

CHAPTER II

THEORETICAL CONSIDERATIONS

Lubricating oil [4,5]

There are two essential sources from which the base lubricant fluids are obtained. These are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties suitable for lubricant purposes.

A lubricant is used to reduce the coefficient of friction between the rubbing surfaces in machinery, thereby reducing energy losses. The lubricant also prevents direct contact of the rubbing surface since under proper condition of lubrication a film of the lubricant is maintained between these surfaces. This prevents failure due to seizure and also reduces wear. The friction heat generated by the rubbing surfaces is removed by the lubricant acting as a coolant or heat transfer medium. In internal combustion engines the lubricant also seals the piston and cylinder wall at the compression rings so that the high pressure gases in the combustion chamber will not leak past the rings and cause power losses. Briefly, the lubricant reduces energy losses from friction, reduce wear, serves as a coolant and may also seal. Most lubricating oils are derived from petroleum; however, some synthetic lubricants are also important in use.

Essential properties of the lubricating oil are viscosity, viscosity temperature relation, viscosity-pressure relation, and oiliness. The changes in these properties are minimized when the oil does not undergo chemical change during use. Therefore, characteristics such as the following are important: stability toward oxidation and other chemical change, resistance to decomposition when exposed to elevated temperatures, and ability to resist emulsification. For various applications special properties are important such as detergency for severe operating conditions in internal combustion engines or extreme pressure load-carrying properties for hypoid gear lubrication.

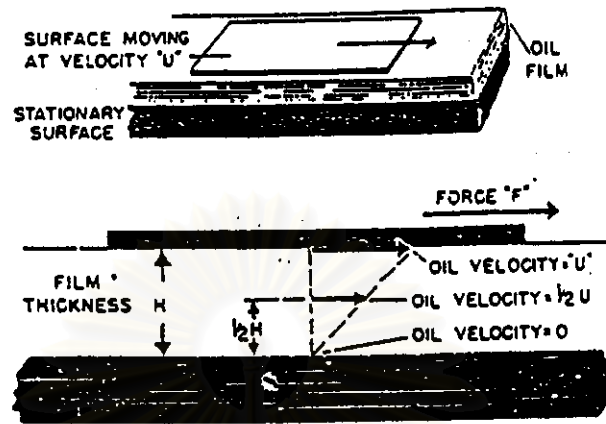


Figure 2-1: Concept of dynamic viscosity[6]

1.2 Heat removal: Another important function of a lubricants is to act as coolant, removing heat generation either 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 remain in a relatively unchanged condition. Change in thermal and oxidation stability which affect its ability to reach the areas involved will materially decreases its efficiency in this respect.

1.3 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, particulate matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

2. Lubricating base oil composition [7,8,9,10]

Materials suitable for the production of lubricating oil are comprised principally of hydrocarbon containing from 25 to 35 or even to 40 carbon atoms per molecule.

The molecule in the lubricating base oil consists essentially of one long carbon atom chain to one or both ends of which a ring system or short branch may be attached. Monocycloalkanes and monoaromatics usually have several short (e.g. methyl) branches on the ring. Most of the compounds are paraffin-naphthenes with cycloparaffinic ring attached to paraffinic chain.

Aromatic compounds usually have cycloparaffinic ring attached to them along with long paraffinic chain. Polyaromatics usually have all their ring in the single condensed nucleus which also might have short branch attached. Polycyclic saturates may have all the ring in a single condensed system or two or more ring system may be separated by alkyl chains. Aromatic compounds may also be in the form of biphenyls and their derivatives. Thus the lubricating oil are made mainly of three general types:

- . Straight- and branched chain paraffinic compounds.
- . Polycyclic and fused-ring saturated hydrocarbons based on cyclopentane prototypic ring structures, collectively known as naphthenes.
- . Aromatics, both mono and polynuclear, which are unsaturated ring structure.

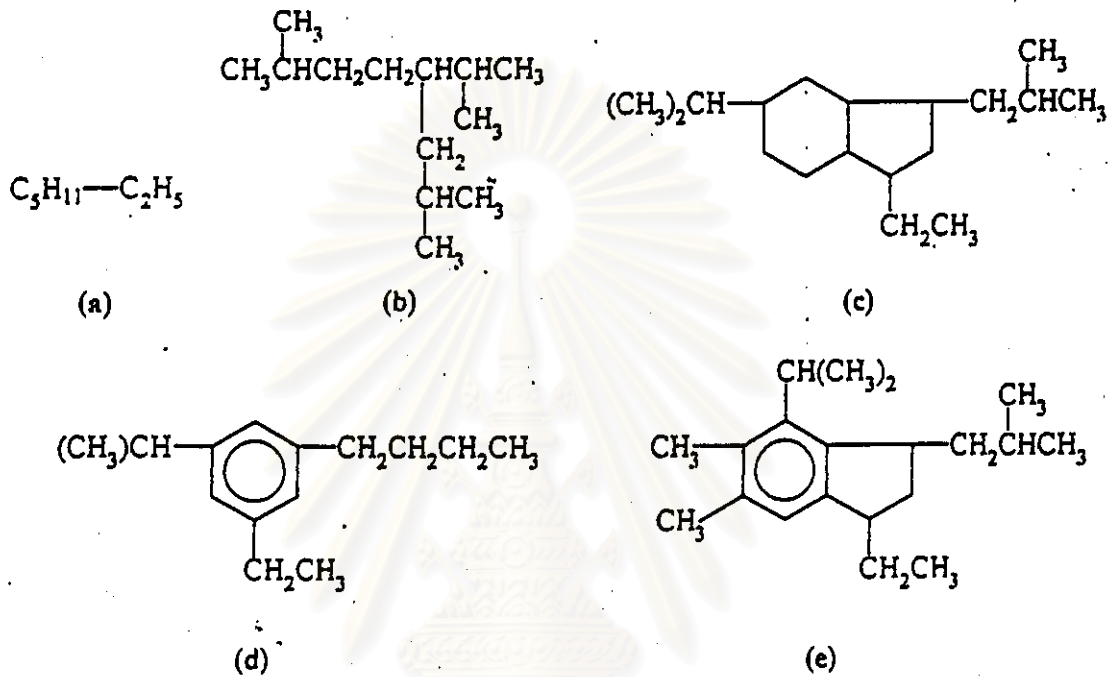


Figure 2-2 : Typical structures in lube oil -(a) n-paraffin , (b) isoparaffin, (c) cycloparaffin, (d) aromatic hydrocarbon, (e) mixed aliphatic and aromatic ring [8]

3. Properties and Test of Lubricating Base Oil [6,11,12,13]

Some of the most commonly tests for physical or chemical properties of lubricating oil are outlined in the following sections, with brief explanations of significance of the test from the standard point of the refiner and consumer.

For detailed information on methods of test, the reader is referred to the American Society for Testing and Materials Handbooks of "Annual Standards for Petroleum Products and Lubricants," the British Institute of Petroleum Handbook "Standard Methods for Testing Petroleum and its products," The United States Federal Test Method Standard No.791, and similar types of publications used in a number of other countries.

3.1 Physical properties

3.1.1 Specific Gravity : Specific gravity is the ratio of the mass of the volume of the substance at the standard temperature to the mass of the same volume of water at same temperature. The standard temperatures 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 degrees and related to the specific gravity by

$$\text{API gravity} = \left[\frac{141.5}{\text{sp.gr. } 60/60^{\circ}\text{F}} \right] - 131.5$$

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

3.1.2 Viscosity : Viscosity is the most significant property of a lubricating oil to meet a particular application, viscosity is generally the most important for controlling the properties in manufacture and selection.

Viscosity is an index for measuring of internal resistance to the motion of the fluid by reason of the cohesion forces between molecules. It decreases with increasing temperature and increases considerably with large increasing pressure. The extend of the viscosity change depends upon the crude oil source and molecular weight of the constituent components.

Kinematics viscosity is the more common and measured by timing the flow rate of the fixed amount of oil through a capacity tube under gravitational force at the standard temperature (at 40 ° and 100 °C).

The units of viscosity used in conjunction with this method is the centistock (cSt). This unit may be converted to the other viscosity systems (Saybolt, Redwood, Engler) using a suitable tables.

The main objective of lubrication is providing a film between lode-bearing surface. The selection of the correct viscosity for the oil is aimed at the balance between a viscosity high enough to prevent the lubricated surfaces from contacting and low enough to minimize energy losses caused by having too viscous a lubricant.

3.1.3 Viscosity Index : The viscosity index (VI) is an empirical number which indicates the effect of temperature changing on the viscosity of the oil. When the temperature increase, all lubricating oils thin out or have lower viscosity. Likewise, oils become thicker or more viscous as the temperature decrease. An oil having a higher VI is less sensitive to temperature than does an oil with the lower VI. The VI of an oil is calculated from viscosities determined at two temperatures by means of tables published by ASTM. Table based on viscosities determined at both 100 °F (40 °C) and 212 °F (100 °C) are available.

3.1.4 Pour Points : Most oil contain some dissolved wax and, as 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 stop flowing from a gravity-fed system or container. Since the size and shape of the container, the head of the oil, and the physical structure of the solidified oil all influence the tendency of the oil flow, the pour point of the oil is, and not an exact measure of, the temperature at which flow ceases under the service condition of the specific system. The importance of the pour point is limited to applications where low temperatures are likely to influence oil flow.

3.1.5 Flash points : The flash points test gives an indication of the presence of volatile components in the oil, and it is the temperature to which the oil must be heated under specified test conditions to give off sufficient vapor to form a mixture which will ignite in the presence of an open flame.

3.1.6 Color : The color of lubricating oil is measured in a standardized glass container by comparing the color of the transmitted light with that transmitted by the series of numbered glass standards. Color variation in lubricating oil is resulted from difference in crude oils, viscosity, method, and degree of treatment during refining. The test is use for manufacturing control purpose and is important since the color is readily observed by the customer.

3.2 Chemical properties [13]

3.2.1 Oxidation Stability : The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can led to the development of corrosive organic acids and insoluble

resinous matter, and a marked increase in viscosity of the lubricant, all of which seriously impaired the efficiency of the lubricant.

The thermogravimetric balance (TG) is one of the recent techniques 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.

The Oxidation points can be used as an indication for base oil thermoxidation stability. From Figure 2.2, the difference between typical model curve for (TG) thermal and thermoxidation stability of lubricating oil usually include the following variable or parameter :



Figure 2-2 : Comparison between typical model curves for both thermal and thermoxidation stabilities. [13]

- Oxidation points ; i.e., temperature at which the rate of weight loss decrease due to the formation of high molecular weight oxygenated compounds.

- Oxidative compounds ; i.e., weight of oxygenated compound in milligrams which remains in the pan of the balance at the oxidation point. Higher than that point, the oxidative compounds start to carbonize and finally evaporate completely as CO_2 .

The thermal stability curve shows that the sample first evaporates gradually, and then faster indicating that sample decomposition occurred and continued over the temperature range from 300°C up to 400°C where nearly 90 percent of the original sample weight is lost. Above 400°C , the residue and impurities start to be continued then remain stable up to about 600°C .



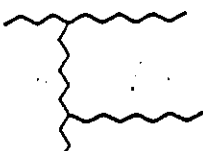
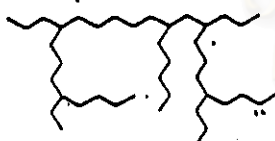
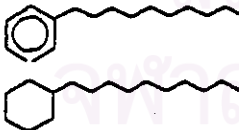
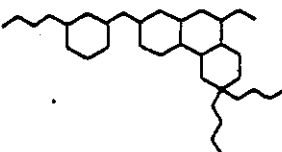
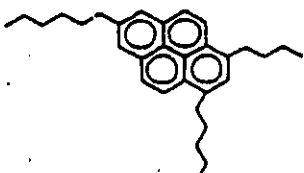
4. Property and Structure Relationship [14]

The most important characteristics of oils 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. The effect of difference type of compounds on the properties of lubricating oil can be seen from table 2-1.

Table 2-1 shows qualitatively that the most interesting structure for hydrocarbons containing 20 to 40 carbon atoms are the highly branched isoparaffin and monocyclic hydrocarbon preferably, saturate or not, with long aliphatic chain preferable five carbon atoms in the ring.

The straight, long-chain paraffins wax-like must be minimized, especially in those oils for application at low temperature. On the other hand, branched -chain paraffins can be very desirable constituents in a lubricant because of their good stability and viscosity temperature

Table 2-1 : Lubricating oil properties of some typical hydrocarbon structures [15]

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 (< 0)	Low	Weak	Nil

characteristics. The longer the side chains in the molecule, the more marked do does attractive fraction become.

The desirable properties still exist in those naphthenes in which the number of ring per molecule is low, but the side chains and connecting links are long and paraffinic. With increasing ring condensation and shortening of paraffinic chain, the viscosity/temperature characteristics of hydrocarbons progressively worsen in respect of lubricants stability.

Synthetic Lubricants [6,15,18]

Synthetic lubricants have been used for many years in the early 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 polymerisation 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 improvement in the performance of lubricants based on mineral oils. In Germany, low temperature performance was one of the driving forces behind the development of similar products by Zene 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 simulated 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 :

- polyalphaolefins
- alkylated aromatics
- polybutenes
- aliphatic diesters
- polyolesters
- polyalkylene glycols
- phosphate esters

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

Some of the primary applications for synthetic lubricants are listed in Table 2.2

The primary performance advantage of synthetic lubricants is the extended range of service temperatures. Their outstanding flow characteristics at extremely low temperatures and their stability at extremely high temperatures mark the preferred use of these lubricants. The comparison of some important physical and chemical properties of the most important synthetic lubricants are shown in Table 2.3. [16]

Table 2.2: Primary applications for synthetic lubricants

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

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

Table 2-3: Comparison of some important properties of major synthetic lubricants

Properties	Type							
	A	B	C	D	E	F	G	H
Viscosity Index	4	5	2	4	2	2	2	3
Pour Point	5	4	1	3	3	1	2	3
Liquid range	4	5	2	3	3	2	2	2
Oxidation stability	4	4	2	4	3	2	2	3
Thermal stability	4	4	4	4	3	3	2	2
Volatility	4	4	2	3	3	1	1	2
Flash temperature	5	5	5	5	4	4	4	2
Hydrolytic stability	1	1	1	1	3	4	4	3
Corrosion protection	1	1	1	1	3	4	4	4
Miscibility with mineral oil	-	1	1	1	5	2	2	4
Solubility of additive	1	1	2	1	4	2	2	1
Toxicity	3	1	1	5	3	3	3	4
Biodegradability	4	5	5	5	2	1	1	2

Types of major synthetic lubricants

- A : Mineral oils
- B : Polyisobutenes
- C : Polyalphaolefins
- D : Alkylated aromatics
- E : Polyalkylene glycol
- F : Dicarboxylic acid esters
- G : Polyol esters
- H : Phosphate esters

Evaluation

- 1 : Excellent
- 2 : Very Good
- 3 : Good
- 4 : Moderate
- 5 : Poor

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Synthetic Organic Esters [8,12,16,17,18]

Synthetic organic esters come into importance as lubricants during World War II. They were used in Germany in mineral oil blends to improve low temperature properties and to supplement scarce supplies of petroleum. There have been used as jet engine lubricants since the early 1950s. Ester used in lubricants have excellent physical properties compared with an SAE 10 weight grade mineral oil [Table 2.4].

Table 2-4 : Physical properties of synthetic organic esters [17]

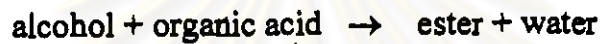
properties	Ester	Mineral oil
Viscosity		
@ 100 °C	4.6	5.2
@ 40 °C	21.0	29.5
@ -17.8 °C	474	a
@ -40 °C	5465	a
Viscosity index	140	102
Pour point, °C	-57	20
Flash point, °C	243	218
Distillation,		
% overhead @ 400 °C	3	20

The ester and the mineral oil have similar viscosities at 100 °C. The ester, however, has a very low pour point because it contains no wax, so it retains its fluidity at much lower temperatures. It has at much higher viscosity index, which is indicative of its excellent viscosity temperature characteristics. The ester also has very low volatility, apparent from the high flash point and low percentage distilled at 400 °C. It readily dissolves most additives and helps retain deposit precursors in solution. This solvency property renders ester based lubricant unsuitable for use with various compounds commonly found in

paints and elastomers. The major type of esters and their feedstocks are reviewed in Table 2-5 and Table 2-6.

1. Manufacture of Ester

An ester is an organic, oxygen-containing material formed by the reaction of alcohol and organic acid.



This reaction is reversible, but is driven to completion by the used of excess alcohol and removal of the water as it forms. The used of azeotropic agent, e.g. toluene, to aid water removal is optional.

The acid and alcohol can be reacted thermally, usually in the present of a catalyst in an esterification reaction. 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 was neutralized using sodium carbonate or calcium hydroxide and removed by filtration.

Typical reaction conditions are 230 °C and 50-760 mmHg pressure. A significant amount of alcohol vaporized along with water 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 monobasic acid.

Table 2-5 The major types of ester [17]

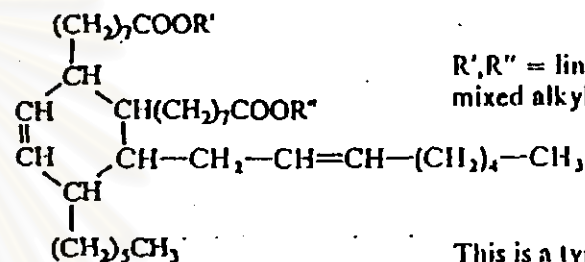
Diesters (dioates)



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

- n = 4 = adipates
- n = 7 = azelates
- n = 8 = sebacates
- n = 10 = dodecanedioates

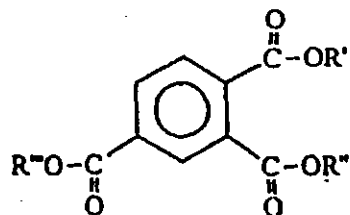
C₃₆ dimer acid esters



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

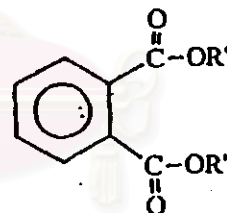
This is a typical structure encountered in dimer acids, the ester can also be fully hydrogenated

Trimellitate esters (1,2,4-benzene tricarboxylate)



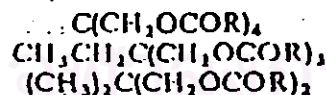
R',R'',R''' = linear, branched or mixed alkyl chain

Phthalate esters (1,2-benzene dicarboxylate)



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

Polyols (hindered esters)



Pentaerythritol esters
Trimethylolpropane esters
Neopentylglycol esters

R = Branched, linear or mixed alkyl chain

Table 2-6 : Summary of ester properties [12]

	Diesters	Phthalates	Trimellitates	C ₃₆ dimer esters	Polyols	Polyoleates
Viscosity at 40 °C	6 to 46	29 to 49	47 to 366	13 to 20	14 to 35	8 to 95
Viscosity at 100 °C	2 to 8	4 to 9	7 to 22	90 to 185	3 to 6	10 to 15
Viscosity index	90 to 170	40 to 90	60 to 120	120 to 150	120 to 130	130 to 180
Pour point, °C	-70 to -40	-50 to -30	-55 to -25	-50 to -15	-60 to -9	-40 to -5
Flash point, °C	200 to 260	200 to 270	270 to 300	240 to 310	250 to 310	220 to 280
Thermal stability	Good	Very good	very good	Very good	Excellent	Fair
Conradson carbon	0.01 to 0.06	0.01 to 0.03	0.01 to 0.40	0.20 to 0.70	0.01 to 0.10	-
% Biodegradability	75 to 100	46 to 88	0 to 69	18 to 78	90 to 100	80 to 100
Costs (PAO =1)	0.9 to 2.5	0.5 to 1.0	1.5 to 2.0	1.2 to 2.8	2.0 to 2.5	0.6 to 1.5

2. Physicochemical properties of ester lubricants

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 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 affect a number of lubricant properties including :

2.1 Viscosity

The viscosity of an ester lubricant can be altered by :

- increasing the molecular weight of molecule by
 - 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 the tendency to shear into smaller fragments under stress.

2.2 Flow properties

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

- increasing the carbon chain length of the acid

- increasing the carbon chain length of the alcohol
 - increasing the linearity of the molecule
 - no cyclic groups in the backbone, which lowers the VI even more than aliphatic branches
- molecular configuration-viscosity indices of polyol esters tend to be somewhat lower than their 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
- decreasing the carbon chain length of the acid
- decreasing the internal symmetry of the molecule
- the position of the branch in which branching in the center of the molecule gives better pour points than branch near the end

As can be seen from the above lists, there is a natural trade-off between VI and pour point. For instance by increasing the linearity of the ester the VI improves but the pour point increases. Ester 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 either branched or normal acid.

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 instead of anti-wear additive. 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.

Ester can be classified in terms of their polarity, or non polarity by using the following formular (Van der Waal, 1985) :

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

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 general rule, increasing molecular weight improves overall lubricity. Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids/alcohols have lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/alcohols.

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 diester is well documented and has been investigated on a number of occasions. It has been found that the absence of hydrogen atoms on the β -carbon atom of the alcohol portion of an ester leads to superior thermal stability.

2.5 Hydrolytic stability

The hydrolytic stability of esters depends on two main features that is processing parameters and 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 esters. Such processing parameters include acid value, degree of esterification, and catalyst used during esterification and the level remaining in the ester after processing. Ester must have a low acid value, a vary 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 serveral 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, germinal 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 acid esters.

2.6 Solvency

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

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

2.6.2 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 rare) and physical. During physical interactions two different processes occur :

- absorption of the lubricant by the elastomer, causing swelling.
- extraction of soluble components out of elastomer, causing shrinkage.

The degree of swelling of elastomeric material can depend on :

- size of lubricant - the larger the lubricant the smaller the degree of swelling
- molecular dynamics of the lubricant in which linear lubricant diffuse in to 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 trends for specific ester types.

2.7 Environmental aspects

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

2.7.1 Ecotoxicity : In Germany esters are classified according to their water endangering potential or Wassergährdungsklasse (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

Ester are generally in the following ranking :

polyols, polyoleates, C ₃₆ dimer esters, diesters	WGK 0
phthalates and trimellitates	WGK 0 - 2

This shows esters to have a low impact on the environment

2.7.2 Biodegradability : The general biochemistry of microbial attack on esters is well known and has been well reviewed. The main step of ester hydrolysis, beta-oxidation of long chain hydrocarbons and oxygenase 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 reduced β -oxidation)

- degree to which ester hydrolysis is inhibited
- degree of saturation in the molecule
- increase in molecular weight of ester

Figure 2-4 show the biodegradability of a wide range of lubricants as measured using the CEC-L-33-T-82 test.

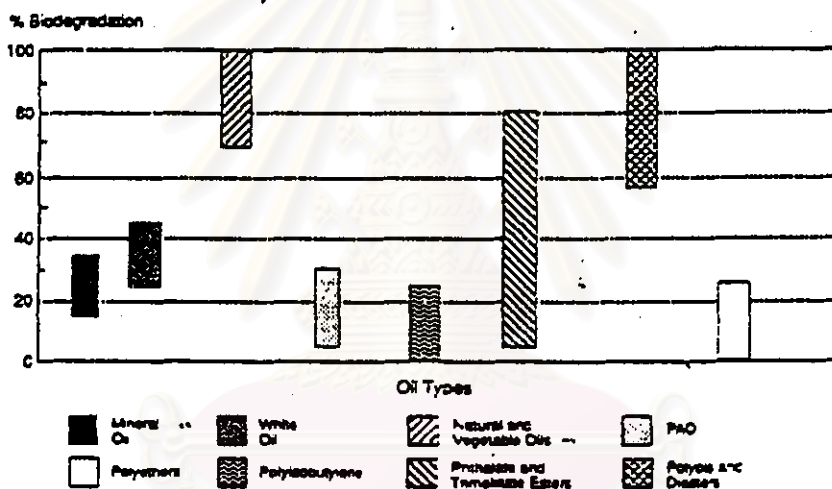


Figure 2-4 : Biodegradability of lubricants as measured by using the CEC-L-33-T-82 test.[17]

3. Application areas

3.1 Engine oil : It is now widely accepted that synthetic fluids, such as polyalphaolefin / ester blends, offer a number of inherent performance advantages over conventional petroleum based oil 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 crankcase oils, either commercialized or considered for commercialization, include polyalphaolefins (POAs) : more correctly hydrogenated olefin oligomers, organic dibasic esters, polyolesters, alkylated aromatic hydrocarbons, and polyglycols. Experience from numerous laboratories of engine bench and vehicle test programmes 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 synthetic crankcase oils.

Low temperature viscosity is perhaps the single most important technical feature of modern crankcase lubricant. Cold starts are a prime cause of engine wear which can be mitigated only by immediately effective lubricant circulation. Furthermore, motor vehicle 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 oil : 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 mixture. 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 lift are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils. Mineral oil has oil : fuel dilution ratio 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 PAH (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. PAHs have been found to be one of the major contributors to the carcinogenic nature of exhaust emissions. Esters 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, trimellitate esters can be used. Diesters and polyol esters may be blended with PAOs for used in the various compressor types.

Diesters have inherently good oxidation resistance and low volatilities (3-10 % according to viscosity) when compared to mineral oil. Coupled with their higher flash and auto-ignition temperatures, and low order of the toxicity for vapour inhalation, ingestion and skin irritation, these properties make them considerable safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradabilities can also lessen their environmental impact. Diesters generally have high viscosity indices, giving them a wide temperature range without the use of viscosity improvers. (The latter can shear in this application.) A further advantage of esters is their good thermal conductivity which allows them to conduct 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 Aviation oils : 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 (Type 1) were met by diesters. However, 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 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.

4. Future trend

The requirement for lubricants to operate at high temperature is causing a move away from mineral oil to esters. In particular, due to the better temperature stability of polyols, there is a growing tendency to use these in preference to diesters. In response to increase environmental pressure, the chemistry of ester is being modified so as to produce compounds which have high biodegradability, low toxicity, and clean engine emissions.

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