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ESTER LUBRICANT

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9 Claims 10

ABSTRACT OF THE DISCLOSURE

A blend of (a) about 1.5-2.5 parts of a trimethylolpropane ester of a mixture of aliphatic monocarboxylic acids containing from 4-12 carbon atoms with (b) about 0.75-2 parts of a dipentaerythritol ester of a mixture of aliphatic monocarboxylic acids containing 4-10 carbon atoms gives an ester blend useful as a synthetic lubricant, especially in turbines and turbojet engines.

This application is a continuation-in-part of application Ser. No. 840,835, filed July 10, 1969 now abandoned.

BACKGROUND

With the development of gas turbine aircraft engines, which must operate at peak efficiency at extremely high altitudes, there has developed needs for lubricants which can endure the extremely high temperatures encountered in these engines for long periods of time and yet remain fluid at the very low temperatures to which these engines are exposed in arctic regions or when the engine is shut down during flight. Engine manufacturers and operations personnel dealing with these engines require a lubricant possessing exceptionally low viscosity at low temperatures and, at the same time, possessing a satisfactory lubricating viscosity at higher temperatures. During the period from about 1940-45, ester lubricants were developed for use primarily in the early turbine engines. The development of these lubricants is described in such publications as Zorn, "Esters as Lubricants," available from the Air Documents Division, T-2 AMC Microfilm No. RC-718 F-18614, Wright Field, Dayton, Ohio, released in July 1947. Until recently, turbojet aircraft have operated at subsonic speeds. The lubrication of turbojet engines in this service has generally been satisfied using diesters of aliphatic dicarboxylic acid such as di-2-ethylhexyl sebacate. Newer aircraft now in service and other aircraft now under development will be required to operate at supersonic speeds requiring higher output turbojet engines. This will place greater stress upon lubricant stability and requires the development of new lubricants which can be used in this service.

SUMMARY

The present invention relates to a synthetic ester useful as a lubricant under extreme operating conditions. The ester is a blend of esters consisting essentially of substantially fully esterified trimethylolpropane esters of mixtures of aliphatic monocarboxylic acids containing 4-12 carbon atoms and substantially fully esterified dipentaerythritol esters of aliphatic monocarboxylic acids containing 4-10 carbon atoms.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

An object of this invention is to provide synthetic ester blends useful in the lubricant field. A further object is to provide blends of synthetic esters having physical properties making them ideally suited as lubricants for turbine engines. Another object is to provide a lubricant

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having a very high viscosity index. A still further object is to provide ester blends having good stability and physical properties that meet the Navy MIL-L-23699-A and Air Force MIL-L-27502 specifications.

The above and other objects are accomplished by providing a synthetic ester blend of:

- (a) 1.5-2.5 parts by weight of a substantially fully esterified trimethylolpropane ester of a mixture of aliphatic monocarboxylic acids containing from 4-12 carbon atoms in proportion such that the average number of carbon atoms in said acids in said mixture is from 6-9, and
- (b) 0.75-2 parts by weight of a substantially fully esterified dipentaerythritol ester of a mixture of aliphatic monocarboxylic acids containing from 4-10 carbon atoms in proportion such that the average number of carbon atoms in said acids in said mixture of acids containing from 4-10 carbon atoms is from 5-9.

Trimethylolpropane (TMP) is the compound 1,1,1-trimethylolpropane and dipentaerythritol (DiPE) is the mono-ether formed from two molecules of pentaerythritol. Small amounts of monopentaerythritol and higher condensation products of pentaerythritol can be present.

In a more preferred embodiment, the acids used to esterify the trimethylolpropane consist of at least 90 weight percent of a mixture consisting essentially of hexanoic, octanoic and decanoic acids, and the acids used to esterify the dipentaerythritol consist of at least 90 weight percent of a mixture consisting essentially of pentanoic, hexanoic, octanoic and decanoic acids. In a still further embodiment, the acid portion of the esters are substantially normal aliphatic monocarboxylic acids. By "substantially normal" is meant that the major portion of the acid mixture is of the normal or straight-chain type. Generally, over 75 percent of the acids are normal, and preferably, over 90 percent of the aliphatic acids are normal.

In a highly preferred embodiment, the trimethylolpropane ester is a substantially fully esterified trimethylolpropane ester of a mixture of substantially normal aliphatic monocarboxylic acids consisting of at least 90 weight percent of a mixture consisting essentially of about 20-30 weight percent hexanoic acids, about 38-48 weight percent octanoic acids, and about 25-35 weight percent decanoic acids, and the dipentaerythritol ester is a substantially fully esterified dipentaerythritol ester of a mixture of substantially normal aliphatic monocarboxylic acids consisting of at least 90 weight percent of a mixture consisting essentially of about 30-60 weight percent pentanoic acids, about 8-20 weight percent hexanoic acids, about 15-32 weight percent octanoic acids, and about 10-25 weight percent decanoic acids.

Both synthetic ester components of the blend are separately prepared by well-known methods. The hindered polyol (trimethylolpropane or dipentaerythritol) is generally mixed in proper proportions with the desired aliphatic monocarboxylic acid mixture and subjected to esterification conditions. There should be enough acid equivalents in the acid mixture to at least esterify substantially all of the hydroxyl radicals in the polyol. A small excess of the acid mixture is generally used, although a large excess is not recommended, because it must be removed after the esterification is complete or the product will have too high an acid number. Removal of large amounts of unreacted acids is not economical and also is troublesome because of emulsion formations. Generally from 1-1.25 equivalents of acid mixture are used for each hydroxyl equivalent of the polyol.

As stated above, the esters are prepared by subjecting the polyol-acid mixture to esterification conditions. By esterification conditions is meant that the reaction is carried out under conditions well known in the art to cause

an organic carboxylic acid and an alcohol to form an ester by eliminating a molecule of water. This is generally promoted by heating the mixture containing the organic carboxylic acid and the polyol. A temperature range of from about 75–300° C. is employed. Preferably the reaction is carried out at a temperature high enough to cause the water formed to distill out, but not so high as to cause decomposition of the reactants or products. Frequently, removal of the water is facilitated by including a water-insoluble azeotroping solvent in the reaction mixture. Suitable solvents include aliphatic or aromatic hydrocarbons. The aromatic hydrocarbons such as benzene, toluene, xylene, mesitylene, and the like, are especially useful. When these are used esterification is generally conducted at the boiling point of the mixture and the water removed from the distillate by phase separation. The solvent is returned to the reaction mixture until esterification is complete. If higher temperatures are desired during an azeotroping solvent the reaction can be carried out under pressure sufficient to raise the boiling point of the mixture to the desired reaction temperature.

The esterification rate can be increased by adding an esterification catalyst to the mixture. Acidic catalysts have been found to be most useful. These catalysts include sulfuric acid, phosphoric acid, p-toluene sulfonic acid, sodium bisulfate, potassium bisulfate, sulfonated polystyrene acidic ion exchange resins, and the like. Other useful catalysts include esters of titanium or zirconium such as tetraalkyl titanates or zirconates (e.g. tetraethyl titanate, tetrabutyl titanate, tetra-n-propyl zirconate, etc.). Also, metal oxides such as zinc oxide, alumina, and the like, can be used. The amount of catalyst is not critical. Only enough is required to promote a reasonable esterification rate. A useful range is from 0.001 to 5 weight percent, based on the weight of the reaction mixture. A preferred catalyst concentration is from 0.1 to 3 weight percent.

The esterification is conducted until the hydroxyl number of the mixture is reduced below about 10. Following this, the ester can be subjected to various treatments to remove undesirable material. Solvents or excess aliphatic carboxylic acids can be removed by heating the ester, preferably under vacuum, to a temperature high enough to cause them to distill out. Temperatures of from 100–250° C. at vacuums under 50 mm. of Hg, preferably under 10 mm. of Hg, are usually sufficient. Residual acid can be removed by washing the ester with an aqueous base such as sodium hydroxide or sodium carbonate. Alternatively, the ester can be first washed with aqueous base prior to distilling out the solvent. This latter method allows the removal of residual water with the solvent. Further drying of the ester can be accomplished by treatment with any of the known drying agents such as anhydrous sodium sulfate. It is generally desirable to subject the final ester to further treatment with an adsorbent material such as activated clay, alumina or charcoal, to remove trace acids and other impurities.

The aliphatic monocarboxylic acid mixtures useful in preparing the esters are mixtures of aliphatic monocarboxylic acids containing, in the case of the trimethylolpropane ester component, from 4–12 carbon atoms per acid molecule, and in the case of the dipentaerythritol ester component, from 4–10 carbon atoms per molecule. The proportion of the individual acids in the mixture is adjusted so that on a mole basis the average number of carbon atoms in the acids of the mixture of acids used to make the trimethylolpropane esters is from 6–9 and the average number of carbon atoms in the acid mixture used to make the dipentaerythritol esters is from 5–9. The average number of carbon atoms is readily calculated by multiplying the number of carbon atoms of each acid by the mole fraction of that acid in the mixture and adding the products. For example, an equal mole mixture of hexanoic and octanoic acids has an average of 7 carbon atoms per molecule on a mole basis.

The aliphatic monocarboxylic acids may be straight or branched chain. Some examples of typical acids used to prepare the esters include n-butyric acid, isobutyric acid, 2-methyl-n-butyric acid, 3-methyl-n-butyric acid, n-pentanoic acid, 2-methyl-n-pentanoic acid, 2-ethyl-n-butyric acid, n-hexanoic acid, 2-methyl-n-hexanoic acid, 2-ethyl-n-pentanoic acid, 3-methyl-n-hexanoic acid, n-heptanoic acid, 2-ethyl-n-hexanoic acid, 2-methyl-n-heptanoic acid, 3-methyl-n-heptanoic acid, 2,3-di-methyl-n-hexanoic acid, n-octanoic acid, 2-methyl-n-octanoic acid, 2-ethyl-n-heptanoic acid, 2,3-dimethyl-n-heptanoic acid, n-nonanoic acid, 2-methyl-n-nonanoic acid, 2-ethyl-n-octanoic acid, 2,3-dimethyl-n-octanoic acid, 2,3,5-trimethyl-n-heptanoic acid, n-decanoic acid, 2-methyl-n-decanoic acid, 2-ethyl-n-nonanoic acid, 2,3-dimethyl-n-nonanoic acid, n-undecanoic acid, 2-methyl-n-undecanoic acid, 2-ethyl-n-decanoic acid, 2,5-dimethyl-n-decanoic acid, and n-dodecanoic acid.

The preferred aliphatic monocarboxylic acids used in making the esters are normal or straight chain acids. Examples of these are n-butyric, n-pentanoic, n-hexanoic, n-heptanoic, n-octanoic, n-nonanoic, n-decanoic, n-undecanoic, and n-dodecanoic. In the most preferred esters the acids used in making the tri methylolpropane ester are mixtures of n-hexanoic, n-octanoic and n-decanoic acids, and the acids used in making the dipentaerythritol esters are n-pentanoic, n-hexanoic, n-octanoic and n-decanoic.

A most preferred mixture of acids for preparing the substantially fully esterified TMP blending component is a mixture consisting of at least 90 weight percent of a mixture consisting essentially of from 20–30 weight percent hexanoic acid, from 38–48 weight percent octanoic acid, and from 25–35 weight percent decanoic acid. A most preferred mixture of acids for preparing the substantially fully esterified DiPE blending component is a mixture consisting of at least 90 weight percent of a mixture consisting essentially of from 30–60 weight percent pentanoic acid, from 8–20 weight percent hexanoic acid, from 15–32 weight percent octanoic acid, and from 10–25 weight percent decanoic acid. As stated above, best results are obtained when the acids are substantially all of the normal configuration.

The amount of the trimethylolpropane ester component and the dipentaerythritol ester component used to prepare the blend is adjusted so that from 1.5–2.5 parts by weight of trimethylolpropane ester is employed for each 0.75–2 parts of the dipentaerythritol ester. Ester blends having superior physical properties are generally obtained when from about 1.9–2.2 parts by weight of the trimethylolpropane ester are used for each 0.9–1.1 part by weight of the dipentaerythritol ester. When using this narrowly-defined ratio of trimethylolpropane ester to dipentaerythritol ester best results are obtained when the trimethylolpropane ester component is a substantially fully esterified trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture consisting essentially of about 20–30 weight percent hexanoic acids, about 38–48 weight percent octanoic acids, and about 25–35 weight percent decanoic acids, and the dipentaerythritol ester component is a substantially fully esterified dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture consisting essentially of about 30–60 weight percent pentanoic acids, about 8–20 weight percent hexanoic acids, about 15–32 weight percent octanoic acids, and about 10–25 weight percent decanoic acids.

An especially preferred class of ester lubricants of this invention is a blend of from about 1.9–2.2 parts by weight of a substantially fully esterified trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of from about 24–28 weight percent hexanoic acid, about 41–45 weight percent octanoic acid, and about 29–33 weight percent decanoic

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acid, and from 0.9–1.1 parts by weight of a substantially fully esterified dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of from about 45–55 weight percent pentanoic acid, about 11–15 weight percent hexanoic acid, and about 13–18 weight percent decanoic acid.

Another highly preferred embodiment is a blend of (a) from about 0.9 to 1.1 parts by weight of a trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture consisting essentially of from 20–30 weight percent hexanoic acid, from 38–48 weight percent octanoic acid, and from 25–35 weight percent decanoic acid, and (b) from about 1.15 to 1.35 parts by weight of a dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture consisting essentially of from 30–60 weight percent pentanoic acid, from 8–20 weight percent hexanoic acid, from 15–32 weight percent octanoic acid, and from 10–25 weight percent decanoic acid.

An especially preferred embodiment is a blend of (a) from about 0.9 to 1.1 parts by weight of a trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of about 24–28 weight percent hexanoic acid, about 41–45 weight percent octanoic acid, and about 29–33 weight percent decanoic acid, and (b) from about 1.15 to 1.35 parts by weight of a dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of about 45–55 weight percent pentanoic acid, about 11–15 weight percent hexanoic acid, about 18–24 weight percent octanoic acid, and about 13–18 weight percent decanoic acid.

The following examples will serve to illustrate the manner in which the esters are prepared. All parts are by weight unless otherwise specified.

EXAMPLE 1

Preparation of TMP ester

In a reaction vessel equipped with stirrer, thermometer, heating means and equipped with a Dean-Stark water separator was placed 67 parts of trimethylolpropane, 235 parts of an acid mixture consisting essentially of 26 weight percent hexanoic acids, 43 weight percent octanoic acids, and 31 weight percent decanoic acids. The acids are substantially normal. There was then added 170 parts of xylene and 6 parts of sodium bisulfate. The mixture was refluxed for 8 hours, during which period water which collected in the separator was removed. At this point, infrared analysis indicated that the hydroxyl content was below 0.1 percent, showing complete esterification. The mixture was then cooled, diluted with an equal volume of petroleum ether, washed twice with 10 percent caustic and then with water until neutral. The solution was dried over anhydrous calcium sulfate and filtered. The petroleum ether solvent was removed by heating the mixture to about 100° C., and the remaining volatile material was distilled out by heating the mixture to about 130° C. at a pressure of under 0.25 mm. Hg. The remaining TMP ester was filtered, giving a blending stock for preparing the ester blends of this invention. Its viscosity was 4.0 cs. at 210° F. and 17.9 cs. at 100° F. Its viscosity index was 134 (ASTM D2270–64).

EXAMPLE 2

Preparation of DiPE ester

In the reaction vessel used in Example 1 was placed 220 parts of n-pentanoic acid and 220 parts of a mixture consisting essentially of 26 weight percent hexanoic acids, 43 weight percent octanoic acids, and 31 weight percent decanoic acids. The acids are substantially all normal. There was then added 143 parts of dipentaerythritol and 2 parts of p-toluene sulfonic acid in 180 parts of xylene.

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The mixture was refluxed for 72 hours, during which period water was continuously removed in the water trap. At this time, infrared analysis indicated less than 0.1 weight percent hydroxyl. The mixture was then cooled, diluted with an equal volume of petroleum ether, washed twice with 10 percent caustic and then with water until neutral. It was then dried over anhydrous calcium sulfate and filtered. The petroleum ether was distilled out up to a liquid temperature of about 100° C. and the remaining volatile material removed by heating to about 130° C. at a vacuum of 0.25 mm. Hg. Finally, the product was filtered, giving a DiPE blending stock useful for preparing the ester blends of this invention. Its viscosity was 9.1 cs. at 210° F., and 59.5 cs. at 100° F. Its viscosity index was 144.

EXAMPLE 3

The following example shows the preparation of a useful TMP ester blend component without employing a catalyst.

To the reaction vessel of Example 1 was added 134 parts of TMP and 475 parts of a substantially normal acid mixture consisting essentially of 26 weight percent hexanoic acids, 43 weight percent octanoic acids, and 31 weight percent decanoic acids. The mixture was heated rapidly to 188° C. and then slowly heated to 240° C., during which period water was removed in the water trap. Heating was continued for 8 hours at a temperature of 240–250° C., at which time infrared analysis showed the hydroxyl content to be less than 0.5 weight percent. The mixture was cooled and diluted with 400 parts of hexane and washed with aqueous caustic. It was then washed with water until neutral and dried over anhydrous calcium sulfate. It was filtered and the hexane and other volatiles removed by heating and then reducing the pressure by heating slowly to 130° C. and lowering the pressure to about 0.5 mm. Hg.

EXAMPLE 4

This example illustrates the preparation of a DiPE ester blend component without the use of a catalyst.

To the reaction vessel of Example 1 was added 59.33 parts of dipentaerythritol, 165 parts of a substantially normal acid mixture consisting essentially of 50 weight percent pentanoic acids, 13 weight percent hexanoic acids, 21.5 weight percent octanoic acids, and 16.5 weight percent decanoic acids. While stirring, the mixture was heated rapidly to 165° C. and then, over a 2.25 hour period, raised to 233° C. while continually removing water in the water trap. The mixture was then slowly heated to 244° C., during the following 5 hour period, at which time the infrared analysis indicated the esterification was complete. It was then cooled, diluted with 100 parts of hexane and washed with 10 percent aqueous caustic. It was then washed with water until neutral and dried over anhydrous sodium sulfate. It was filtered and hexane and other volatiles distilled by heating to 130° C. at 0.5 mm. Hg. The final product was treated with a mixture of activated alumina and decolorizing carbon and then filtered through a filter containing a "Celite" filter mat. The product is a useful blending stock of this invention.

Other fully esterified TMP and DiPE blending components can readily be made following the above procedures by merely varying the amount and types of aliphatic monocarboxylic acids employed within the parameters already described.

EXAMPLE 5

In a glass-lined reaction vessel was placed 9.4 parts of trimethylolpropane, 2.15 parts of xylene and 32.9 parts of an acid mixture consisting essentially of 26 weight percent n-hexanoic acid, 43 weight percent n-octanoic acid, and 31 weight percent n-decanoic acid. The mixture was heated to reflux (150° C.) while stirring and refluxed for 7 hours while removing water from the distillate. The temperature reached 251° C. It was then cooled and diluted with 30 parts of hexane. It was washed with

10 parts of 10 percent aqueous caustic and a second time with 5 parts of 10 percent aqueous caustic. It was washed with water until neutral, dried over 5 parts anhydrous sodium sulfate and filtered. Then 0.5 part of activated alumina was added and the mixture stirred for 10 minutes. Volatiles were distilled out up to a liquid temperature of 160° C. at 73 mm. Hg. Finally, the ester was filtered, giving a useful TMP ester blending component.

EXAMPLE 6

In a glass-lined reaction vessel was placed 6.36 parts of dipentaerythritol, 1.33 parts of xylene and 20 parts

- (p) n-nonanoic
(q) 2-methyl-n-octanoic
(r) n-decanoic
(s) 2-ethyl-n-octanoic
(t) 2,2-dimethyl-n-octanoic
(u) n-undecanoic
(v) 2-methyl-n-decanoic
(w) 3-ethyl-n-nonanoic
(x) n-dodecanoic
(y) 2,2-dimethyl-n-decanoic
(z) 2-ethyl-n-decanoic

TABLE 1.—TMP ESTERS

A	B	C	D	E	F
24.2 parts (a)	5 parts (a)	63.8 parts (e)	100 parts (e)	110 parts (e)	11 parts (e)
63.8 parts (f)	4.7 parts (b)	14.3 parts (f)	20 parts (f)	17 parts (g)	21 parts (e)
71.5 parts (k)	11.2 parts (d)	200 parts (l)	8 parts (g)	14 parts (k)	21 parts (f)
158 parts (o)	16 parts (o)	10 parts (m)	110 parts (l)	140 parts (l)	200 parts (l)
95 parts (r)	16 parts (g)	10 parts (n)	50 parts (o)	19 parts (m)	37 parts (o)
55 parts (x)	200 parts (l)	17 parts (o)	120 parts (r)	110 parts (r)	30 parts (r)
	100 parts (m)	110 parts (r)	50 parts (s)	23 parts (s)	7 parts (b)
	17 parts (n)	60 parts (s)	9 parts (t)	30 parts (x)	21 parts (v)
	8.7 parts (q)			14 parts (z)	
	50 parts (r)				
	45 parts (s)				

TABLE 2.—DIPE ESTERS

G	H	I	J	K	L
48 parts (b)	200 parts (c)	10 parts (a)	340 parts (e)	350 parts (e)	450 parts (e)
200 parts (e)	24 parts (d)	300 parts (c)	20 parts (f)	33 parts (f)	89 parts (e)
25 parts (d)	205 parts (e)	36 parts (d)	23 parts (h)	290 parts (l)	130 parts (l)
280 parts (e)	50 parts (g)	170 parts (e)	280 parts (l)	16 parts (m)	13 parts (m)
20 parts (f)	50 parts (i)	15 parts (f)	20 parts (m)	10 parts (n)	50 parts (r)
20 parts (h)	21 parts (k)	6 parts (h)	16 parts (o)	110 parts (r)	16 parts (s)
90 parts (l)	140 parts (l)	145 parts (l)	160 parts (r)	40 parts (s)	10 parts (t)
10 parts (m)	10 parts (m)	13 parts (o)	15 parts (s)	39 parts (t)	
19 parts (o)	9 parts (n)	50 parts (r)	14 parts (t)		
35 parts (r)	70 parts (r)	16 parts (s)			
12 parts (s)	24 parts (s)	10 parts (t)			

of an acid mixture consisting essentially of 50 weight percent n-pentanoic acid, 13 weight percent n-hexanoic acid, 21.5 weight percent n-octanoic acid, and 15.5 weight percent n-decanoic acid. The mixture was heated to reflux (150° C.) while stirring and refluxed for 11 hours while continuously removing water from the distillate. The temperature reached 245° C. It was then cooled and diluted with 16.5 parts of hexane. It was washed with 8 parts of 10 percent aqueous caustic and a second time with 4 parts 10 percent aqueous caustic. It was washed with water until neutral and then dried over 5 parts anhydrous sodium sulfate and filtered. Hexane was distilled out to a temperature of 129° C. and then 0.25 part of activated alumina added. Distillation of volatiles was continued up to 140° C. while reducing pressure to 4 mm. Hg. Final filtration gave a useful DiPE ester blending component.

Individual TMP and DiPE ester blending components are prepared following the general procedures of Examples 3 and 4 but using the various acid mixtures shown in the following tables. The amount of acid used is based on the use of 134 parts of TMP in the TMP ester table and 136 parts of DiPE in the DiPE ester table. The aliphatic monocarboxylic acids shown in the table by letters are identified as follows:

- (a) n-butyric
(b) isobutyric
(c) n-pentanoic
(d) 2-methyl-n-butyric
(e) n-hexanoic
(f) 2-methyl-n-pentanoic
(g) 2,2-dimethyl-n-butyric
(h) 2-ethyl-n-butyric
(i) n-heptanoic
(j) 2-methyl-n-hexanoic
(k) 2,2-dimethyl-n-pentanoic
(l) n-octanoic
(m) 2-methyl-n-heptanoic
(n) 2,2-dimethyl-n-hexanoic
(o) 2-ethyl-n-hexanoic

Blends useful as lubricants of this invention are prepared by mixing the TMP esters and DiPE esters selected from the foregoing tables in the proportion shown in the following table.

TABLE 3.—BLENDED ESTERS

Blend	TMP ester	DiPE ester
I.....	250 parts (A).....	75 parts (K).....
II.....	150 parts (D).....	125 parts (L).....
III.....	200 parts (B).....	100 parts (H).....
IV.....	225 parts (C).....	75 parts (J).....
V.....	190 parts (E).....	110 parts (G).....
VI.....	210 parts (F).....	100 parts (H).....
VII.....	230 parts (B).....	110 parts (L).....
VIII.....	160 parts (D).....	90 parts (K).....
IX.....	170 parts (E).....	110 parts (I).....
X.....	210 parts (F).....	120 parts (G).....

In like manner, many other useful ester blends can be obtained by blending other combinations of the TMP and DiPE esters shown in the above table. Likewise, other useful esters can be obtained by varying the amount of each type ester within the range of from 1.5–2.5 parts of TMP ester for each 0.75–1.25 parts of DiPE ester.

An unusual feature of the present blends is their exceptionally high viscosity index. In fact, it has been surprisingly found that the viscosity index of the blend is higher than that of either blend component. Viscosity index is a standard industry-recognized criteria for measuring the ability of an oil to resist change in viscosity with change in temperature (ASTM method D-2270-64). Thus, a lubricant with a high viscosity index tends to maintain a lubricating viscosity at higher temperature and still not become too viscous at low temperature. This is an especially important property of the lubricant in turbine use. Turbines must be able to be started under arctic conditions but must still have a lubricant that will protect at the temperature reached under maximum output.

Blends were prepared which illustrate the improved viscosity index of the blends of this invention. The following table summarizes the viscosity properties of the pre-

ferred blend components and those two of the preferred blend. These preferred blends not only have higher viscosity indices than that of either component but have the other physical properties required to satisfy MIL-L-23699-A and MIL-L-27502 specifications.

TABLE 4

	Viscosity (cs.)		Viscosity index ¹
	210° F.	100° F.	
1. dipentaerythritol ester of Example 2...	9.1	59.5	144
2. trimethylolpropane ester of Example 1...	4.0	17.9	134
3. blend of 2 parts TMP ester and 1 part DIPE ester.....	5.1	25.0	147
4. blend of 1 part TMP ester and 1.25 parts DIPE ester.....	6.0	32.3	148

¹ ASTM method D-2270-64 (Reapproved 1968). Also a standard of the Institute of Petroleum under the designation IP 226.

The above results show that the blend components have a viscosity index of from 134-144. Surprisingly, the blends have a viscosity index of 147-148, which is significantly higher than that of either blend component.

Other blends of the esters prepared in Examples 1-6 are readily made by merely mixing the esters in the proportions previously described.

Tests were carried out to demonstrate the stability of the ester blends of this invention under high temperature oxidative conditions. These tests, called "Oxidative Stability Tests," are carried out by first formulating the ester lubricant to contain 0.8 weight percent dioctyl diphenylamine, 0.8 weight percent phenyl- α -naphthylamine, 0.04 weight percent benzotriazole, and 2.0 weight percent tricresylphosphate. Then 100 ml. samples are placed in test cells along with copper and steel coupons. They are heated to 400° F. and air is bubbled through the fluid at a rate of 5 l./hr. for 72 hours. Following this, the weight loss of the coupons is determined and also the acid number, viscosity increase, visual appearance and pentane insolubles are determined. Results obtained with the above blended ester lubricants are as follows:

TABLE 5

Ester No.	Mg. wt. loss		Acid No.	Percent visc. increase	Vis. ual ¹	Pentane insolubles ²
	Cu	Steel				
5. Blend of 70 parts of TMP ester of Example 3 and 30 parts of DIPE ester of Example 4.....	0	0	0.7	10	A	0.02
6. Blend of 67 parts of TMP ester of Example 3 and 33 parts of DIPE ester of Example 4.....	0	0	0.8	14	A	0.02

¹ On the basis where A is unchanged and E is very dirty.

² Mg./100 ml. sample.

As the above results show, the ester blends of this invention not only possess excellent physical properties but are also highly stable under severe oxidative conditions.

In preparing turbine lubricants using the esters of this invention it is preferred to include other additives to improve the properties of the lubricants. These include antioxidants, metal passivators, extreme pressure agents, anti-foam agents, and the like. A useful antioxidant range is from 0.1 to 5.0 weight percent. The preferred antioxidants include:

phenothiazine
phenyl- α -naphthyl amine
phenyl- β -naphthyl amine
dioctyldiphenyl amine
N-alkylphenothiazines
dipyridyl amine

5-ethyl-10,10-diphenylphenazasilane

3,7-dialkylphenothiazines

diphenyl amine

dinaphthyl amine

5 butyl- α -naphthyl amine

ditolyl amine

phenyl tolyl amine

tolyl naphthyl amine

dicyclohexyl amine

10 diphenyl p-phenylene diamine

4-tert-butyl catechol

2,6-di-tert-butyl-p-cresol

hexyl gallate

tri-nonylphenyl phosphite

15 polymerized trimethyl dihydroquinoline

p,p'-dioctyl diphenyl amine

octylphenyl- β -naphthyl amine

octylphenyl- α -naphthyl amine

p-amino diphenyl amine

20 o-aminophenol

hydroxy diphenyl amine

dodecyl aniline

3-pentadecyl-4-aminophenol

10-methyl-3,7-dioctyl phenothiazine

25 10-n-octyl-3,7-dioctyl phenothiazine

10-phenyl-3,7-dioctyl phenothiazine

10-tolyl-3,7-dioctyl phenothiazine

10-cyanoethyl-3,7-dioctyl phenothiazine

10-cyanobutyl-3,7-dioctyl phenothiazine

30 10-benzyl-3,7-diisopropoxy phenothiazine

10-benzyl-3,7-butoxy phenothiazine

Metal passivators are used in concentrations from 0.001 to 2.0 weight percent. Useful metal passivators include:

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1,4-dihydroxy anthraquinone

1-salicylaminoguanidine

benzotriazole

benzimidazole

40 butylbenzothiazole

methylene-bis-benzotriazole

C₁₄₋₁₈ aliphatic carboxylic salt of 1-salicylaminoguanidine

polyhydroxyanthraquinone

45 N,N'-disalicylidene-1,2-propane diamine

N,N'-disalicylidene-1,2-ethane diamine

quinizarin

alizarin

50 Extreme pressure agents are used in concentrations from 0.1 to 5.0 weight percent. Typical extreme pressure agents

are the esters of acids of phosphorus including triarylphosphates such as triphenylphosphate, tricresylphosphate, phenyldicresylphosphate, tritolylphosphate, and the tri-alkylphosphates and phosphonates such as tri-n-butylphosphate, tri-(2-ethylhexyl)phosphate, tri-methylcyclohexylphosphate, tri-butylphosphonate, tri-(β -chloroisopropyl)phosphonate, and the like.

Silicones such as dimethyl silicone, diethyl silicone, and the like, are used in small amounts, from about 1 to 50 p.p.m., to inhibit foam.

The following examples illustrate the blending of typical turbine lubricants using the esters of this invention.

EXAMPLE 7

In a blending vessel is placed 100 parts of ester No. 3 from Table 4. To this is added one part of phenyl- α -naphthyl amine, one part of dioctyldiphenyl amine, 0.1 part of a fatty acid salt of 1-salicylaminoguanidine, 0.02 part of 1,4-di-hydroxy anthraquinone, 3 parts of tricresylphosphate and 5 p.p.m., based on the total, of dimethyl silicone. The mixture is stirred until homogenous and then filtered through a fine filter, resulting in an ester lubricant suitable for use in lubricating turbine bearings.

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EXAMPLE 8

In a blending vessel place 1000 parts of ester No. 4 from Table 4, 50 parts of tricresylphosphate, 30 parts of 3,7-dioctylphenothiazine, 1 part of quinizarin and 0.05 part of dimethyl silicone. Stir the mixture until homogeneous and then filter, giving a suitable formulated ester lubricant.

EXAMPLE 9

In a blending vessel place 1000 parts of ester No. 5 from Table 5, 10 parts of phenyl- α -naphthyl amine, 10 parts of dioctyldiphenyl amine, 5 parts of benzotriazole and 20 parts of tricresylphosphate. Stir the mixture until homogenous and filter to obtain a synthetic lubricant suitable for use in turbine engines.

Although the principal use for the ester blends described herein is as lubricants for turbine engines, they are also eminently useful in other applications. For example, they are readily thickened by fatty acid soaps such as the alkali or alkaline earth metal stearates to form synthetic ester greases. Addition of about 10–20 weight percent of lithium stearate to the hot ester followed by cooling gives a useful synthetic ester based grease.

They are also useful as plasticizers in a wide range of plastics. For example, adding 5–50 parts per 100 of ester to a calendering grade of polyvinyl chloride resin gives a useful flexible product.

They are also useful in various specialty applications which require a liquid that does not freeze and maintains good flow characteristics over a wide temperature range. For example, they can be used as damping fluids in instruments having moving parts that require damping, such as compasses. Another example is their use as the liquid in bubble type levels. They can also be used as fluid in hydraulic shock absorbers.

Useful automatic transmission fluids are readily formulated from the ester blends by addition of an antioxidant such as phenyl- β -naphthyl amine, a wear agent such as tricresylphosphate, and a small amount of a methyl silicone foam agent.

The ester can be used to lubricate internal combustion engines including both spark ignited and diesel engines. In this use they can be used as the sole base stock or they can be blended with mineral lubricating oils to obtain the desired properties at the least cost. In this use, typical additives can be included such as zinc dialkyl-dithiophosphates, calcium sulfonates, barium salts of phosphosulfurized high molecular weight olefins and dispersants such as high molecular weight alkenyl succinimides and succinamides of ethylenepolyamines such as tetraethylenepentamine and mixtures thereof.

We claim:

1. A synthetic ester consisting essentially of a blend of:

(a) 1.5–2.5 parts by weight of a substantially fully esterified trimethylolpropane ester of a mixture of aliphatic monocarboxylic acids containing from 4–12 carbon atoms in proportion such that the average number of carbon atoms in said acids in said mixture is from 6–9, and

(b) 0.75–2 parts by weight of a substantially fully esterified dipentaerythritol ester of a mixture of aliphatic monocarboxylic acids containing from 4–10 carbon atoms in proportion such that the average number of carbon atoms in said acids in said mixture of acids containing from 4–10 carbon atoms is from 5–9.

2. An ester blend of claim 1 in which:

(a) said ester of trimethylolpropane is a substantially fully esterified trimethylolpropane ester of an aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture of hexanoic, octanoic and decanoic acids, and

(b) said ester of dipentaerythritol is a substantially fully esterified dipentaerythritol ester of an aliphatic

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monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture of pentanoic, hexanoic, octanoic and decanoic acids.

3. An ester blend of claim 2 in which said aliphatic monocarboxylic acids have a substantially normal configuration.

4. An ester blend of claim 3 in which:

(a) said ester of trimethylolpropane is a substantially fully esterified trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture consisting essentially of from 20–30 weight percent hexanoic acid, from 38–48 weight percent octanoic acid, and from 25–35 weight percent decanoic acid, and

(b) said ester of dipentaerythritol is a substantially fully esterified dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting of at least 90 weight percent of a mixture consisting essentially of from 30–60 weight percent pentanoic acid, from 8–20 weight percent hexanoic acid, from 15–32 weight percent octanoic acid, and from 10–25 weight percent decanoic acid.

5. An ester blend of claim 4 in which said blend consists essentially of:

(a) from 1.9–2.2 parts by weight of said trimethylolpropane ester, and

(b) from 0.9–1.1 parts by weight of said dipentaerythritol ester.

6. An ester blend of claim 5 in which:

(a) said trimethylolpropane ester is a substantially fully esterified trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of about 24–28 weight percent hexanoic acid, about 41–45 weight percent octanoic acid, and about 29–33 weight percent decanoic acid, and

(b) said dipentaerythritol ester is a substantially fully esterified dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of about 45–55 weight percent pentanoic acid, about 11–15 weight percent hexanoic acid, about 18–24 weight percent octanoic acid, and about 13–18 weight percent decanoic acid.

7. An ester blend of claim 4 in which said blend consists essentially of:

(a) from about 0.9–1.1 parts by weight of said trimethylolpropane ester, and

(b) from about 1.15–1.35 parts by weight of said dipentaerythritol ester.

8. An ester blend of claim 7 in which

(a) said trimethylolpropane ester is a substantially fully esterified trimethylolpropane ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of about 24–28 weight percent hexanoic acid, about 41–45 weight percent octanoic acid, and about 29–33 weight percent decanoic acid, and

(b) said dipentaerythritol ester is a substantially fully esterified dipentaerythritol ester of a substantially normal aliphatic monocarboxylic acid mixture consisting essentially of about 45–55 weight percent pentanoic acid, about 11–15 weight percent hexanoic acid, about 18–24 weight percent octanoic acid, and about 13–18 weight percent decanoic acid.

9. A formulated ester blend comprising at least 90 weight percent of a synthetic ester blend of claim 1 and

(a) from about 0.01–5 weight percent of an antioxidant for synthetic ester lubricants,

(b) from about 0.001–2 weight percent of a metal passivator, and

(c) from about 0.1–5 weight percent of an extreme pressure wear agent.

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,694,382 Dated September 26, 1972

Inventor(s) Joseph P. Kleiman, Robert E. Malec and Larry Plonsker

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading on the patent, "Larry Lonsker" should read -- Larry Plonsker -- . Column 5, line 5, after "about 11-15 weight percent hexanoic acid," insert -- about 18-24 weight percent octanoic acid, -- .

Signed and sealed this 13th day of February 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents