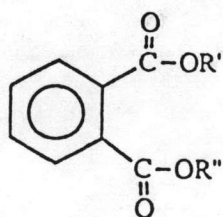R',R'' = linear branched or mixed alkyl chain

This is a typical structure encountered in dimer acids, the ester can also be fully hydrogenated
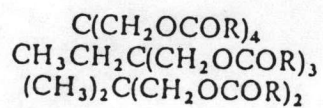
Trimelliatate ester (1,2,4- benzene tricarboxylate)

R',R'',R''' = linear, branched or mixed alkyl chain

Phthalate esters (1,2- benzene dicarboxylate)

R',R'' = linear, branched or mixed alkyl chain

Polyols (hindered esters)

C(CH$_2$OCOR)$_4$
CH$_3$CH$_2$C(CH$_2$OCOR)$_3$
(CH$_3$)$_2$C(CH$_2$OCOR)$_2$

Pentaerythritol esters
Trimethylolpropane esters
Neopentylglycol esters

R = Branched, linear or mixed alkyl chain

Figure 2-2 : Ester type

1. Manufacture of ester

The manufacturing process of esters consists of three distinct processes. They are esterification, filtration and distillation. The fundamental reaction process is that :

$$\text{Acid} \quad + \quad \text{Alcohol} \quad \rightleftharpoons \quad \text{Ester} \quad + \quad \text{water}$$
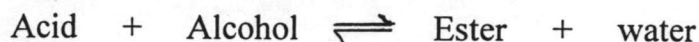
This reaction is reversible, but is driven to completion by the use of excess alcohol and removal of water as it forms. The use of an azeotroping agent, e.g. toluene, to aid water removal is optional.

The acid and alcohol can be reacted thermally, usually in the presence of a catalyst in an esterification reactor. Possible catalysts include sulfuric acid, p-toluene sulfuric acid, tetra alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorus oxides and stannous octanoate. After the ester has been formed, unreacted acid is neutralized using sodium carbonate or calcium hydroxide and removed by filtration.

Typical reaction condition are 230°C and 50-760 mmHg pressure. A significant amount of alcohol vaporizes along with the water and must be recovered. This is accomplished by condensing the reactor vapors and separating the resulting two-phase liquid mixture. The alcohol is then returned to the reactor.

Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol(NPG), trimethylol propane(TMP) or pentaerythritol(PE), with a monobasic acid to give the desired ester. When making neopolyol esters, excess acid is used because the acid is more volatile than the neopolyol and is therefore easy to recover from the ester product.

2. Physicochemical Properties of Ester Lubricant

Mineral oil base stocks are derived from crude oil and consist of complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the otherhand, are prepared from man-defined properties that can be tailored to specific applications.

Many lubricant requirements are translated into specific properties of an oil measurable by conventional laboratory tests, e.g. viscosity, evaporation, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricants of the lubricant, and many of these can only be measured satisfactorily by elaborate and expensive rigs specially developed to simulate performance.

A wide variety of raw materials can be used for the preparation of ester type base fluids and this can effect a number of lubricant properties including:

2.1 Viscosity

The viscosity of an ester lubricant can be altered by:
- increasing the molecular weight of the molecule be
    * increasing the carbon chain length of the acid
    * increasing the carbon chain length of the alcohol
    * increasing the number of ester groups
- increasing the size or degree of branching
- including cyclic groups in the molecular backbone
- maximizing dipolar interactions

One disadvantage of very long chain molecules is their tendency to shear into smaller fragments under stress.

2.2 Flow Properties

The viscosity index(VI) of an ester lubricant can be increased by:

- increasing the acid chain length
- increasing the alcohol chain length
- increasing the linearity of the molecule
- not using cyclic groups in the backbone, which lowers the VI even more than aliphatic branches
- molecule configuration-viscosity indices of polyol esters tend to be somewhat lower than diester analogues due to the more compact configuration of the polyol molecule

The pour point of the lubricant can be decreased by:

- increasing the amount of branching
- the positioning of the branch-branching in the center of the molecule gives better pour points than branches near the end
- decreasing the acid chain length
- decreasing the internal symmetry of the molecule

As can be seen from the above lists, there is a natural trade-off between viscosity index and pour point. For instance by increasing the linearity of the ester the viscosity index improves but the pour point increases. Esters made from mixtures of normal and branched acid (having the same carbon number) have viscosity indices between those of the normal and

branched acid esters, but have lower pour points than esters used from eighter branched or normal acids.

2.3 Lubricity

Ester groups are polar and will therefore affect the efficiency of anti-wear additives. When a too polar base fluid is used, it, and not the anti-wear additives, will cover the metal surfaces. This can result in higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives.

Esters can be classified in terms of their polarity, or non-polarity by using the following formula(Vander Waal,1985)

$$\text{Non-polarity index} = \frac{\text{total number of C atoms} \times \text{molecular weight}}{\text{number of carboxylic group} \times 100}$$

Generally, the higher the non polarity index, the lower the affinity for the metal surface. Using the above formula it can be seen that as a general rule, increasing molecular weight improves overall lubricity. Esters terminated by normal acids or alcohol have better lubricities than those made from branched acids/alcohol, while esters made from mixed acids/alcohol have lubricities intermediate between esters of normal acids/alcohol and esters of branched acids/alcohol.

2.4 Thermal Stability

The ester linkage is an exceptionally stable one; bond energy determinations predict that it is more thermally stable than the C-C bond.

The advantage in thermal stability of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. It has been found that the absence of hydrogen atoms on the beta-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of such hydrogen atoms enables a low energy decomposition mechanism to operate via a six-membered cyclic intermediate producing acids and 1-alkenes . When beta-hydrogen atoms are replaced by free radical mechanism. This type of decomposition requires more energy and can only occur at higher temperature .

Short linear chains generally give better thermal stability than long branched chains, while esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight also increases flash points.

2.5 Hydrolytic Stability

The hydrolytic stability of esters depends on two main features:

- processing parameter
- molecular geometry

If the final processing parameters of esters are not tightly controlled they can have a major effect on the hydrolytic stability of the ester.

Such processing parameters include: acid value, degree of esterification, and catalyst used during esterification and the level remaining in the ester after processing.

esters must have a low acid value, a very high degree of esterification and a low ash level before the effects of molecular geometry will begin to assert themselves.

Molecular geometry can affect hydrolytic stability in several ways. By sterically hindering the acid portion of the molecule (hindrance on the alcohol portion having relatively little effect) hydrolysis can be slowed down. To this purpose, terminal di-branched acids (e.g. neoheptanoic acids) have been used. However, when using these feedstocks, there are penalties to be paid, namely very long reaction times to achieve complete esterification, and poor pour points. The hydrolytic stability of neopolyol esters can generally be regarded as superior to that of dibasic esters.

2.6 Solvency

This can be divide into compatibility with additives and other lubricants, and elastomer compatibility.

(I) Compatibility with additives and other lubricants : Esters are generally fully compatible with mineral oils. This gives them three major advantages. First, there are no contamination problems therefore esters can be used in machinery that previously used mineral oil. In addition, they can be blended with mineral oil (semi-synthetics) to boost their performance. Second, most additive technology is based on mineral oil and this technology is usually directly applicable to esters. Third, esters can be blended with other

synthetics such as polyalphaolefins(PAOs). This gives esters great flexibility, whilst blending with other oils gives unrivalled opportunities to balance the cost of a lubricant blend against its performance.

(II) Elastomer compatibility : Elastomers brought into contact with liquid lubricants will undergo an interaction with the liquid diffusing through the polymer network. There are two possible kinds of interaction, chemical (which is are) and physical. During physical interactions two different processes occur:

- absorption of the lubricant by the elastomer, causing swelling

- extraction of soluble components out of the elastomer, causing shrinkage

The degree of swelling of elastomeric material can depend on:

- size of the lubricant-the larger the lubricant the smaller the degree of swelling

- molecular dynamics of the lubricant-linear lubricants diffuse into elastomers quicker than branched or cyclic lubricants

- closeness of the solubility parameters of the lubricant and the elastomer. The 'like dissolves like' rule is obeyed

- polarity of the lubricant. It is known that some elastomers are sensitive to polar ester lubricants. The non-polarity index can be used to modal elastomeric seal-swelling trends for specific ester types.

Several polar esters are well known industrial plasticisers. Non-polar base stocks, such as PAOs, have a tendency to shrink and harden

elastomers. By carefully balancing these compounds with esters, lubricants which are neutral to elastomeric materials can be formulated.

2.7 Environment Aspect

Growing environmental awareness has turned the threat to our waters into a major issue. The environment can become polluted in many ways, for example oils and oil-containing effluent can have devastating consequences for fish stocks and other water fauna.

(I) Ecotoxicity : In Germany materials are classified according to their water endangering potential of Wassergahrdungklasse(WGK). Substances are given a ranking of between 0 and 3.

WGK 0 Not water endangering

WGK 1 Slightly water endangering

WGK 2 Water endangering

WGK 3 Highly water endangering

Esters generally have the following rankings:

Polyols, polyoleates, C_{36} dimer esters, diesters   0

Phathalates and trimellitates   0-2

This shows esters to have a low impact on the environment.

(II) Biodegradability : The general biochemistry of microbial attack on esters is well known and has been well reviewed. The main steps of ester hydrolysis, beta-oxidation of long chain hydrocarbons and oxygenates

attack on aromatic nuclei have been extensively investigated. The main features which slow or reduce microbial break down are:

- position and degree of branching (which reduces β-oxidation)

- degree to which ester hydrolysis is inhibited

- degree of saturation in the molecule

- increase in molecular weight of the ester

3. Application Areas

3.1 Engine Oils

It is now widely accepted that synthesized fluids, such as polyalphaolefin/ester blends, offer a number of inherent performance advantages over conventional petroleum base oils for the formulation of modern automotive engine oils.Practical benefits which may derive from their use include improved cold starting, better fuel and oil economy, together with improved engine cleanliness, wear protection and viscosity retention during service. Fluid types used in the development of automotive oils, eighter commercialized or considered for commercialization, include PAOs - more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkelated aromatic hydrocarbons, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programs conducted over the last ten years has shown that a blend of PAO and an organic ester provides an excellent base fluid for the formulation of synthesized crankcase oils.

Low temperature viscosity perhaps the single most important technical feature of a modern crankcase lubricant. Cold starts are a prime cause of engine wear which can be mitigated only by immediately

effective lubricant circulation. Furthermore, motor vehicles are increasingly required to operate reliably in arctic conditions. Esters provide this essential low temperature fluidity and, because of their low volatility, do so without any sacrifice of lubricant efficiency at high operating or ambient temperatures. Low volatility is especially important in the context of the modern trend towards smaller sump capacities and longer oil change intervals.

3.2 Two-Stroke Oils

Ester lubricants (such as C_{36} dimer esters and polyoleates) offer a number of advantages over mineral oils as the lubricant component of two-stroke engine mixtures. First, the clean-burn characteristics result in less engine fouling with much reduced ring stick and lower levels of dirt build-up on ring grooves, skirts and undercrowns. Ignition performance and plug life are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil fuel dilution ratios of 50:1 whereas esters can be used at 100:1 and even 150:1. This higher dilution factor results in reduced oil emissions which is a benefit in environmentally-sensitive applications such as marine outboard engines and chainsaw motors. Third, in some applications, such as engines used to power snowmobile-type vehicles, low temperature performance is important. In these applications, esters with low pour point (down to -56°C) are very suitable.

Finally a 25% decrease in the amount of PHAs (polyaromatic hydrocarbons) in the exhaust emissions of a two-stroke engine has been found when a carboxylic ester has been used in place of a mineral oil. PHAs have been found to be one of the major contributors to the carcinogenic nature of

exhaust emissions. Ester can also be used to reduce the level of smoke emitted by the engine.

3.3 Compressor Oils

This sector of the market covers a wide range of compressor types, used for a number of different gases. Diesters and phthalates have found their major application in air compressor lubricants, but are also used in compressors handling natural gas. In reciprocating compressors, where oils of rather higher viscosity are preferred, trimelliate esters can be used. Diesters and polyol esters may also be blend with PAOs for use in the various compressor types.

Diesters have inherently good oxidation resistance and low volatility (3-10%, according to viscosity) when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, and low order of toxicity for vapor safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradability can also lesson their environment impact. Diesters generally have high viscosity indices, giving them a wide temperature range without the use of viscosity improves. A further advantage of esters is esters is their good thermal conductivity which allows them to conduct heat away from heat sources more effectively than mineral oils. Specific heat values of 5-10% higher than mineral oils enable esters to "soak" up heat and allow the compressor to operate at cooler temperatures.

3.4 <u>Aviation Oils</u>

The bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The requirements placed on jet engine oils, namely lubricating, oxidation and aging stability, cannot be met by hydrocarbon oils. The first generation of oils (type 1) were diesters but, over the last 25 years, these have slowly lost ground to the more expensive (type 2) polyol esters. Some diesters are still used in less-demanding applications, e.g. for small private aircraft, turbo-prop engines, etc. Type 2 aviation gas turbine lubricants are produced to a viscosity of 5 cSt (at 100 °C). For some military applications, where operability at low temperatures is vital, the corresponding viscosity is reduced to 3 cSt.

Industrial Lubricant [11-14]

Industrial lubricants comprise a wide variety of products which, depending on their application, differ widely in their chemical and physical properties. With respect to properties, one can say that industrial lubricants involve all classes of lubricants applied in practice.

1. Bearing Lubricant

Bearing are the most important machine elements used in all branches of industrial machinery. They permit smooth, low-friction linear or rotary motion between two surfaces. Bearings function by applying a sliding or rolling action. Bearings based on sliding action are called plain bearings,

whereas those involving rolling action are referred to as rolling-element bearings or antifriction bearing.

Bearing can be lubricated by gases, liquid lubricants, greases, or solid lubricants. The main function of the lubricant is to keep the surfaces apart so that no interaction can occur, thus reducing friction and wear. Bearing lubricated by gassed include aerodynamic and aerostatics bearing(externally pressurized feed). Generally, in externally pressurized bearings the solids are separated by a fluid film supplied under pressure to the interface. The fluid may be a liquid, in which case the mode of lubrication is called hydrostatic.

2. Compressor Lubricants

In industry, compressors are widely used for compressing many types of gases in order to store and/or transport them, eighter as compressed gas or as liquids. There are three main types of compressors, namely reciprocating, rotary and turbo-type air compressors. Reciprocating compressors employ a piston and cylinder with valves. Rotary compressors can be further divided into two types: sliding vane and screw. The former operate by trapping gas in a succession of cells, the latter by compressing gas in intermeshing screws. Reciprocating and rotary compressors bring lubricant and gas into intimate contact over a large area of exposed surface under high pressure and high temperature. Such conditions promote chemical reactions. Consequently, when compressing air, lubricants with excellent oxidative stability must be used. Turbo-type air compressors operate continuously by the velocity of gas. In these compressors the lubricant does not come into contact with compressed air, therefore the requirements are less severe.

There are three main groups of compressor lubricants for gas compressors, lubricants for vacuum pumps. Depending on the application, various classes of lubricating oils, including mineral oils of various levels of refining, semi-synthetic, and/or synthetic oils are used. Some of the oils for gas compressors may contain a wide variety of additive.

3. Hydraulic Lubricants

Hydraulic systems (i.e. hydraulic power transmission equipment) serve a wide range of purpose where multiplication of force is required, or where correct and reliable control gear must be provided.Developments in automation have significantly extended the use of hydraulic equipment. Typical hydraulic equipment consists of a circulating system. Usually sliding vane pumps, piston pumps and gear pumps are used. Although lubricants for hydraulic systems must also reduce friction and prevent wear of the mating elements, especially pump components, in practice they are usually called hydraulic fluids.

Hydraulic fluids represent one of the most important groups of industrial lubricants, being widely used in industrial hydraulic fluids are also applied in land, sea and airborne transport , as well as in brake system. The selection of hydraulic lubricants and the specifically required properties depends on the hydraulic system operating conditions. In systems with a high leakage rate, non-toxic hydraulic lubricants with adequate biodegradability must be employed in order to avoid polluting the environment. Hydraulic lubricants can be divided into four classes mineral oil based products, synthetic lubricants, emulsions, and water-based fluids.

4. Industrial Gear Lubricant

The main functions of a gear lubricant are wear prevention and friction reduction by providing a lubricating film between the gear mating elements. In the case of enclosed gears, the lubricant also has to carry away the heat developed during friction.

The choice of oil viscosity depends on the transmitted power and pinion speed. Generally, the lubricant viscosity decreases as the speed increases, and increase as the power increases. This relates mostly to lowloaded spur gears. In cases where conditions of the tooth engagement are particularly severe or where gears are subjected to shock load, the use of tribological additives is essential.

For highly loaded spur, helical, worm and bevel gears, lubricants containing tribological additives such as sulphurised and phosphorous-containing additives are used. These provide excellent anti-wear and extreme pressure protection over a wide range of conditions.

High viscosity residual lubricants with good adhesion are used for open gears. Industrial gear lubricants for more severe conditions are based on polypropylene glycol, their characteristics being high load-carrying capacity, very high viscosity index and low pour point. They also possess low frictional characteristics which provide more power transmission. Special greases and semi-fluid gear lubricants are also employed. For example, a lithium soap/synthetic oil based lubricant provides outstanding low steel/bronze frictional characteristics in wide temperature ranges, and long life properties.

5. Turbine Lubricant

There are three main categories of turbines ; gas turbines, steam turbines, and water turbines. Gas turbines are mostly used in aircraft, though some aircraft-derived gas turbines are used for propulsion of naval vessels or for industrial purposes, e.g. stand-by generation of electricity. Industrial gas turbines are usually robust. The same is true of steam turbines.

In steam turbine lubrication systems, a pump transports the lubricant from the storage tank through a filter and oil cooler to all lubrication points. Consequently, the lubricant must not only provide reliable lubrication, but must also serve as a coolant, hydraulic fluid, gear lubricant for geared turbines, and prevent rusting of the turbine components. Since the oil is in intimate contact with steam, condensation water, metals, and air, it requires high oxidative stability and satisfactory separation from water. In order to prevent malfunction of turbine hydraulic system a low tendency to air entrainment is essential.

These requirements have been met by special turbine lubricants, usually formulated from highly refined paraffinic base oils, with high viscosity temperature characteristics, and adequate oxidation and corrosion inhibitors. Such oils have excellent oxidation stability, very high demulsibility and resistance to foaming, and are also able to rapidly release entrained air.

6. Metalworking Lubricants

One of the purposes of metalworking processes is that of creating a new shape. Usually the processes bring into contact two solids; the tool and the workplace. The contact involves either the plastic flow of metals (metal

forming processes) or the creation of a new shape by controlled removal of excess material(metal cutting process). The creation of new shapes by metalworking processes involves high friction, high temperatures and tool wear. Consequently, metalworking lubricants influence both the effectiveness of these processes, and the overall efficiency of the manufacturing operation.

By removing material in the form of chips, the operation is referred to as metal cutting which involves two important processes ; the formation of a chip from the workpiece by the tool, and movement of the chip across the face of the tool. Thus, it is extremely important to provide a lubricant that reduces friction and removes heat as rapidly as possible.

7. Process Oil

Process oils are not typical lubricants and are mostly used as processing aids in manufacture. They are generally additive-free mixtures of crude oil hydrocarbons and include products such as medicinal white oils, technical white oils, bright process oils, and dark process oils. Medicinal white oils are composed exclusively of isoparaffins and alkylnaphthenes. Technical white oils are less refined products than medicinal white oils and are composed of saturated hydrocarbons, though they may also contain a slight amount of aromatic compounds. Bright process oils include both yellow raffinates and brown distillates. Dark process oils are extracts from solvent refining of mineral base oils.

Process oils are widely used in various industrial processes, including rubber, plastics, pharmaceutical, food, cosmetics, printing ink, textile and other industries.

8. Textile Oils

These oil are used in the fibers and textile industries either to lubricate the textile machinery, or as components of process oils used for the working of natural fibers, the production and processing of synthetic fibers, or the finishing of intermediate of final products. Textile oils are often made from technical white oils and oxidation inhibitors, plus agents ensuring removal of the oils by washing, even after a long period of use. High quality products also contain additives that assist in removing oil stains from the fabrics.

9. Slideway Oils

Slow moving slides and tables in machine tools are subject to a jerky motion due to alternating slipping and sticking of the sliding surfaces. Consequently, specially developed lubricants are required to prevent and/or reduce the stick-slip phenomenon. Slideway oils usually contain polar surface-active compounds, mostly fatty acid derivatives, together with anti-wear additives and oxidation inhibitors. The polar surface-active agents form oriented boundary layers which prevent adhesive friction.

10. Cylinder Oils

These products are highly viscous mineral oils produced from raffinates of high boiling vacuum residues, or from brightstocks and fatty oils. The latter improve water displacement characteristics of the cylinder oil and provide better adhesion of the lubrication film to the cylinder walls. Cylinder

oils, also known as compounded cylinder oils, are used for lubrication cylinders, values, and other moving parts of steam engines.

Transesterification [15]

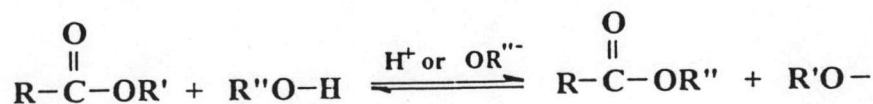$$R\text{-}CO\text{-}OR' \ + \ R''OH \ \rightleftharpoons \ R\text{-}CO\text{-}OR'' \ + \ R'OH$$

Transesterification is catalyzed by acid (H_2SO_4 or dry HCl) or base (usually alkoxide ion). These two reactions occur by mechanisms that are identical with alcoholysis of esters as follow.
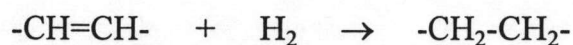
1. For Acid-Catalyzed Transesterification
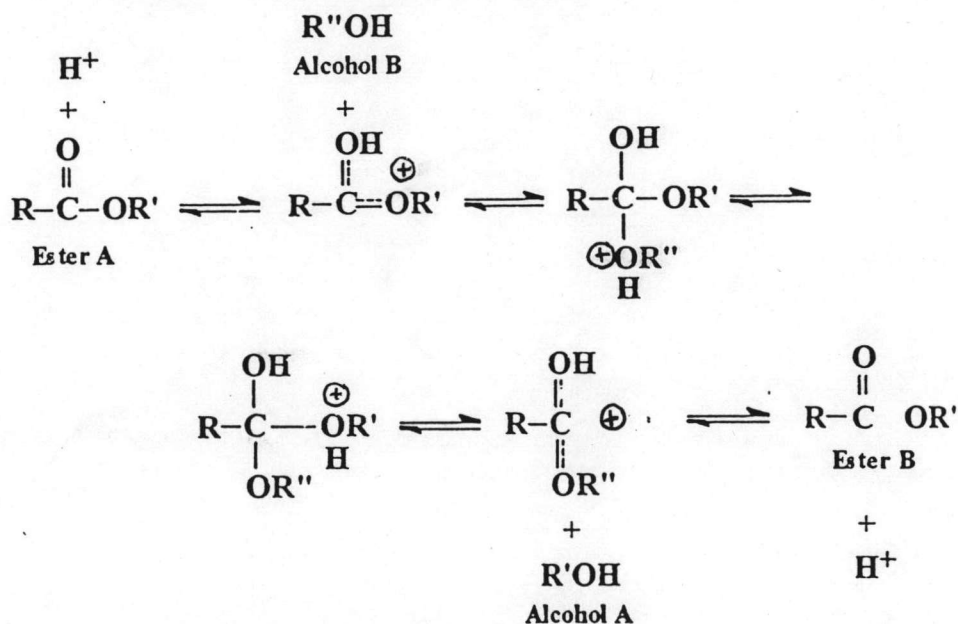
2. For Base-Catalyzed Transesterification

Hydrogenation [16]

1. Mechanism of Hydrogenation

The basic of hydrogenation of and unsaturated carbon-carbon double bond appears to be very simple but is extremely complex.

$$-CH=CH- \quad + \quad H_2 \quad \rightarrow \quad -CH_2-CH_2-$$

As this reaction shows, hydrogenation can take place only when the three reactants, the unsaturated oil, the catalyst and hydrogen gas, have been brought together in a heated stirred reactor with hydrogen available under pressure in the headspace of the reactor. In general, a heterogeneous reaction involves the following series of steps

1. diffusion of reactant(s) to catalyst surface
2. adsorption
3. surface reaction
4. desorption
5. diffusion of product(s) from catalyst surface

Each unsaturated group of the fatty acid chain can transfer back and forth between the main body of the oil and the bulk surface of the catalyst. These unsaturated groups can be adsorbed on the catalyst surface and can react with a hydrogen atom to an unstable complex that is a partially hydrogenated double bond. Some of the complexes may react with another hydrogen atom to complete the saturation of double bond. If the complexes does not react with

another hydrogen atom, a hydrogen is removed from the adsorbed molecule and the new unsaturated bond is desorbed. Thus not only are some of the bonds saturated, but some may also be isomerized to new positions or new geometric forms.