# Fat-Based Synthetic Lubricants

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## ABSTRACT

Synthetic lubricants derived from fat-based materials are almost exclusively esters of the following type: (a) mono and dibasic acid esters, e.g., laurates, stearates of short chain aliphatic alcohols, azelates and sebacates of oxo alcohols; (b) polyalkylene glycols and glycol esters, e.g., triethyleneglycol dicaprylate caprate and others; (c) branched polyol or nucleic polyol esters derived from pentaerythritol or trimethylol alkanes and saturated short chained acid of the $C_6$, $C_8$, $C_9$ type; (d) triglycerides, specifically tailored by the rearrangement of two or more naturally occurring triglycerides. Among the unique but desirable characteristics of synthetic lubricants are: good lubricity, minimum viscosity change with temperature (high VI), low temperature fluidity, high thermal and oxidation stability, low volatility, excellent additive response, seal and gasket compatability and high fire and flash points.

One of the reasons that the synthetic lubricant field is receiving so much attention these days is its potential to produce and perform in critical energy-related situations. Synthetic lubricants are currently being utilized where no other product will perform, or they are indispensible by satisfying a unique application. In many cases, they are the only product that will do the particular job. Another potential benefit of synthetic lubricants is their ability to stretch out or lengthen current mineral oil base stocks, some of which are forecasted to be in short supply over the next few years. Synthetic lubricants are generally divided into four categories: (a) synthetic hydrocarbons, which would include alkylated aromatics, and olefin oligomers, such as poly-alpha olefins; (b) organic esters, which include dibasic acid esters, polyolesters and polyesters; (c) others, which include halogenated hydrocarbons, phosphate esters, polyglycol esters, polyphenol esters, silicate esters and silicones; (d) any blend of the above three.

The title of this paper is *Fat-Based Synthetic Lubricants,* which includes dibasic acid esters, polyakalene glycols and glycol esters, branched polyolesters and other polyhydric esters. It is difficult to discuss only the fat or fatty-derived synthetic lubricants without including their counterparts that are derived synthetically and indeed make up a substantial portion of the synthetic lubricant esters and/or lubricant package. However, we will try to isolate and target several of the more widely utilized fat-based fatty acid esters specifically. Almost all fatty and synthetic-based lubricants are esters of the following types.

The first group is the monobasic acid esters, which can be best illustrated by the simple esters; e.g., methyl stearate; methyl oleate, methyl 12-hydroxystearate, butyl stearate, butyl oleate and hexyl laurate.

Second, we have the typical dibasic acid esters; several examples are: ditridecyl azelate, dioctyl azelate, and di-2-ethylhexyl sebacate. Specific applications of the monobasic acid ester include their use in lithium base greases, textile fiber lubricants, mold release agents and rolling and cutting oils.

The dibasic acid esters' applications include gas turbines, compressors, hydraulic and other functional fluids, instruments, turbo and jet aircraft engines, and two- and four-cycle engines. The dibasic acid esters contribute to specific improvements in engine lubrication through their two significant characteristics of high viscosities and low pour points. In the synthetic formulation, they also contribute improved thermal and oxidative stability compared to mineral oils, which will be discussed later.

The third group of esters that is utilized in the field of synthetic lubricants is the glycol esters. Several of the fat-based esters would include dipropylene glycol dicaprylate, dipropylene glycol dipelagonate, triethylene glycol diheptanoate, triethylene glycol dicaprylate/caprate.

The next and probably the most important ester group is the branched polyol or nucleic polyol esters derived from neopentyl alcohol, neopentyl glycol, trimethylolpropane, pentaerthritol, and dipentaerythritol. The structure of this group of esters includes an important chemical feature in that on the alcohol portion of the molecule there are no hydrogen atoms on the beta carbon. This is the chemical structure that provides the esters of this group of alcohols a high degree of oxidative and thermal stability. The esters produced from this type of polyol exhibit excellent low temperature fluidity, low volatility at high temperatures, high flash and fire point, and compatibility with other esters and additives. As an example, the TMP esters are widely used in synthetic lubricant formulations, and are excellent base stocks for crank case lubricants, 2-cycle oils, high temperature greases, compressor oil, gear lubes, hydraulic fluids, and many other industrial applications where a combination of the following properties are required: (a) mineral oil compatability; (b) excellent lubricity and anti-wear properties; (c) good thermal and oxidative stability; (d) high viscosity index; (e) low evaporation losses and low flammability; (f) excellent antifoaming & demulsification properties; (g) high solvency and dispersancy; (h) low toxicity and high biodegradability; and (i) wide temperature range.

These properties make them excellent candidates for any future development of other functional fluids including transmission, hydraulic brake, and electrical refrigeration fluids, and transformer and other gas turbine lubricants.

The last group of fat-based esters includes the mono-, di- and triglycerides. Their applications include cutting oils, textile fiber lubricants, food-processing lubricants and plastic film slip agents. Many of these products are derived by the interesterification or glycerolysis of naturally occurring lauric, tallow and vegetable oils to a triglyceride or a mixture of mono- and diglycerides.

While we have noted many lubrication applications of the fatty-based synthetic esters, such as textile, cutting oils, greases, rolling oils, the latter part of the presentation will be directed primarily to their utilization as engine lubricants. To reiterate, the properly formulated synthetic lubricants possess the following properties: good lubricity; minimum viscosity change with temperature; high thermal and oxidation stability; low volatility; excellent additive response; seal and gasket compatability; and high fire and flash points.

Synthetic lubricants must undergo several critical physical tests. Lubricity is generally determined by actual metal friction tests in which the metals involved are scored or worn away. The Shell 4-Ball wear, Timken, and Falex tests are among the standard methods used to evaluate lubricity. Oil viscosity is critical. For instance, if the crank case viscosity is too high, starting will be increasingly difficult at lower temperatures. There will be inadequate lubrication at the bearing or race sights. With low viscosity, excessive ring wear and oil consumption will shorten the mechanical life of the system. Viscosity measurement is primarily by the Kinematic method following ASTM-D445.

TABLE I

Synthetic Mono and Diester Base Stocks Typical Properties

| Composition | 210 F | Kinematic viscosity CST<br>100 F | -40 F | V.I. | Pour Pt. F |
|---|---|---|---|---|---|
| Mono and dibasic acid esters | | | | | |
| Hexadecyl laurate | 3.30 | 13.95 | 2,033 | 121 | <-80 |
| Di-2-ethylhexyl adipate | 2.38 | 8.22 | 807 | 121 | <-90 |
| Di-isooctyl adipate | 2.72 | 9.55 | 870 | 141 | <-80 |
| Di-isodecyl adipate | 3.63 | 15.80 | 2,880 | 132 | <-75 |
| Di-tridecyl adipate | 5.30 | 28.40 | 20,000 | 132 | <-75 |
| Di-2-ethylhexyl azelate | 2.96 | 11.00 | 1,150 | 138 | <-80 |
| Di-isooctyl azelate | 3.34 | 12.70 | 1,300 | >150 | <-80 |
| Di-tridecyl azelate | 6.50 | 36.50 | 18,700 | 136 | <-70 |
| Di-2-ethylhexyl sebacate | 3.34 | 12.80 | 1,400 | 147 | <-80 |
| Glycol esters | | | | | |
| Dipropylene glycol dicaprylate | 2.50 | 8.90 | 420 | 121 | -75 |
| Dipropylene glycol dipelargonate | 2.70 | 9.80 | 963 | 129 | -75 |
| Triethylene glycol diheptanoate | 2.50 | 8.70 | 400 | 128 | -65 |
| Triethylene glycol dicaprylate-caprate | 2.60 | 9.50 | 800 | 120 | -65 |

TABLE II

Physical and Chemical Testing of a Jet Engine Synthetic Lubricant[a]

| Test | | Requirements | |
|---|---|---|---|
| Viscosity, cs @ 210 F. | | 5.00-5.50 | |
| 100 F. min. | | 25.0 | |
| -40 F. max. | | 13,000 | |
| -40 F. Stability, % change after 72 hr. | | 6 | |
| Flash point °F. min. | | 475 | |
| Pour pt. °F. max. | | -65 | |
| Total acid no., max. | | 0.50 | |
| Evaporation, 400 F/6-½ hr., % wt. max. | | 10 | |
| Foaming | | | |
| Seq. I, ml initial, ml final | | 25-0 | |
| Seq. II, ml initial, ml final | | 25-0 | |
| Seq. III, ml initial, ml final | | 25-0 | |
| "H" rubber swell, 158 F/72 hr., % change | | 5.0 to 25.0 | |
| "F" rubber swell, 400 F/72 hr, % change | | 5.0 to 25.0 | |
| Thermal stability, % corrosivity @ 525 F. 96 hr | | | |
| Viscosity change at 100 F. % max. | | 5.0 | |
| Total acid no. change, max. | | 6.0 | |
| Metal weight change mg/cm$^2$, max. | | 4.0 | |
| Corrosion and oxidation stability 72 hr. | 347 F | 400 F | 425 F |
| Viscosity change @ 100 F., % | -5 to +25 | -5 to +25 | Report |
| Total acid no. change, max. | 2 | 3 | Report |
| Contamination mg/100 ml max. | 50.0 | 50.0 | Report |
| Metal weight change mg/cm$^2$, max. | | | |
| Steel | ±0.2 | ±0.2 | ±0.2 |
| Silver | ±0.2 | ±0.2 | ±0.2 |
| Aluminum | ±0.2 | ±0.2 | ±0.2 |
| Magnesium | ±0.2 | ±0.2 | — |
| Copper | ±0.4 | ±0.4 | -- |
| Titanium | — | — | ±0.2 |

[a] Lubricating oil, aircraft turbine engine synthetic base – MIL-L-23699.

All lubricants show viscosity changes with temperature. As temperature rises, viscosity falls. The smaller the change in viscosity with temperature changes, the higher the viscosity index (VI), and therefore the oil is applicable for use over a wider range of temperatures.

Low temperature fluidity is determined by pour point. Many synthetic ester lubricants have pour points of -60 C and lower with comparable low viscosities. In addition, most synthetic lubricants have low volatility. Combined with their low viscosity, these fluids widen the practical temperature range to which they can be used, offering significant economy as well as functional value. Hydrocarbon oil of the same low viscosity is much more volatile, demanding more frequent replenishment. Table I shows several examples of mono-, dibasic and glycol esters, their respective viscosities, viscosity indices and pour points. Thermal and oxidative stability are the most critical requirements for synthetic lubricants, particularly with the advent of aircraft engines that operate at increasingly higher temperatures. Within the limit of obtainable organic compounds, structurally designed carboxylic esters offer reasonably good thermal stability at service in the 275 to 310 C range.

An example of a military specification is MIL-L-23699,

TABLE III

Physical and Chemical Testing of a Jet Engine Synthetic Lubricant[a]

| Test | Requirements |
|---|---|
| Shear stability, viscosity change, % max. | 4.0 |
| Sediment | |
| 1.2 micron filter, mg/l, max. | 10.0 |
| Total ash, mg/1, max. | 1.0 |
| Ryder gear, average relative rating | |
| Two determinations, % min. | 112 |
| Reference oil absolute rating | |
| Current average, lb./in. | Report |
| Bearing test 100 hr. | |
| Overall demerits, max. | 80 |
| Filter deposits, % max. | 3 |
| Oil consumption, ml, max. | 2,000 |
| Viscosity change, % cs, 100 F. | -5 to +30 |
| TAN, change, max. | 2 |
| Trace metal content | |
| Metal | PPM |
| Al | 2 |
| Fe | 2 |
| Cr | 2 |
| Ag | 1 |
| Cu | 1 |
| Sn | 4 |
| Mg | 2 |
| Ti | 2 |
| Ni | 2 |

[a]Lubricating oil, aircraft turbine engine synthetic base – MIL-L-23699.

TABLE IV

Oxidation Inhibition, One Percent Phenyl Alphanapthyl Amine

| Ester | 0 | 1% |
|---|---|---|
| Di-2-Ethyl hexyl azelate AN change | 18.5 | 1.1 |
| % Visc. increase 37 C | 50.8 | 5.3 |
| % Wt loss | 11 | 3.5 |
| PE Ester | | |
| AN change | 3.6 | 0.3 |
| % Visc. increase 37 C | 102 | 5.5 |
| % Wt. loss | 6.5 | 1.3 |

TABLE V

Synthetic Lubricant Additive Packages for Gas Turbine Engines

| | | |
|---|---|---|
| Antioxidant | Hindered amines | 2.0% |
| Antioxidant | Quinazarin | 0.1% |
| Anticorrosion | Sebacic acid | 0.02% |
| Antiwear | Substituted phosphate ester | 1-2% |
| Antifoam | Polysiloxane | --- |

"Military Jet Engine." (Table II.) It demonstrates the minimal requirements of a syn jet engine lube required to meet that specification. The properties of viscosity, flash, pour points, thermal and oxidation stability, shear, Ryder gear, are very critical in meeting requirements of this specification, (Table III).

Critical to thermal stability is the strict adherence to the principal of a hydrogen-free beta carbon atom in the polyol component. As an example, three esters were heated for 150 hr at 260 C. The acid number was measured and the $C_9$ pentaerythritol ester gave only 4% decomposition, while a comparable molecular weight $C_9$-trimethylpentane-1,3-diol ester decomposed to the extent of 45% and a dibasic ester, di-isooctyl azelate, decomposed to the extent of 14%. As an example of a simple ester that contains a beta hydrogen, ethyl stearate probably decomposes to stearic acid and ethylene. This decomposition probably follows an ionic mechanism. Esters without a beta hydrogen in the alcohol portion can decompose by a free radical mechanism.

Because free radicals require substantially more energy to form, a higher initiating temperature is required for this path of decomposition. As a consequence, the polyol esters without the beta hydrogen are more thermally stable. The diol ester and the dibasic acid ester both contain a beta hydrogen. Decomposition of the azelate is probably less because primary alcohol esters are more stable than secondary alcohol esters.

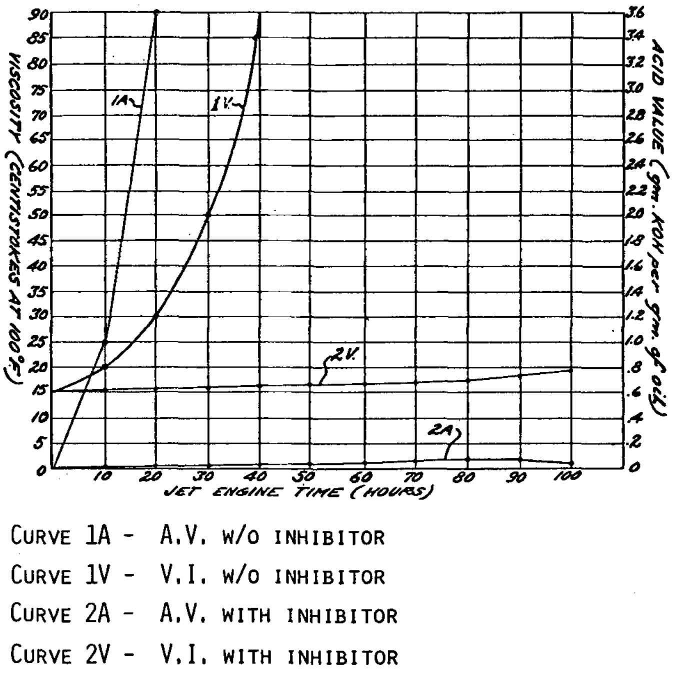

FIG. 1. Jet engine lube test using TMP-$C_7$ ester with and without the antioxidant package.

The dominant factor in ever-increasing high temperature performance is oxidative stability. An example of a dibasic acid ester is di-2-ethylhexyl sebacate exposed to air for 24 hr at 215 C, giving a viscosity increase of 200% at 37 C and a corresponding acid number increase of 32. A trimethyolpropane $C_9$ triester gave a viscosity increase of 380% and a corresponding acid number increase of 16. The pentaerythritol ester gave a viscosity increase of 500%, and an acid number increase of only 7. A generalization can be drawn from this in that the polyol esters can withstand a more stringent combination of time and temperature than can the dibasic acid esters. However, on the other hand, viscosity buildup is substantially less for the dibasic acid esters than for the hindered polyol esters once significant oxidative breakdown has occurred.

There are several postulated mechanisms with air or oxygen in the decomposition and polymerization of this type of ester. The excited state of oxygen reacts to form alkyl free radical plus a hydroperoxide free radical group. The resultant alkene polymerization can occur in any of three ways: (a) the combination of two free radicals which further combine until chain termination occurs; (b) cationic polymerization, which takes place normally in the presence of Lewis acid or a hydrogen source, which can be produced from the oxidation of a metal, and the resultant carbonium ion is the basis for polymerization; (c) an anionic polymerization mechanism that would apply to oxidation of esters if selective ions were present to form a strong base.

All gas turbine engine ester lubricants require antioxidants; PANA is a commonly used antioxidant. In Table IV is shown the AN change, viscosity and weight loss percent of a dibasic acid and a pentaerythritol ester with 1% PANA

TABLE VI

Current and Projected Synthetic Lubricant Estimated Consumption, Synthetic and Fat-Based

| Industry | Chemical type | 1979 MMLBS | 1985 MMLBS |
|---|---|---|---|
| Aerospace | Polyol | 32-35 | 42 |
| Aerospace | Dibasic | 6 | 5 |
| Automobile crankcase | Polyol | 4-6 | 16 |
| Automobile crankcase | Dibasic | 8-10 | 12 |
| Others (stationary turbine, hydraulic air compressors, textile, auto) | Dibasic and polyol | 34-37 | 43 |

addition, under 202 C, 24 hr. Additive packages for gas turbines usually contain, in addition to one or more hindered amines as an antioxidant, an anticorrosion agent, an antiwear agent and antifoaming agent (Table V). The necessity for oxidation inhibitors in fully formulated jet engine lubricants is shown graphically in Figure 1.

Illustrated is a TMP-$C_7$ ester with and without an antioxidant package. The viscosity and the acid value increase rapidly for the polyol ester and greatly retard the effectiveness of the lubricant after ca. 10 hr of jet engine running time. The inhibited lubricant ester system shows excellent retention of viscosity and minimal AN buildup from decomposition.

The outlook for fatty-derived (nonsynthetic) lubricant base ester stocks is of diminishing market share in a total market growing an estimated 6-8% a year. Several factors contribute to this decline in market share: (a) production of fractionated coconut fatty acids ($C_8$–$C_{10}$) is static while demand for lauric acid continues to decline; (b) there is increased world value of coconut oil and tallow; (c) there is limited growth potential and uncertain availability of byproduct heptanoic acid from castor oil in the production of nylon; (d) domestic pelargonic acid growth rate is dependent on azelaic demand; (e) there is no forecast for additional azelaic acid capacity; (f) sebacic acid demand is diminishing due to higher costs.

With all the higher costs coupled with static capacity, it is of little surprise to see the following activity in the synthetic fatty acid sector: (a) increased capacity of $C_5$ production; (b) new installation of $C_7$ and $C_9$ acid plant; (c) rapid growth of adipic acid and oxo-alcohol dibasic acid esters.

Synthetic lubricant projections (Table VI) for specific industries – aircraft, automobile and other industrial applications – show an overall growth rate from 6-8% for the next five years. This overall growth rate is mostly due to the automobile crankcase application of synthetics and partial synthetics. These automobile market projections are clouded by several factors which include consumer acceptance, automobile manufacturers' approval, and government regulatory compliances. As an example, by 1985 the average mile per gallon of the automobiles produced is to be 27.5 mpg.

One of the options being seriously considered and under testing at this very moment are fuel-efficient lubrication systems. These include total and partial synthetics as well as various mineral oil blends. No one knows who is going to win, but the rewards are great – there is a forecast of a total of 2,590 million gallons of all classes of petroleum-based lubricants. Synthetics of all types (esters, polyalphaolefins, alkylated aromatics, etc.) have ca. a 2.5% share of this current market. Consequently, small market share growth of synthetic fatty-based lubricants would severely tax the existing fatty and synthetic acid production capabilities, as well as ester manufacturing capacities. This is the prime feature of the market for synthetic lubricants – unlimited opportunities for technological advances.

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