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A Technical Publication Devoted to the Selection and Use of Lubricants

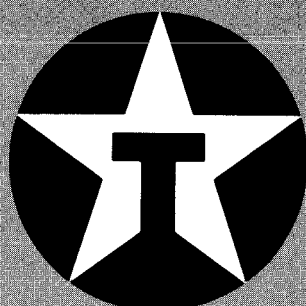
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Synthetic Lubricants



Better protection for the long run.



LUBRICATION

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SYNTHETIC LUBRICANTS

Douglas H. Culpon and Theodore C. Mead

INTRODUCTION

Because of the prevalence of petroleum-based lubricants in modern times, we may forget that through most of history man has used a variety of natural oils and greases for his lubrication needs. Olive oil was used to lubricate wooden planks on which Egyptian monuments were moved in 1650 B.C., and ancient Egyptian chariot axles were greased with mutton tallow. By Roman times, non-petroleum stocks such as rapeseed, castor and palm oils were used as lubricants, as were oils from whale, porpoise and cattle ("neat's-foot" oil). In Western societies, these natural lubricants were replaced by cheaper petroleum waxes and oils, which became available when the first petroleum dewaxing process was developed in 1880.

The first true synthetic lubricants, derived from silicones and polyolefins were developed in the United States in the early 1930's. World War II accelerated synthetic lubricant development, especially in petroleum-short Germany. The Germans experimented with synthetic hydrocarbons, alkylbenzenes and polyglycols derived from furan. Farben Industries screened more than 3500 esters as potential aviation lubricants during the

war years. The United States reported on extensive work with fluorinated lubricants in 1951.

The current interest in synthetic lubricants follows from environmental regulations issued by international, federal and state bodies which stress biodegradability, non-toxicity, environmental friendliness and recyclability. In addition, equipment manufacturers are requiring lubricants with longer service lives, lower volatilities and increased energy efficiency; such lubricants are, in some cases, required to function in more severe temperature and pressure regimes.

Synthetic lubricants are, in the strict sense, chemical products, although some vegetable and plant oils are loosely included in the general category. Most are, however, manufactured or "synthesized" in chemical plants by reacting components to make a desired product. Examples include poly-alpha-olefins, diesters, polyol esters and silicone fluids. In contrast, conventional lubricants, often known as "mineral oils", are obtained from petroleum crude oils by distillation and other refining procedures. Additives are blended into the synthetic or mineral oil base fluids to impart properties

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needed for specific applications.

Synthetic base fluids are often well-defined materials. In formulated products they may offer:

- utility over wide temperature ranges,
- good stability,
- long service life and
- unique performance traits.

Synthetic lubricants have both desirable and undesirable properties. Hence, matching the correct lubricant with the intended application is important. The wide variety of synthetic lubricants available in the marketplace attests to the fact that one type of synthetic lubricant will not work for all applications.

Properties of conventional paraffinic and naphthenic mineral oils are described in the next section to provide a frame of reference for the subsequent discussion of synthetics; a description of "unconventional" mineral oils is included. This is followed by a section describing specific synthetic lubricant types, with an assessment of the strengths and weaknesses of each. The important subject of biodegradability is described separately and the paper concludes with a summary of four major applications of synthetic lubricants.

The authors acknowledge frequent reference to the classic work in synthetic lubricants, that edited by Gunderson and Hart.¹

MINERAL OILS

Mineral oils are chemical components obtained from petroleum crude oil. A variety of refining steps remove most of the undesirable materials in crude oil and isolate the desired hydrocarbons that form the bulk of most lubricants in use today. Crude oil is a complex mixture of hydrocarbons, substances made with hydrogen and carbon, as well as some substances that also contain phosphorus, sulfur and/or metal atoms. The overall mix of hydrocarbons present in crude oil depends on its source, with each crude oil having its own unique properties. Once preferred crudes are identified, they are treated with appropriate processing steps to isolate lubricant base oils.

Distillation separates crude oil into gases, fuel liquids, lubricant fractions and "heavier" components such as asphalt. Further processing of the lubricant fractions removes many impurities, including most of the phosphorus, sulfur and metals. Solvent refining removes less desirable hydrocarbons, while leaving those with better properties. Dewaxing produces base oils with improved low-temperature properties.

Crude oils have traditionally been classified as "paraffinic" or "naphthenic". Paraffinic crude oils

contain many hydrocarbons with linear and branched arrangements of the carbon atoms. Typical paraffinic hydrocarbon structures are shown schematically in Figure 1, with each straight line representing two linked carbon atoms. Additional hydrogen atoms are present, but not shown. (Subsequent figures also use straight lines to represent two linked carbon atoms.)

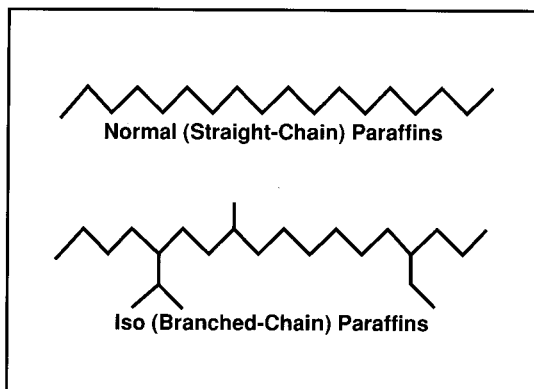


Figure 1

A specific paraffinic base oil from Pennsylvania was used as one of the original standards for Viscosity Index (VI) measurement and was assigned a VI value of 100. The viscosity index is an indication of an oil's tendency to decrease in viscosity with increasing temperature; higher numbers, associated with smaller changes in viscosity with temperature, are desirable. Most present-day paraffinic base oils have good viscosity-temperature behavior with VI's of 90 or higher.

Since paraffinic crude oils contain relatively large amounts of wax, dewaxing processing steps are essential to provide paraffinic base oils with acceptable low-temperature properties.

Naphthenic crude oils contain few of the long-chain "wax-like" hydrocarbon components and more hydrocarbons with carbon atoms linked in rings. These ring-like materials are known as cycloparaffins. A schematic structure of a typical cycloparaffin or naphthenic hydrocarbon is shown in Figure 2.

Naphthenes, because of their low wax content, have excellent low-temperature properties, including low pour points. A typical naphthenic base oil was assigned a viscosity index of zero at the time the VI scale was developed. Even with improved processing, most present-day naphthenes have VI's below 60.

The structures above represent only a few of the

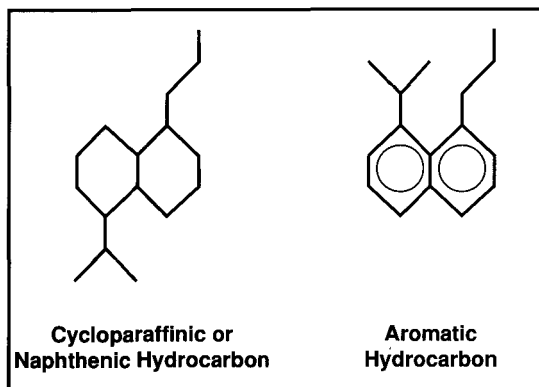


Figure 2

millions of carbon and hydrogen arrangements found in paraffinic and naphthenic mineral oils. While various processing steps improve many of the properties of these base oils, a wide variety of chemical components remain. This variation includes both the size of the molecules (i.e., the number of carbon atoms per molecule present) and the structural arrangements of the molecules. Variations in size affect properties such as volatility, viscosity and pour point. Variations in structural arrangements affect properties such as oxidative stability, thermal stability and crystallinity.

"High VI" or "unconventional" mineral oils represent an oil type that is intermediate between conventional paraffin mineral oils and synthetic poly-alpha-olefins (to be discussed in the next section). These oils have properties approaching those of the poly-alpha-olefins, but are somewhat less expensive. High VI oils are prepared by either (a) severely hydrogenating paraffin distillates or (b) isomerizing wax available from the solvent dewaxing process used in lubricant manufacturing. Severe hydrogenation of paraffin distillates converts undesirable components containing multiple ring structures (polynuclear compounds) or atoms such as nitrogen, oxygen and sulfur to desirable hydrocarbons containing paraffinic structures with high VI's. Isomerization of waxes, which are predominately straight-chain paraffinic hydrocarbons, transforms them into lower-melting branched-chain paraffinic hydrocarbons at some VI penalty, but with much lower, acceptable pour points.

Severe hydrogenation requires considerable capital investment to accommodate the required high hydrogenation pressures. Wax isomerization requires a source of petroleum wax; usually a solvent dewaxing unit in the refinery lubricant processing train. Solvent dewaxing, however, is being replaced by catalytic dewaxing, which affords no waxy by-products. This development will affect the

availability of wax by-product for isomerization to high VI base oils.

For further information on mineral oil processing, the reader is referred to LUBRICATION magazine, Vol. 75, No. 1 (1989) on Lubricant Base Oil Processing.

SYNTHETIC LUBRICANT BASE STOCKS

Poly-Alpha-Olefins

Poly-Alpha-Olefins (PAO's) are the most widely-used synthetic industrial lubricants in the U.S. and Europe. They are similar to a "super-pure" paraffinic mineral oil and consist of identical molecules of pure hydrocarbons. PAO's are made by combining two or more decene molecules into an "oligomer", or short-chain length polymer. Decene, a linear molecule with 10 carbons, is synthesized first by linking together 5 molecules of ethylene, each of which contains two carbons. The 10-carbon decene molecule is unsaturated (deficient in hydrogen) at the terminal ("alpha") position. The second synthesis step involves polymerization of decene through this unsaturated or olefinic function. PAO base oils have the structure shown in Figure 3.

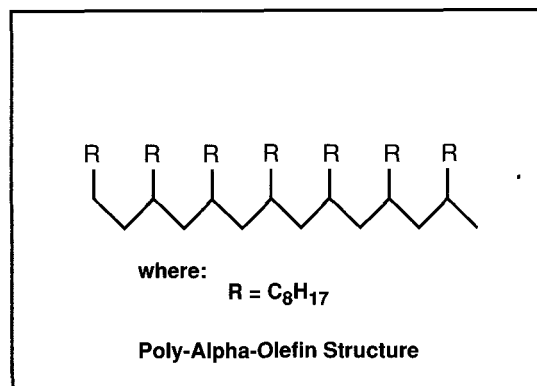


Figure 3

The two-step manufacturing process impacts the economics of PAO's. Decene manufacture is a capital-intensive process and requires the sale of by-product materials, which limits the number of suppliers. The conversion of decene to PAO's, however, can be done in small or large systems,

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making it attractive to a variety of manufacturers.

PAO's are all-hydrocarbon structures. They contain no sulfur, no phosphorus and no metals. Being wax-free, they have low pour points generally below -40°F, ranging as low as -90°F. The viscosity indices of these materials are high, with all but the lowest viscosity grades exceeding 140 on the VI scale. They are available in viscosity grades from 2 cSt (2 cSt @ 100°C) to 100 cSt. The 4, 6 and 8 cSt grades are manufactured in higher volumes for automotive applications and are considerably less expensive than the 40 and 100 cSt grades.

PAO's have good thermal stability; they can withstand high temperatures without decomposing. PAO's also resist oxidation in a well-formulated product containing suitable antioxidants. In the absence of antioxidants, PAO's and many other synthetic lubricants are less resistant to oxidation than are mineral oils. Apparently, some of the sulfur present in mineral oils serves as a natural antioxidant. Antioxidants are needed for both mineral oil and synthetic lubricants to withstand high-temperature use and to provide an adequate service life without thickening and forming harmful acids. The presence of antioxidants throughout product life is especially important for PAO's. Rapid oxidation can otherwise be a problem.

PAO's have some disadvantages, including limited ability to dissolve necessary additives and a tendency to shrink seals. Both of these problems can be overcome via the addition of a suitable quantity of a synthetic ester base fluid. Most PAO-based products contain 5 to 20% of a diester or polyol ester. Researchers have recently reported development of a base fluid in which alpha-olefins are polymerized with methacrylic acid, which builds the ester function directly into the PAO structure.²

Applications for PAO's include crankcase engine, gear, turbine, compressor and automotive accessory oils. PAO's are used in both fully synthetic and semi-synthetic automotive lubricants. Semi-synthetic lubricants contain both mineral oils and synthetic base fluids. PAO's in these blends afford improved low-temperature properties with less volatility than is seen in corresponding mineral oils.

In 1992, poly-alpha-olefins cost four to eight times as much as the corresponding conventional mineral oil base stocks.

Diesters

Esters are synthesized by reacting an acid and an alcohol, forming water as a by-product which must be removed. Diesters draw their names from

the diacids used to make them. Common examples include the manufacture of adipate esters from adipic acid and phthalate esters from phthalic acid (see Figure 4). The alcohols reacted with the diacids have much higher viscosities than ethyl alcohol and are often refinery or chemical plant by-products. Diester base oil prices are usually higher than those of PAO's of the same viscosity.

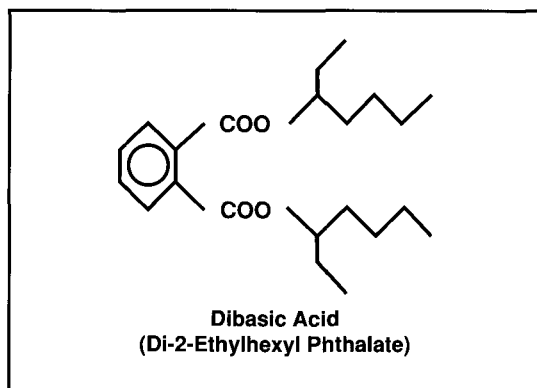


Figure 4

As mentioned earlier, water is generated when an ester is made and must be removed from the ester. Unfortunately, under some conditions when water is present as a contaminant, the reverse reaction of water with an ester lubricant can occur, reforming the parent alcohols and acids. If strong acids (e.g., adipic and phthalic) are formed as a result of hydrolysis, corrosion can become a problem. Proper additive selection is crucial to avoid this problem, since some additives can increase the likelihood of hydrolysis. The presence of iron and zinc in wet systems can also promote hydrolysis.

Diesters, like PAO's, do not contain sulfur, phosphorus, metals or wax. Chemically they have more varied structures than PAO's, since the alcohols used are often mixtures of chemically-related materials. They have low pour points, generally ranging from -60 to -80°F. Diesters exhibit good thermal stability and, with the right additives, can be made oxidatively stable.

Another benefit of diesters is their excellent solvency, both for additives and potential deposit-forming substances. Diesters are clean-running lubricants, as they tend to dissolve varnish and sludge rather than leave deposits. In fact, diesters often clean up prior deposits formed with mineral oils or other products.

Diesters of low viscosity are sold as plasticizers. In this application, their function is to soften plastics to facilitate manufacturing. Lubricant range diesters can also soften plastics, which can lead to seal compatibility problems. Chemically resistant seals like Viton, Flourel, Hytrel and medium-to-high nitrile Buna-N are recommended in systems employing diester lubricants. Natural rubber, neoprene and low nitrile Buna-N elastomers should be avoided.

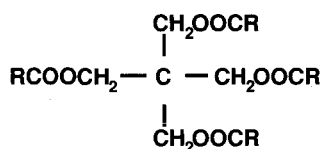
Applications for diesters include compressor lubricants, misting oils, bearing lubricants and some high temperature hydraulic oils. Diesters are often used in small quantities with PAO's to provide neutral seal swell and adequate solvency for additives.

Diesters are five to seven times more expensive than the corresponding viscosity grade mineral oils.

Polyol Esters

Like diesters, polyol esters are formed by the reaction of an acid and an alcohol to form an ester and water. The term "polyol" refers to a molecule which contains two or more alcohol functions (-OH groups) in its structure. Polyol esters derive their names from the polyol alcohols used. Most of the polyol esters used in lubricant applications are derived from "hindered" polyols. Esters of these polyols have improved thermal stability characteristics because of the lack of hydrogen atoms on the carbon atom beta to the alcohol functions. This is the tetra-substituted central carbon in Figure 5. Examples include trimethylolpropane (TMP), neopentylglycol (NPG) and pentaerythritol (PE).

TMP, NPG or PE ester lubricants are formed by reaction of these polyols with relatively weak organic acids derived from refinery or chemical sources. The structure of a pentaerythritol ester is indicated in Figure 5.



Polyol Ester Derived from Pentaerythritol

Figure 5

Polyol esters contain no sulfur, phosphorus or wax. Typical pour points range from -20 to -95°F, depending on the blend of compounds found in the specific base fluid. Viscosity indices are generally above 140, with a range of 120 to 160. With suitable additives, polyol esters are slightly more oxidatively stable than diesters or PAO's.

Polyol esters resist hydrolysis somewhat better than diesters. Hydrolysis is unlikely with the polyol esters, and if it does occur, less corrosive materials are formed relative to those obtained from the hydrolysis of diesters. Seal-swell behavior of polyol esters is similar to that seen in diesters for most elastomers.

Polyol esters are manufactured in large quantities for use as aviation lubricants, especially high temperature aircraft turbine oils, and as hydraulic oils. The largest application is as aviation lubricants, with PE esters being preferred. The outstanding high-temperature performance of these fluids and their very low pour points are ideal for the wide temperature ranges encountered between cold outside air and hot turbine systems.

TMP esters biodegrade much faster than mineral oils, PAO's or diesters.

Polyol esters are ten-to-fourteen times more costly than mineral oils in the same viscosity range.

Alkylbenzenes

Alkylbenzenes are formed by the reaction of olefins or alkyl halides with benzene or other "aromatic" materials. These materials came into prominence during the oil shortages in the 1970's. Because of their good low-temperature properties, they found application in arctic engine oils, compressors, transformers and refrigeration systems. Alkylbenzenes may have either linear or branched alkyl chains attached to the aromatic ring. Linear alkylbenzenes ("LAB's") are by-products of detergent manufacture. The lubricant range material is the heavy end of the product used to make detergent and will also contain some dialkylated aromatics, diaryl alkanes and more complex products. Branched alkylbenzenes have substituted alkyl side-chains; these are often formed from the reaction of propylene tetramer and benzenes. Examples of both structures are shown in Figure 6.

In Figure 6, the two alkyl groups are shown "para" to each other; that is, in the 1- and 4-positions on the benzene ring. Substitution may also occur in the "ortho" position (i.e., the 1-and 2-positions on the ring); 1,3 or "meta" disubstituted products are seldom encountered. Both types of alkylbenzenes have good additive solubility. The linear types have viscosity indices of about 50,

while those with branched side chains can have VI's of zero or lower. These are considerably lower values than those seen in esters and PAO's.

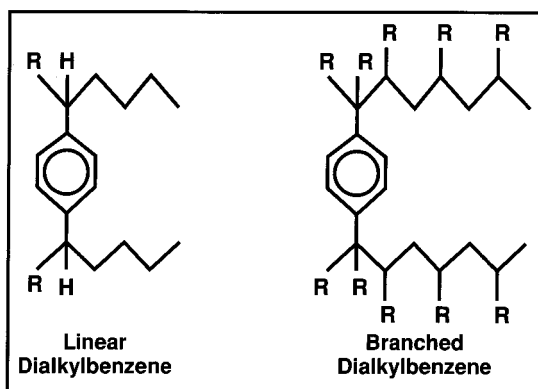


Figure 6

The LAB's are more prone to oxidation than the branched chain analogues. This is due to the presence of a reactive tertiary ("benzylic") hydrogen atom on the side-chain carbon attached to the aromatic ring. The thermal stability (i.e., the resistance to heat in the absence of oxygen) of commercial alkylbenzenes has been shown to be similar to that of PAO's but inferior to that of silahydrocarbons. Specially prepared pure, trisubstituted benzenes can, however, be extremely stable.³

The lubricity of alkylbenzenes is similar to that of naphthene oils, as measured in standard laboratory test methods.

Alkylbenzenes and semi-synthetic mixtures of linear alkylbenzenes and naphthene base oils are marketed in Europe as refrigeration oils. When these oils are used in compressors after conventional lubricants have been used, the higher solvency of the alkylbenzenes may lead to a flushing and decarbonizing action. Initially, such changeovers may initially require more frequent filter changes and close monitoring of the unit.

Polyalkylene Glycols (PAG's)

Polyalkylene glycols, commonly known as PAG's, are polymers of alkylene oxides, such as ethylene oxide or propylene oxide (see Figure 7). As such, a more accurate name for these materials is polyalkylene oxides or polyethers.

These polymers contain oxygen, as do the low-molecular weight glycols found in antifreeze (ethylene glycol) or aircraft deicer fluids (propylene

glycol), but few of their properties are similar.

Manufacture of PAG's by polymerization of alkylene oxides is ordinarily base catalyzed. If the initiator is a glycol or water, the polymer will contain terminal hydroxy groups; these polymers are known as "diols." If the initiator is an alcohol, the end product is a monoether; these polymers are referred to as "end-capped." Because of the higher degree of hydrogen bonding in diols, the viscosity of a given molecular weight diol is much higher than that of an end-capped monoether analogue. Thus, a 32 cSt polypropylene glycol would have molecular weights of 390 and 750, respectively, for the diol and monoether forms.⁴ Densities of diols tend to be higher than those of the end-capped versions.

The lubricating performance and physical properties of PAG's depends on the monomer(s) used in its manufacture, the molecular weight and the nature of the terminal groups. PAG's made from ethylene oxide are water soluble and oil insoluble, while those made from propylene oxide are water insoluble and oil soluble. Some PAG's are denser than water; with such lubricants any separated water will float on the lubricant. The interaction of PAG's with water, as well as other properties of PAG's, can be "customized" with special combinations of ethylene oxide, propylene oxide and other building blocks.

Water-soluble PAG's may separate from aqueous solution at high temperatures. In metal-working fluids, this can result in the PAG coming out of dilute aqueous solution to provide lubricity at the hot surfaces of the tool and work piece. In quenching fluids, coating of a hot metal surface by the PAG will control the cooling rate. In antifoamants, PAG insolubility at high temperatures contributes defoaming properties.⁵

PAG's tend to leave little residue after thermal decomposition. This makes them excellent carriers

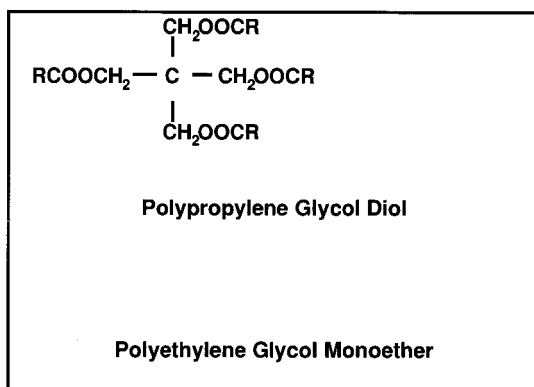


Figure 7

for graphite dispersions at very high temperatures. Kiln car wheels, which are subjected to temperatures of 2000°F for several hours in porcelainware manufacture, provide a dramatic example for the use of this combination lubricant.⁶

PAG's typically comprise 20% of an automotive brake fluid and are used in hydraulic systems in which the leakage of petroleum-based fluids cannot be tolerated and fire-resistance is crucial. The United States Navy pioneered the use of water-based hydraulic systems in which PAG's were included to impart shear-stable thickening and lubricity.

PAG's have low toxicity. Those with molecular weights above 1500 have been given FDA status #178.3570 with reference to incidental contact, which means they are suitable for the lubrication of food processing machinery. Low orders of fish toxicity have been reported for "most random PAGs" (however, see "Hydraulics" section, following). PAG's do not inhibit the growth of bacteria in aqueous solution at concentrations of up to 1000 mg/l and are said to be "20% biodegradable in 20 days."⁵

Like most synthetic lubricants, neat PAG's can react in the presence of oxygen. With the use of proper additives, however, PAG's can form stable, long-life lubricants; amine antioxidants have been shown to be more effective than phenolic antioxidants.⁷ Because of their high viscosity indices, PAG's may be used over a wide temperature range. Deposit formation is low, since at temperatures above 500°F, PAG's tend to volatilize rather than form solid deposits. The oils also tend to solubilize their decomposition products. Under conditions of very high surface temperature, polyalkyleneglycols will give rise to coke or carbon deposits, as may be seen from panel coking data.⁴

The ability to "customize" the properties of PAG's has led to their use in specialty applications include metalworking fluids and quenchants, as noted earlier. In addition, their good high temperature stability has led to their use in air compressor lubricants, and their insolubility with natural gas makes them useful in process gas compressors. PAG's have found some use as industrial gear oils in Europe, particularly where their water solubility and non-persistence in the environment are important.

Prices for PAG's cover a wide spectrum, since an enormous number of special products can be made. Simple polymers of ethylene oxide or propylene oxide are six to eight times as expensive as corresponding mineral oils.

Phosphate Esters

Phosphate esters are synthesized from phosphorus oxychloride and alcohols or phenols. They are used as synthetic base oils and also as antiwear additives for mineral or synthetic lubricants. Phosphate ester base fluids are used particularly where fire resistance is desired. Hydrocarbon groups (indicated as R in Figure 8) range from methyl to alkyl aromatics.

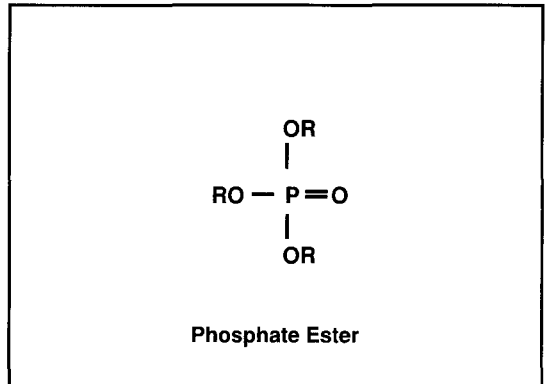


Figure 8

The antiwear function of these fluids is believed to result from the reaction of the phosphate ester with iron surface asperities, forming low melting phosphide alloys or eutectics. These reaction products deform or "smooth out" under pressure, yielding more surface area to support the load; this process is described as "chemical polishing."⁸ Phosphate esters generally offer good lubricity as a result of this chemical polishing characteristic, particularly as measured by antiwear testing. In some bearing applications, however, it has been shown that the use of phosphate ester as lubricants or additives can degrade performance relative to neat mineral oil.

The thermal stability of phosphate esters is good. Pour points range from -15 to +25°F.

The most common application for phosphate esters is as fire resistant hydraulic fluids. Key properties include:

Flash Point	470°F (minimum)
Fire Point	620°F minimum)
Autoignition Temperature	950°F (minimum)

A limitation to the high-temperature performance of the phosphate esters is their extremely low viscosity indices, which range from zero to -30. As a result, viscosities often become too low at high temperatures to allow the oil to function as a lubri-

cant. As with most esters, hydrolysis may be a problem in the presence of water.

Phosphate esters are slightly more expensive than polyol esters and about ten times as expensive as mineral oils in the same viscosity grade.

Silicone Fluids

Silicones are organic compounds built on a backbone of silicon-oxygen bonds. Various alkyl or aryl groups are attached directly to the silicon atoms as shown in Figure 9.

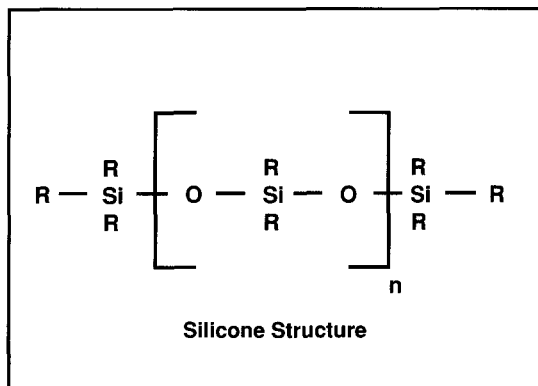


Figure 9

In contrast to the phosphate esters, silicone fluids have VI's that are off the high end of the scale, with typical values of 350 and above. Silicone fluids also have other outstanding characteristics; they operate over extremely wide temperature ranges, completely repel water, resist chemical attack and are compatible with a wide range of plastics and elastomers.

Silicone fluids, however, offer little wear protection for metal surfaces. The poor wear protection provided by the silicon fluids limits their use to fully hydrodynamic lubrication modes, where a complete film of liquid separates the metal surfaces.

If temperatures are high or chemical environments are severe, the use of silicone fluids may be justified, even with costs generally above \$50/gallon. Examples of appropriate applications include oven and kiln fan bearings, chemical plant valve lubricants, low torque instruments, clocks, timers, etc.

Fluorinated Lubricants

Replacement of the hydrogen atoms in polyethylene with fluorine atoms results in polytetrafluoroethylene (e.g., "Teflon"®). Likewise, replacement of the hydrogen atoms with fluorine

atoms in a polypropyleneoxide polymer gives a lubricant with outstanding stability and lubricity. These materials operate over a temperature range from as low as -40°F to as high as 450°F. They carry loads extremely well and are nearly impervious to chemical attack. Fluorocarbons are available as both oils and greases at prices of about \$75 per pound.

The ultimate in cost and performance, especially at ultra-low vacuums is a fully fluorinated polyphenylether. These materials are custom aerospace lubricants for satellites and other applications where extremely low volatility is needed at high temperatures. Costs are around \$1400 per pound, which is over \$10,000 per gallon.

Natural Esters

Naturally occurring esters, such as those derived from the rape or castor plants, find application as lubricants in agriculture and in the wood and food industries. Their limitations of relatively short life time and low operable working temperatures are compensated for by their biodegradability.

About fourteen million metric tons of rapeseed were produced in 1985, affording 4.6 million tons of oil. About half of this production was in India and China, where it is used for food. European production was 1.6 million metric tons per year between 1980 and 1985; about 1% of this amount was used as lubricant.

Rapeseed oil is expressed from the dehulled and steamed seeds of the plant, *Brassica campestris*, and is degummed, steam-refined, bleached with acid-activated earth and deodorized. Hydrogenation of rapeseed oil affords a product more resistant to oxidation and thermal degradation.

Rapeseed oil is a glyceride [a triester of glycerin (1,2,3-trihydroxypropane) and oleic, linoleic and linolenic acids (C-18 mono-, di- and tri-unsaturated acids, respectively)]. The generalized structure is shown in Figure 10. The glyceride also contains varying amounts of ester groups derived from erucic acid (a C-22 mono-unsaturated acid). The erucic acid content can comprise more than fifty percent of the acid groups in some varieties of rape oil, but is less than 25% in the "Montana" variety. Because of concern over possible physiological effects of the erucic acid component in rapeseed oil, a "zero-erucic" strain has been developed, known as "canbra" or "canola" oil.

Rapeseed oil has a viscosity of 36 cSt at 40°F and is compared to a typical Neutral 150 mineral oil in Table I.

Another naturally-occurring glyceride, which most closely approaches a pure product, is castor

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oil. The acid component of castor oil is about 90% ricinoleic acid, a mono-unsaturated 18-carbon acid with a hydroxyl substituent. While the castor bean is highly toxic to humans, castor oil is used as a "non-toxic" component in cutting oils, high temperature steel-rolling lubricants and other metal working fluids. Castor oil has a room temperature viscosity of 6-8 cSt.

An oxidized and esterified modification of castor oil finds application as an aviation lubricant.⁹

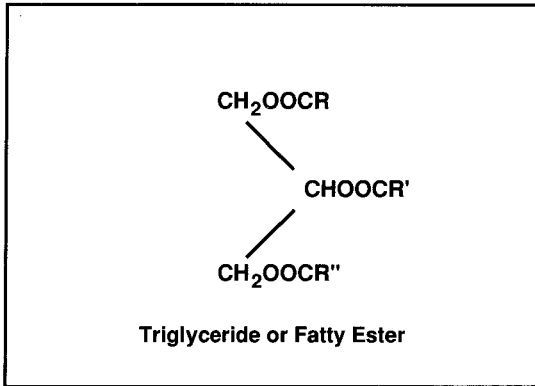


Figure 10

Natural esters are principally produced as food-stuffs. Annual worldwide production figures for the mid-1980's follow:

<u>Source</u>	<u>Production (MM Metric Tons)</u>
soy	11.3
sunflower	4.5
palm	3.7
peanut	3.3
cotton seed	3.2
coconut	3.2
rapeseed	2.9 - 4.6
olive	1.8

The USDA figures quoted may be low, especially for rapeseed oil production. About 14 million hectares of rape are planted world-wide, with half of this in China and India. Since one hectare of rape can yield a metric ton of oil, potential oil production from this crop is as high as 14 million metric tons.

Oil extracted from the jojoba seed is exceptional in that it is not a triglyceride. It is a simple ester derived from C-20 and C-22 straight-chain hydrocarbon acids and alcohols. It closely resembles sperm oil

TABLE I
Rapeseed Oil vs. Paraffinic Mineral Oil

	<u>Rapeseed Oil</u>	<u>Paraffinic Oil</u>
Density, 15°C	0.919	0.872
Viscosity, 40°C, cSt	36.0	30.0
Viscosity, 100 °C, cSt	8.19	5.26
Viscosity Index	214	105
Flash, COC	318°C (604°F)	215°C (419°F)
Cloud	-9°C (15°F)	-10°C (14°F)
Pour	-20°C (-4°F)	-15°C (5°F)
Neut. Number, mg KOH/g	0.3	< 0.01
Sap. Number, mg KOH/g	195	0.03
Ash, wt%	0.001	0.001
Color, ASTM	< 2.0	< 1.0
Aniline Point	9.5°C (49°F)	105°C (221°F)
Sulfur, ppm	19	3000
Nitrogen, ppm	22	150
Demulsibility, 54°C		
Time to separation (min)	9;12	5;8
Foam (DIN 51381), ml ¹		
24°C	0/0	300/0
93.5°C	0/0	30/0
50°C	0/0	70/0
Air Release (DIN 51381), min	< 1	2
FZG (DIN 51354T2)		
Damage load stage	9	6
Timken (IP 240), lb	12	10

¹At end of blowing period/after 10 minute settling period

LUBRICATION

and has been suggested as a lubricant in high pressure applications. Jojoba oil is remarkable for its resistance to bacterial degradation. It can be stored for years without becoming rancid.¹⁰

Prices of vegetable oils range from 14 cents per pound for palm oil to 43 cents per pound for peanut oil. Canola is priced at about 23 cents per pound. On a "per pound" basis, a typical petroleum base stock would be about 15 cents.

Summary

Table II summarizes some of the properties of typical synthetic lubricants. The assessments refer to formulated products, not necessarily to the base oils:

BIODEGRADABILITY OF MINERAL AND SYNTHETIC OILS

Any mineral oil or hydrocarbon-based synthetic lubricant will eventually degrade to carbon dioxide and water with the evolution of energy. The processes of ignition, digestion and decomposition are similar in this respect. Biodegradation refers to the last of these processes; oxidative decomposition of

carbon, hydrogen and oxygen compounds by micro-organisms. While all such compounds biodegrade, the rate of disappearance of lubricants in nature varies widely, and, within the same class of compounds, those of lower molecular weight tend to biodegrade more rapidly. The general order of decreasing biodegradability of common lubricants is:

- vegetable oils (most degradable)
- synthetic esters
- mineral oils and alkylbenzenes
- polyalkyleneglycols
- poly-alpha-olefins (least degradable)

While there is a general trend between the oxidative instability of the uninhibited fluids and their biodegradability, exceptions are noted. The most degradable "synthetic" fluid, rapeseed oil, cannot be used at high operating temperatures because of its susceptibility to oxidation. In contrast, polyalkyleneglycols, which oxidize readily in the absence of an inhibitor, resist microbiological action. These anomalies, as suggested above, may relate to the relative occurrences of the molecular types in nature. Esters and hydrocarbons commonly occur in nature; hence, classes of organisms have evolved which exploit them as

TABLE II
Relative Properties of Synthetic Lubricants¹

	Viscosity <u>Index</u>	High Temperature <u>Stability</u>	<u>Lubricity</u>	Low Temperature <u>Properties</u>	Hydrolytic <u>Stability</u>	Fire <u>Resistance</u>	<u>Volatility</u>
Poly-alpha-olefins	Good	Good	Good	Good	Excellent	Poor	Good
Diesters	Varies	Excellent	Good	Excellent	Fair	Fair	Average
Polyol Esters	Good	Excellent	Good	Good	Good	Poor	Average
Alkylbenzenes	Poor	Fair	Good	Good	Excellent	Poor	Average
Polyalkylene Glycols	Excellent	Good	Good	Good	Good	Poor	Good
Phosphate Esters	Poor	Excellent	Good	Varies	Fair	Excellent	Average
Silicones	Excellent	Excellent	Poor	Excellent	Fair	—	Good
Fluorinated Lubes	Excellent	Excellent	Varies	Fair	Excellent	Excellent	Average

(1) Comparisons made for typical formulated products with additive packages, not for the base oils alone.

energy sources. Polyalkyleneglycols and halogenated compounds rarely occur in nature and are "biostable".¹¹ Recent studies have indicated that PAG's are less biodegradable than are mineral oils.¹²

The lubricant technologist is clearly in a dilemma in attempting to formulate a biodegradable lubricant, since the ideal type would be oxidatively stable in service, but oxidatively unstable in nature. As noted, biodegradation is an oxidative phenomenon. Industry's problem is compounded by the lack of an accepted international standard for biodegradability. To avoid potential legal difficulties, terms like "environmentally aware," "environmentally considerate," "biofriendly" and the like have proliferated in the early 1990's.

In the absence of clear EPA and FTC guidelines, state regulators have begun to promulgate rules and procedures for the marketing of "green" products. New York and California have legislation in place restricting the use of terms such as biodegradable, "ozone friendly," and "photodegradable." Therefore, environmental claims are best specified as to the test methods involved, supported by adequate documentation.

The most frequently quoted test method is that developed by the Coordinating European Council, referred to as CEC-L-33-T-82. This method was developed specifically to test the aerobic aquatic biodegradation potential of two-stroke cycle engine oils, but has been widely used in Europe to test the biodegradability of lubricants in general. A second widely-used test was promulgated by the Environmental Protection Agency. This test, called the "Shake Flask" method, was published under the Agency's Chemical Fate Testing Guidelines and also measures aerobic aquatic degradation. Both tests use municipal sewage plant inoculum; the "Shake Flask" test also uses a soil inoculum. The CEC method measures remaining hydrocarbon via infrared absorption at 2930 cm⁻¹ (C-H stretching). The Shake Flask test measures carbon dioxide evolved over a 28-day period. These tests are used in conjunction with toxicity tests, which often include fish toxicity measurements, to assess a product's overall environmental acceptability.

Biodegradable hydraulic oils are discussed in the applications section. Biodegradable synthetic gear oils based on natural and synthetic esters and polyalkyleneglycols are commercially available, as are biodegradable outboard engine lubricants, chain gear and power saw oils. Mould-release agents and other "lost lubricants" are also obvious candidates for biodegradable formulations.

APPLICATIONS FOR SYNTHETIC LUBRICANTS

Synthetic lubricants may justify their higher costs or be essential in cases in which the lubricant is

- subjected to temperature extremes,
- used under severely oxidizing conditions, required to give long service life and/or
- used in severe chemical environments.

They may also be justified under circumstances in which conventional lubricants are ruled out because of regulatory, environmental or toxicity considerations. Requirements for energy efficiency, ease of disposal, food-compatibility or other special needs may also dictate the use of synthetics.

Applications in which synthetics are often considered include:

Crankcase Lubrication,
Compressor Lubrication,
Gear Lubrication and
Hydraulic Fluids.

Crankcase Lubrication

Synthetic crankcase engine oils have been marketed in the United States since the 1970's, but their origins go back to the early 1940's when they were first used in Germany to alleviate wartime shortages of crude oil-derived lubricants. While synthetic crankcase engine oils offer certain performance advantages over conventional lubricants, their relatively high cost (three-to-five times that of conventional mineral oil-based products) has prevented them from capturing a significant share of the domestic engine oil market. In 1991, synthetic lubricants accounted for less than one percent of the total motor oil market.

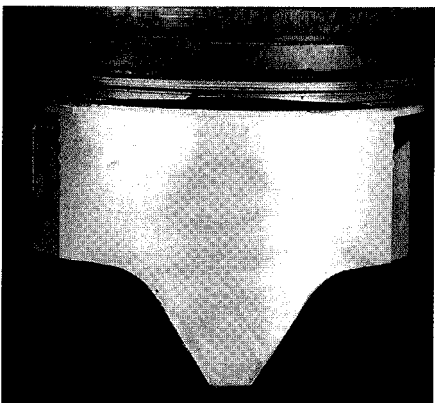
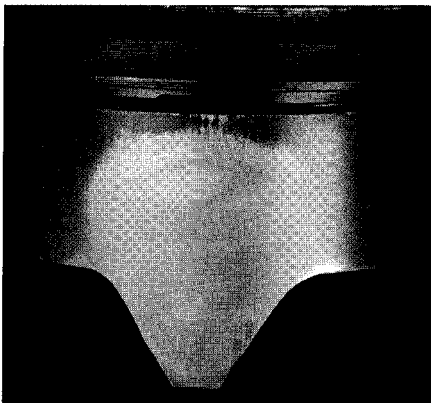
Another reason that synthetic motor oils have not achieved greater market share is that engine manufacturers have not permitted longer oil-drain intervals in their warranty maintenance schedules when synthetic motor oils are used. This is because the operating environment of motor oils - relatively hostile when compared to that experienced by most industrial oils - can vary considerably, depending on engine operating conditions. Crankcase engine oils are constantly contaminated by combustion byproducts during engine operation. Some of these byproducts are acidic in nature and cause corrosion, rust and wear, while others contribute to the formation of sludge and varnish deposits. To counteract these harmful effects, engine oils are formulated with additive packages designed to protect the engine from these contaminants. The

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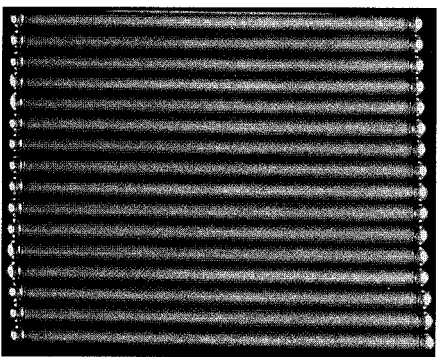
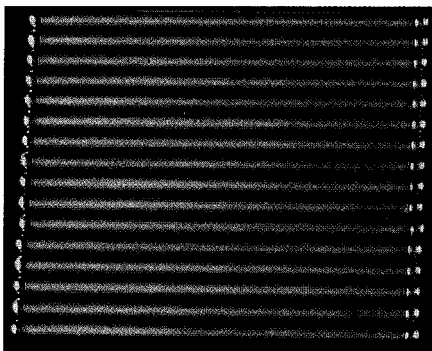
MINERAL MOTOR OIL

SYNTHETIC MOTOR OIL

Piston Skirts:



Push Rods:



Front Covers:

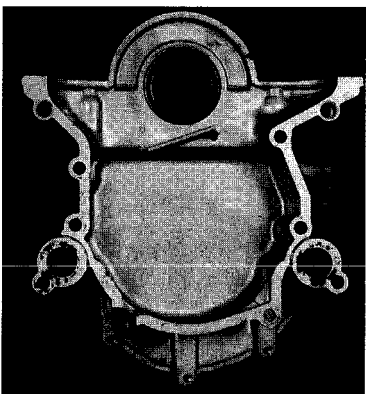
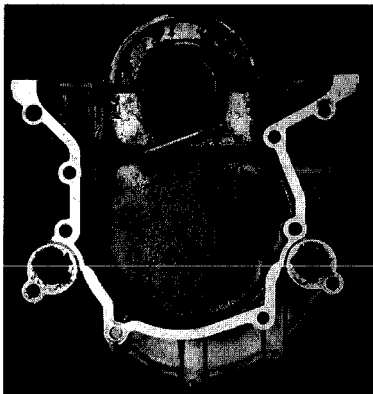


Figure 11– Comparison of engine cleanliness of API SG/CD mineral vs. synthetic motor oils at the conclusion of a severe service taxi field test.

additive packages are chemically similar for either synthetic or mineral oil-based engine oils and are depleted with use. When the additive packages are depleted, the engine oils are unsuitable for further use, requiring oil and filter changes.

Early PAO-based synthetic engine oils tended to harden and shrink elastomer seals, resulting in oil leakage. Conversely, ester-based engine oils - in addition to being more costly than comparable PAO-based products - tended to soften and swell elastomer seals excessively. Most synthetic oils marketed today contain primarily PAO base stocks in combination with lesser amounts of synthetic esters to provide neutral or slightly positive seal swell, thereby preventing oil leaks.

The performance advantages of synthetic motor oils result from their thermal stability, low temperature flow properties and low volatility.

Fully formulated synthetic motor oils have better high-temperature properties than do conventional engine oils and are notably more resistant to thermal and oxidative degradation. This is an important factor in maintaining engine cleanliness since the products of lubricant decomposition and oxidation are precursors to harmful engine sludge and varnish deposits. Oxidative degradation also causes oil thickening. The effects of these advantages on engine cleanliness may be seen in Figure 11.

Synthetic motor oils remain fluid at temperatures of -50°F and below. This ability makes the fluids attractive in regions where winter temperatures drop below zero. At these temperatures, synthetic lubricants permit quicker engine starts and provide lubricant flow quickly throughout the engine, thereby maintaining a protective lubricant film over critical valve-train areas.

Volatility is also an important physical property of an engine oil, since there is a direct correlation between volatility and oil consumption. The low volatility of synthetic motor oils translates to reduced oil consumption, thereby reducing or eliminating the need for oil additions between changes.

Synthetic motor oils on the market today meet the performance requirements of API service categories SG or SG/CD for gasoline and diesel engine oil applications, as do high-quality mineral-oil based motor oils. They are used by consumers who need the superior performance capabilities of these products under extreme high- and low-temperature operating conditions or who simply wish to use the highest quality oil in their vehicle's engine.

Compressor Lubrication

Compressors, whether reciprocating, rotary or centrifugal, may have special operating require-

ments which necessitate the use of synthetic lubricants. In these units, the oil is called upon to seal and cool, as well as to lubricate. In addition, the possibility of lubricant entrainment in the compressed gas stream where it can encounter high-temperature or reactive regimes may dictate the use of thermally stable or chemically inert synthetics. The reader is referred to an excellent short article by D. D. Schnack, for some general considerations in compressor lubrication.¹³

Phosphate esters are often used as cylinder lubricants in air compressors where build-up of carbonaceous residues in valve areas or piping may lead to fire and explosion hazards. These lubricants can reduce or eliminate such residues. In addition, they are fire resistant⁸; that is, they minimize the propagation of a fire if one is started.

Polyalkylene glycol lubricants are not recommended for air compressor service unless operating temperatures and discharge pressures are low. However, PAG's are used in gas compressors and vacuum pumps in which lubricant entrainment or solubility in the gas stream is a problem. In the compression of low-molecular weight hydrocarbons, the relatively poor solubility of light hydrocarbons in the polar polyalkyleneglycols is an asset in eliminating excessive lubricant thinning or wash-off from moving parts. Water soluble (polyethylene glycol) lubricants can be removed from gas streams via a water wash. The inherent chemical purity and clean burning characteristics of PAG's also indicates their use when catalyst contamination is a problem in the subsequent processing of the compressed gas stream.

The extraordinary chemical inertness of fluorocarbon lubricants makes these especially suitable for use in oxygen compressors. In such systems, the piston rings, cylinder walls and bearings are not constructed of aluminum, magnesium, copper or copper alloys. This is necessary because of the possible rapid reaction of freshly sheared, hot surfaces of copper, aluminum and magnesium with halogenated oils in an oxygen environment.¹

Diesters, as well as PAO's incorporating some ester content for seal swelling and additive solubility, have found applications in compressor lubrication. Long service life in air compression units is the rationale behind the use of synthetics in flood lubricated rotary valve and screw type units due to the severe oxidation environment. Problems were encountered in early formulations of PAO-based compressor lubricants. These problems are related to the narrow range of molecular weight and chemical types in these lubricants. The formulations gave a long service life, but eventual oil degradation tended to be rapid and catastrophic, without

the usual warning signs of incipient oil deterioration, such as gradual viscosity and acid number increase. Although improvements have been made in the formulation of synthetics, the operator should always adhere to the equipment manufacturer's drain schedules.

The lubrication of refrigeration compressors with synthetic oils will be reviewed in detail in a future issue of LUBRICATION. This is a complex subject related to the implication of some chlorofluorocarbon refrigerants in the depletion of the earth's atmospheric ozone layer. The American Society of Heating, Refrigerating and Air-conditioning Engineers (ASHRAE) has published a series of publications dealing with the specific problems associated with the replacement of chlorofluorocarbon refrigerants with hydrochlorofluorocarbons (HCFC's) and hydrofluorocarbons (HFC's) and the lubrication problems associated with these replacement refrigerants.¹⁴ Here we will merely note that in those systems in which refrigerant R-134a (asymmetric tetrafluoroethylene) is used as a replacement for the proscribed R-12, conventional naphthene-based lubricants are not acceptable because of their limited solubility in R-134a. In most refrigeration systems, particularly hermetic types, some mutual solubility of refrigerant and lubricant is needed to assure proper compressor lubrication and return of lubricant to the compressor. Since the mid-1980's, intensive research has been under way in Europe and the United States to identify replacement lubricants. Polyalkylene glycol- and polyol ester-based formulations are now available for this application.

Poly-alpha-olefin and dialkylbenzene lubricants have been used for refrigeration systems over the last several decades, especially in Europe. Problems related to a "fractionation" of PAO's between evaporator and condenser have, however, lead to declining sales in this application in Europe. The use of linear dialkylbenzenes and "semi-synthetic" mixtures of dialkylbenzenes and naphthene oils have reportedly given rise to sludge-related problems in Europe when used in certain types of ammonia compressors. Both PAO's and alkylbenzenes have been used for years in special refrigeration applications in the United States without reported problems. As always, the lubricant recommendations of the compressor manufacturer should be followed.

Gear Lubrication

Five major classes of conventional lubricants (i.e., rust and oxidation inhibited oils, extreme pres-

sure lubricants, tallow-containing compounded oils, heavy-bodied residuum-based open gear oils and greases) are required to lubricate spur, helical, bevel, worm and hypoid gears under the variety of conditions encountered in industry.¹⁵ It may be inferred from this that a variety of synthetic lubricants would be employed for the very general term of "gear lubrication."

Polyalkyleneglycols, because of their excellent load-carrying capacity and low deposit-forming properties have been used to lubricate heavily loaded or high-temperature worm gears for many decades.⁴ The long service life of PAG's and their lack of persistence (in the event of spills) make them particularly suitable for use in mines and mills. Sugar mill operators have also shown interest in PAG-based gear oils.

Natural esters, particularly rape-derived, and the more expensive polyol ester-based formulations are used in the same environmentally-sensitive gear lubrication applications. Polyol ester formulations provide long working lifetimes. Both types of esters can be used in normal-to-high load conditions.

Poly-alpha-olefins have shown promise in closed gear boxes and other applications in which biodegradability of the lubricant is not important. Specific advantages claimed are shear stability in roller-crusher operations in cement mills, low operating temperatures in locomotive traction drive gear boxes, good filterability characteristics and good high temperature stability.

Hydraulic Fluids

Seventeen attributes of an "ideal" hydraulic fluid have been cited in a treatise on this subject, ranging from the obvious desirability of good lubricity and high viscosity index to subtler needs, such as non-hygroscopicity, good dielectric properties and, of course, low cost.¹⁶ This list should be supplemented with two additional attributes that can be of overriding importance in some situations; namely, biodegradability and filterability.

It is clear that no single lubricant can provide all conceivable attributes for a hydraulic fluid. Accordingly, the choice of a synthetic lubricant for a hydraulic system is application specific. The building of missile and advanced weapons systems in the 1950's led to the requirements for hydraulic fluids capable of operating over a temperature range of -65 to 400°F. Alkyl silicate ester fluids were developed to fill this need.⁸ Diesters, especially dioctyl sebacate, were sometimes incorporated into these silicate ester hydraulic flu-

ids to impart sufficient seal-swell for leak-proof, high-pressure systems.¹⁷

Fire-resistant hydraulic fluids are used in die casting, metal and plastic handling and fabrication, heat treating and in other systems, especially aircraft, where hydraulic lines are run close to high temperature areas. Phosphate esters have been the primary fluids of choice for these applications, which are the largest single use for phosphate esters.

A second type of fire-resistant hydraulic fluid incorporates polyalkylene glycols in water-based fluids. PAG's are used in these water-based fluids to impart lubricity and thickening characteristics. The United States Navy developed a series of these fluids, called "hydrolubes," for hydraulic systems on aircraft carriers wherein fire resistance was the primary concern. They are also used in automotive brake fluids.

In Europe and the United States, there is interest in hydraulic fluids which are innocuous when leaked or spilled to the environment. That is, fluids which are both non-toxic and biodegradable. In Europe, especially, lubricant manufacturers have used rapeseed oil-based hydraulic fluids in applications (earth-moving, forestry, etc.) in which oil spillage is common and biodegradation of the fugitive product is essential.

As noted previously, rapeseed oil has a high viscosity index, has good lubricity and is an excellent solvent for additives. As a corollary to its biodegradability, rapeseed does not have good oxidative stability, and an upper working temperature of 125°F is recommended. As in bio-friendly gear oils, where higher operating temperatures are encountered, the more expensive, biodegradable synthetic esters may be used.

Vegetable-based hydraulic oils entered the United States market in 1991, with manufacturers emphasizing the biodegradability and non-toxicity of the products. Vegetable oils have been selected over polyalkyleneglycols in some applications as a result of studies indicating higher fish toxicity for PAG's.¹² Poly-alpha-olefins are preferred in sealed hydraulic systems using gear, piston or vane pumps where severe service conditions are encountered and product biodegradability is not important. The high viscosity index of these fluids affords a wide usable operating range of temperatures. It has been found that backhoes and excavators used in open pit mining applications need shorter warm-up periods, use less fuel and are less susceptible to seal leakage and pipe rupture when PAO-based fluids are used. PAO-based hydraulic systems have also found acceptance in Scandinavia because of their low temperature fluidity properties.

Other applications for PAO-based hydraulic oils include the controls, pumps, variable-pitch propellers and stabilizers in marine systems. Exposed on-deck equipment like trawl net retrievers, cranes and hatch covers are similarly serviced, as are some cranes, oil rigs, refrigeration and cold-storage equipment and automatic hydraulic assemblies (robots). Finally, a PAO-based, fire-resistant hydraulic fluid has replaced a kerosene-based predecessor in most military aircraft applications; a rust-inhibited version is also used in tanks and ordnance units.¹⁸

Contamination control is of paramount importance in all hydraulic systems and is of no less importance in systems using synthetic hydraulic oils than it is in mineral-oil based systems. Seventy percent of hydraulic system failures can be traced to poor fluid condition.¹⁹ This subject was discussed in depth in LUBRICATION, Volume 63, Number 4, 1977.

CONCLUSIONS

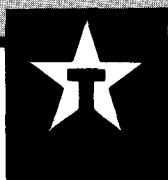
For the majority of lubricant applications, readily available petroleum-based mineral oils continue to provide satisfactory service at low cost. For severe service, long-life and/or specialty applications, three other classes of lubricants are available to the lubricant engineer. These are 1) "unconventional" petroleum-based oils, such as wax isomerate and severely hydrogenated distillates, 2) naturally occurring plant-derived esters and 3) synthetic lubricants. All three are imprecisely, but conveniently, referred to as "synthetics." Probably the only statement that is true of all synthetics is that they are more expensive than the corresponding petroleum-based mineral oils.

Poly-alpha-olefins and esters are the most widely used synthetic lubricant base oils. Suitable esters include those derived from dibasic acids and alcohols, hindered polyols and monobasic acids or natural occurring plant materials. The versatile polyalkylene glycols should assume a more prominent role in lubrication in the near future. Alkylbenzenes, phosphate esters, silicon-based synthetics and fluorinated hydrocarbons will continue to fill specialty niches.

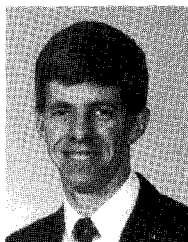
A properly formulated synthetic lubricant can be cost effective in an overall perspective, considering unit down-time, maintenance and the expense of regulatory compliance. In an atmosphere of increasingly stringent equipment manufacturer specifications and environmentally-driven federal, state and international regulatory constraints, the role of synthetic lubricants will increase.

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