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SYNTHETIC LUBRICANT

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This invention relates to synthetic lubricating oils, and particularly to lubricating compositions having outstanding lubricating properties at low and high temperatures and that have outstanding extreme pressure resisting characteristics. More particularly, the invention relates to a synthetic lubricating composition which comprises a blend of a diester, a minor amount of tricresyl phosphate, and a minor amount of a metallic soap of a petroleum sulfonic acid.

In an effort to obtain superior lubricating oils having specific and unusual characteristics made necessary by the technical developments in the last few years, new synthetic lubricants have been developed by the art. One class of materials which has attracted unusual interest as synthetic lubricants are the esters, both the simple esters and the complex type. In general these synthetic lubricating oils are characterized by lower volatility, higher viscosity indices, and lower pour points than mineral oils of a corresponding viscosity level. Lubricants possessing such properties are of special value in the lubricating of moving parts such as combustion turbines, particularly those of the "prop-jet" and "turbo-jet" type for aircraft. Mineral oil lubricants containing added viscosity index improvers, pour point depressors, or other such additives are undesirable for use in such engines because of their tendency to leave a residue which accumulates and interferes with the operation of the turbine. Yet it has been found that these additive materials must be added to mineral oils to give them extreme pressure resistance and viscosity characteristics essential for operating at the extreme temperature differentials experienced. The synthetic lubricants of the ester type are especially adaptable for use under such conditions since these lubricants without additive materials of these types have a desirable combination of low volatility, low pour points, and high viscosity indices.

With the continued development of aircraft engines designed to operate at peak efficiency at high altitudes it has been found that there also exists a problem of lubricity and/or load carrying capacity. It is with this problem of incorporation of desirable viscosity properties with lubricity or load characteristics, which may be termed extreme pressure resistance, in a synthetic oil blend that this invention is concerned.

It has now been found, and forms the object of this invention, that a synthetic lubricating composition having outstanding high and low temperature characteristics and outstanding extreme pressure resistance may be pre-

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pared by blending with a branched chain alcohol ester of a dibasic acid, a minor amount of tricresyl phosphate and a minor amount of the calcium or sodium soap of a petroleum sulfonic acid. The proportions of the resulting blend are critical, and will be specifically illustrated in detail below.

New design "turbo-jet" and "turbo-prop" engines featuring high compression ratios and increased power output have forced temperatures upward and have increased the load on gears and bearings. Oil cooling has also become a problem since bearing temperatures in excess of 450° F. are not uncommon. These factors subject the lubricant to extremely severe conditions with regard to high temperature performance and load handling ability, in addition to the ordinary low temperature requirements. Lubricants designed for these engines, therefore, must exhibit an outstanding combination of physical and chemical properties.

As the temperature increases the lubricant tends to thin out, or decrease in viscosity. It is essential, however, that at the high temperatures experienced the lubricant retain sufficient viscosity to furnish the lubricity necessary for decreasing friction. It has been found that in these new design engines, the viscosity of the lubricant at 210° F. and at 100° F. should be about 3.0 to 11.0 centistokes, minimum, respectively. At the same time, however, the viscosity of the oil at the minimum starting temperature of the engine must be sufficiently low so as to prevent serious reduction in the oil flow rate. The maximum viscosity of the oil which can be pumped in adequate quantity has been found to be about 14,500 centistokes at -65° F.

In order to prevent excessive oil consumption the lubricant must possess a sufficiently low volatility. The ASTM flash point is used as a measure of volatility and it has been found that lubricants possessing flash points in excess of about 390° F. have been found to be satisfactory in this respect.

The load carrying ability of lubricants designed for these new uses must be adequate to properly lubricate the main anti-friction bearings and gears at high speeds. This is particularly true for the reduction gear assembly found in turbo-prop engines. Exhaustive tests have shown that the load carrying capacity for a lubricant for this use should be such as to result in a Shell 4-ball seizure point of about 70 kilograms and a weld point of about 120 kilograms, both values given being minimum values. The explanation of the Shell 4-ball test is set out in detail below.

As was stated above, there are three distinct components in the synthetic lubricating oil composition of this invention. They are:

- (1) A branched chain alcohol ester of a dibasic acid;
- (2) Tricresyl phosphate, and
- (3) A sodium or calcium soap of a sulfonic acid.

It is to be understood, of course, that other additive materials may be added to the basic blend to further enhance the properties of the blend. For instance, oxidation inhibitors, such as phenothiazine, may be added; viscosity index improvers or pour depressants may be incorporated into the finished lubricant. In general, however, for reasons pointed out above, it is desirable to

keep the amount of additive materials to a minimum and only in circumstances requiring special properties will these additive materials be included in the finished product.

A more detailed description of the component parts of the compositions of invention is set out below.

THE BRANCHED CHAIN DIESTER

The dibasic acid which is fully esterified to form the diester portion of the lubricating oil blend may be selected from sebacic, azelaic, and adipic acid. These acids are well known in the art and need no further description.

The branched chain alcohol which is used to form the diester of the acid is selected from a group of alcohols which contain from 6 to 16 carbon atoms in branch chain configuration. It is essential that these be some degree of branching in the carbon chain of the alcohol, and, within limits, the higher the degree of branching the more satisfactory the lubricant. Alcohols such as ethylbutyl, ethylhexyl and other well known branch chain alcohols are operable.

One group of alcohols that have recently become commercially available and that answer the requirements for the esterifying alcohol are the so-called "Oxo" alcohols. These alcohols are preferred and are contemplated in the preferred embodiment of this invention.

The Oxo alcohols are prepared by the catalytic reaction of an olefin with carbon monoxide and hydrogen. The reaction, called "Oxo" synthesis, occurs at temperatures in the order of 300° F. to 400° F. at pressures in the range of about 1000 to 3000 p. s. i. In the presence of a suitable catalyst, ordinarily a heavy metal carbonyl, such as cobalt carbonyl, there is formed an aldehyde, which is subsequently hydrogenated to a primary alcohol. This process is described in U. S. Patent No. 2,327,066, issued to Roelen in 1943.

It has been found that particularly desirable alcohols for the esterification of the dibasic acid to prepare the diester component of the blend of this invention may be prepared by the application of the Oxo synthesis to polymers and copolymers of C₃ and C₄ monoolefins. These monoolefins are readily available in refinery streams and processes for their conversion to liquid copolymers have been worked out by the art. One such process, known as UOP polymerization, consists of passing the olefin-containing stream in liquid phase in contact with an acid catalyst comprising phosphoric acid impregnated on kieselguhr. Other acidic catalysts, such as phosphoric acid or copper phosphate impregnated on silica gel, sulfuric acid, Friedel-Crafts catalysts, activated clays, silica-alumina, copper pyrophosphate, etc. may be used. Suitable conditions when employing phosphoric acid catalysts of the UOP type are temperatures of 300° F. to 500° F., pressures from 250 to 5,000 p. s. i., and feed stocks comprising refinery streams containing propylene and mixed butylenes. Suitable feed stocks, for example, may contain from 15 to 60 mol percent propylenes, from 0.5 to 15 mol percent butylenes, and from 0.1 to 10 mol percent isobutylene, the remaining being saturated hydrocarbons. Other suitable feed stocks for the Oxo reaction are the dimer and trimer of isobutylene.

Of the Oxo alcohols operable, those alcohols having from 6 to 16 carbon atoms are preferred. They are prepared from olefin polymers or copolymers having from 5 to 15 carbon atoms. In preparing these Oxo alcohols, the desired olefin fraction is segregated from the crude olefin polymer product by fractionation.

As was stated above, the Oxo alcohols are especially desirable esterifying alcohols because of their optimum degree of branching. For example, the following table shows the structure and percentage composition of a C₈ Oxo alcohol prepared from a C₇ olefin stream which had been fractionated from the products obtained by the phosphoric acid polymerization of refinery gas streams containing propylene and mixed n- and isobutylenes.

Structure of C ₈ Oxo alcohol	Percent
$\begin{array}{c} \text{C} & & \text{C} \\ & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	29.0
$\begin{array}{c} \text{C} & & \text{C} \\ & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	25.0
$\begin{array}{c} & & \text{C} & & \text{C} \\ & & & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	17.0
$\begin{array}{c} & & \text{C} \\ & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	16.0
$\begin{array}{c} & & & & \text{C} \\ & & & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	
$\begin{array}{c} & & & & \text{C} \\ & & & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	2.3
$\begin{array}{c} & & & & \text{C} \\ & & & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	
$\begin{array}{c} & & & & \text{C} \\ & & & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	1.4
$\begin{array}{c} & & & & \text{C} \\ & & & & \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	
α-alkyl-alkanols.....	4.3
Others.....	5.0
	100.0

It will be noted that Oxo alcohols derived from the olefins produced by C₃-C₄ polymerization are mostly methyl substituted.

Of the preferred Oxo alcohols operable as the acid esterifying agent, that is, those Oxo alcohols having from 6 to 16 carbon atoms, especially preferred are those Oxo alcohols having from 6 to 10 carbon atoms, that is the Oxo alcohols prepared from olefins having from 5 to 9 carbon atoms. Specifically they are the C₆ Oxo alcohol, the C₇ Oxo alcohol, the C₈ Oxo alcohol, the C₉ Oxo alcohol, and the C₁₀ Oxo alcohol.

TRICRESYL PHOSPHATE

The second component of the synthetic lubricating compositions of this invention is tricresyl phosphate. This material is well known to the art and has been sufficiently described in the literature. Its preparation forms no part of the instant invention.

THE METAL SULFONATE

The third component of the synthetic lubricant of this invention may be generally described as being a metallic soap of a sulfonic acid. Although the calcium and sodium soaps are preferred, other metallic soaps, such as barium, strontium, potassium, magnesium, etc. may also be used.

The sulfonic acids used to prepare the metallic soaps used in formulating the compositions of the invention may be prepared by suitable treatment of petroleum oils of the lubricating oil range with strong sulfuric acid. The sulfonic acids are then converted to the desired salts, which in the petroleum industry are well known by the name of petroleum sulfonates. The sulfonic acids employed have molecular weights in the range of from about 300 to about 600, preferably from 350 to 550. These acids can also be derived from relatively pure sulfonic acids having from about 10 to about 33 carbon atoms per molecule. For example, sulfonated products of alkylated aromatics such as benzene, toluene, xylene, etc., alkylated with olefins or olefin polymers of the type of polypropylene, etc. can be used. Likewise, alkyl sulfonic acids of the 300 to 600 molecular weight range are also suitable.

The sulfonates may be added to the composition in the form of a dry powder or they may be added in the form of a mineral oil concentrate, the form with which the art is most familiar.

COMPONENT PROPORTIONS

As was stated above, the proportions of the component parts of the lubricant blend of invention are critical, and optimum results are obtained only by use of proportions in a narrow range. It has been found that from 5.0% to 3.0% by weight of tricresyl phosphate blended with from 0.5% to 2.5% by weight of calcium or sodium sulfonate gives an outstanding combination of properties.

The extreme pressure characteristics of the blends of the invention were determined by the well known Shell 4-ball extreme pressure test developed by the Shell Development Company.

Briefly, the test consists of the following: 3 stainless steel balls in fixed relation are contacted by a 4th ball which is rotated at high speeds. The arrangement is such that the 3 stationary balls are each contacted by the 4th rotating ball. By mechanical linkage extreme pressures are placed on the points of contact through the rotating ball. The lubricant to be tested surrounds the points of contact. As pressure increases it has been noted that the first pitting of the contacting surfaces occurs when the pressure is sufficient to force the lubricant from between the metal contacting surfaces. This initial pitting or scoring, an actual seizing of the metal of the surfaces, is called the "seizure point." As pressure is increased a point is reached at which the metal surfaces actually weld and the 4 balls become one unit. This point is referred to as the "weld point." It is to be seen that an increase in the seizure point and the weld point indicates an increase in the lubricity of the test material. Results of the test are reported in kilograms.

Using as a base oil a C₈ Oxo alcohol diester of adipic acid, twelve blends were prepared using various amounts of tricresyl phosphate, a metallic sulfonate, either calcium or sodium, and a complex ester prepared by reacting one mol of a polyethylene glycol of a molecular weight of about 200 with two mols of a half-ester of sebacic acid and 2-ethylhexanol. The first five blends (1-5) were compounded as taught by the prior art, specifically described in copending application, Serial Number 316,732, filed October 24, 1952. The next seven blends (6-12) were prepared utilizing the metallic sulfonate as a replacement for the expensive complex ester.

The twelve blends were then tested for extreme pressure resistance on the Shell 4-ball machine, as described above. Viscosities at 210° F., 100° F., and at -65° F. were obtained. Target specifications are set out for these values, along with the results of the determinations on the various blends in Table I below.

Table I

PHYSICAL DATA ON SYNTHETIC OIL BLENDS

[Base oil: D1-C₈ Oxo adipate.]

Blend No.	Vol. Percent Diester	Vol. Percent Complex Ester (a)	Weight Percent Tricresyl Phosphate	Weight Percent Metallic Sulfonate	Viscosity in Cs.			Shell 4-Ball E. P. Test, Kg. load	
					210° F.	100° F.	-65° F.	Seizure	Weld
1	100	0	0	0	3.0	11.0	14.500	70	120
2	95	5	0	0	2.88	10.10	6,812	40	95
3	100	0	5	0	3.03	11.18	8,349	45	120
4	95	5	5	0	2.87	10.36	8,679	55	95
5	95	5	0	0	3.08	11.43	10,825	70	130
6	100	0	0	2.5	3.07	11.36	10,105	70	120
7	100	0	3	2.5	3.03	11.14	8,228	45	160
8	100	0	3	1.0	3.05	11.39	9,832	55	170
9	100	0	3	0.75	2.92	10.69	8,668	65	130
10	100	0	3	0.50	2.90	10.56	8,542	75	130
11	100	0	5	1.0	2.87	10.43	8,260	80	110
12	100	0	3	0.75	2.90	10.7	9,281	85	135
								70	130

¹ Includes 1.0 wt. percent phenothiazine.² Sodium sulfonate.³ Calcium sulfonate.⁴ Desired blend properties.

The data of Table I above points out the favorable results obtained with blends which utilize the inexpensive and readily obtainable metallic sulfonates instead of the complex ester component of the blend. The substitu-

tion results in an economically advantageous composition, with no loss of desirable high or low temperature characteristics and no loss in extreme pressure resistance.

It will be noted that blends number 4 and 5 show excellent properties at all temperatures and have extreme pressure resistance characteristics that make them very desirable lubricants. Equally favorable results are obtained, however, by substituting the complex ester component with from 0.50 to 2.5 wt. percent of a metallic sulfonate, such as sodium sulfonate or calcium sulfonate. Blends number 7 to 12 illustrate this point.

In addition to the data given in Table I above blends 4 and 11 were also subjected to standard pour point and flash point determinations and various corrosion tests.

The copper, silver, and lead corrosion tests were performed by placing a weighed specimen of the metal in a beaker of the lubricant, heating to a specified temperature while maintaining the lubricant in a high degree of agitation. At the end of the test period, the metallic specimen was cleaned, weighed, and the loss of weight calculated. The test described in the Table II below as the oxidation-corrosion stability test, consists of submerging four metal plates of known area and weight in a bath of 20 cc. of the sample being tested. The temperature is then raised to 347° F. and air is bubbled through the bath. At the end of 72 hours of test time the metal plates are removed, the weight change is determined, and the weight change in mg. per square centimeter calculated. The percentage of oil sample loss is calculated and the neutralization number change determined.

The data for these determinations, that is, the ASTM pour points, flash point, neutralization number, copper, silver, and lead corrosion, and the oxidation-corrosion stability tests on blends 4 and 11 are set out in Table II below:

Table II

Test	Blend 4	Blend 11
Pour Point.....° F.	-75	-75
Flash Point.....° F.	410	420
Neutralization No. (D-664).....	0.24	0.17
Copper Corrosion, 3 hrs. at 212° F. (mg. loss).....	6.0	5.0
Silver Corrosion, 17 hrs. at 325° F. (mg. loss).....	+0.9	+0.9
Lead Corrosion, 1 hr. at 325° F. (mg. loss).....	-0.3	-17.0
Oxidation/Corrosion Stability at 347° F. (wt. change, mg./cm. ²):		
Copper.....	+0.26	+0.28
Magnesium.....	+0.34	-0.21
Iron.....	+0.14	+0.31
Aluminum.....	+0.34	+0.19
Neutralization No. increase.....	0.9	1.9
Evaporation Loss (percent).....	0.9	0.9

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The data of Table II above point out that the blends in accordance with the concept of this instant invention compares very favorably with the outstanding lubricants which contain the complex ester. These data clearly

demonstrate the very desirable stability properties of the lubricant blends of the invention.

To summarize briefly, the instant invention relates to compounded synthetic lubricants which have outstanding high and low temperature properties. The blends have extreme pressure resistant characteristics which make them very satisfactory for use in lubricating the moving parts of aircraft engines. The compositions of invention comprise a blend of a diester, a minor amount of tricresyl phosphate, and a minor amount of a metallic soap of a sulfonic acid. The diester may be selected from the branched chain esters of dibasic acids, such as adipic and sebacic acid. The alcohol chosen should contain from 6 to 16 carbon atoms, preferably from 6 to 10 carbon atoms. Especially preferred are the C₈ to C₁₀ highly branched chain Oxo alcohol esters of adipic and sebacic acid.

The petroleum sulfonate soap may be selected from the sodium, calcium, barium, strontium, potassium and magnesium soaps of sulfonic acids having a molecular weight within the range of from about 300 to 600. Especially preferred and contemplated in the preferred embodiment of this invention are the sodium and calcium soaps of petroleum sulfonic acids having a molecular weight within the range of from about 350 to about 550.

The proportions of the components are critical and it is preferred to utilize from about 3.0 to 5.0 wt. percent of the tricresyl phosphate and from about 0.5% to 2.5% by weight of the metal sulfonate.

Other additive materials may be blended with the compositions of the instant invention in order to enhance special properties. For instance, oxidation inhibitors, such as phenyl alpha naphthylamine or phenothiazine may be used. Viscosity index improvers, pour point depressants, detergent inhibitors, rust preventative agents, and the like, may also be incorporated with the inventive compositions.

What is claimed is:

1. A synthetic lubricating oil composition which consists essentially of a diester formed by esterification of adipic acid with a mixture of alcohols obtained by subjecting a C₇ olefin to the action of carbon monoxide and hydrogen at a temperature of about 300° to 400° F. and a pressure of about 1,000 to 3,000 p. s. i. in the presence of a cobalt carbonyl catalyst, said mixture of alcohols having the approximate composition of

	Percent
3,5-dimethyl-hexanol-1	29.0
4,5-dimethyl hexanol-1	25.0

	Percent
3,4-dimethyl hexanol-1	17.0
3-methyl heptanol-1, 5-methyl heptanol-1	16.0
4-ethyl heptanol-1	2.3
5,5-dimethyl hexanol-1	1.4
α-Alkyl-alkanols	4.3
Others	5.0

containing combined therein about 3% by weight of tricresyl phosphate, and about 0.75% by weight of a metal soap of a petroleum sulfonic acid, said metal selected from the group consisting of sodium and calcium.

2. The synthetic lubricating oil composition of claim 1 wherein said metal is sodium.

3. The synthetic lubricating oil composition of claim 1 wherein said metal is calcium.

4. A synthetic lubricating oil composition which consists essentially of a diester formed by esterification of adipic acid with a mixture of alcohols obtained by subjecting a C₇ olefin to the action of carbon monoxide and hydrogen at a temperature of about 300° to 400° F. and a pressure of about 1,000 to 3,000 p. s. i. in the presence of a cobalt carbonyl catalyst, said mixture of alcohols having the approximate composition of

	Percent
3,5-dimethyl hexanol-1	29.0
4,5-dimethyl hexanol-1	25.0
3,4-dimethyl hexanol-1	17.0
3-methyl heptanol-1, 5-methyl heptanol-1	16.0
4-ethyl heptanol-1	2.3
5,5-dimethyl hexanol-1	1.4
α-Alkyl-alkanols	4.3
Others	5.0

containing combined therein about 5.0% by weight of tricresyl phosphate, and about 1.0% by weight of sodium petroleum sulfonate.

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