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LOW TEMPERATURE STABILITY OF SYNTHETIC LUBRICANTS

Benjamin T. Fowler and Michael F. Hoare, Abingdon, and Hans G. Krischai, Oxford, England, assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to a composition adapted to lubricate aviation gas turbine engines, in particular it relates to lubricating compositions containing a substantial proportion of synthetic lubricant.

Broadly speaking, the properties required for an aviation turbine lubricant are good high temperature stability, good viscosity temperature characteristics, and load carrying ability, and the coupling of a low viscosity at low temperatures with a low vapour pressure at high temperatures. These qualities are not simultaneously available from any economically attractive refining process applied to a petroleum oil.

However, it has previously been suggested that compositions approaching these characteristics may be formulated by using a major proportion of certain synthetic esters, in particular diesters and complex esters or blends of the two can be found having properties approaching those desired.

The preferred synthetic lubricant base used in this invention contains a major proportion of compounds having the following structural formulae:

$$R_2OOCR_1COOR'_2$$
$$R_2OOCR_1COOR_4OOCR_3$$
$$R_3COOR_4OOCR'_3$$
$$R_2(OOCR_1COOR_4)_nOOCR'_1COOR'_2$$
$$R_3COOR_4(OOCR_1COOR'_4)_nOOCR'_3$$

In all the above formulae R_1 and R'_1 are the residues of dicarboxylic acids: $HOOCR_1COOH$. R_2 and R'_2 are the residues of monohydric alcohols: R_2OH. R_3 and R'_3 are the residues of monocarboxylic acids: R_3COOH. R_4 and R_4' are the residues of glycols: HOR_4OH. n is a number from 1 to 6 which need not necessarily be integral and, where it is fractional, represents the average of a mixture of compounds. It is preferred that the monohydric alcohols are aliphatic alcohols, or ether alcohols, or thio-ether alcohols.

Some branching in the hydrocarbon chain of the radical R_2 is desirable, and the alcohols derived from the Oxo synthesis are particularly effective; generally R_2 has from 4 to 18 carbon atoms and only contains sulphur and oxygen atoms in thio-ether or ether linkages. The monocarboxylic acids are preferably aliphatic acids having up to 22 carbon atoms. The glycols are preferably members of the alkylene or polyalkylene glycol series, particularly useful being the polyethylene glycols from diethylene glycol up to decaethylene glycol, or diols of the formula $(HO(CH_2)_nOH$ where n is from 3 to 12. The molecular weight and structure of the esters should be such that the resulting composition has a viscosity between 1 cs. and 20 cs., preferably 3 to 10, at 210° F.

One disadvantage that has been experienced from the use of lubricating blends based on esters, particularly those containing complex esters in an amount above about 20% by volume, is that they exhibit a tendency to thicken on storage at low temperatures. The reason for this thickening is not clearly understood, but it is undesirable. It is a purpose of the present invention to provide means whereby this thickening at low temperatures is substantially reduced.

A complex ester is considered, for the purposes of the present invention, to be an ester containing three or more ester groups linearly arranged.

It has now been discovered that salts of strong organic bases, and compounds of the formula $Ar(R_1)R_2$ where R_1 and R_2 are each either a hydroxy group, a mercaptan group, an amine group or a carboxylic acid group, *o*, *m* or *p* substituted, and where the oxygen, sulphur or nitrogen atoms of the two substituent groups R_1 and R_2 may form the heterocyclic atoms in a hetero ring joining two *o*-carbon atoms in the aromatic nucleus Ar and where any or all the said groups may be substituted by other groups such as alkyl amine and amide groups able to stabilize the low-temperature viscosity characteristics of lubricating oils based on synthetic esters.

The strong organic base preferably has the general formula:

$$R'''HN{-}C(=N{-}R'){-}NHR''$$

wherein R', R'' and R''' are aliphatic hydrocarbon groups or hydrogen; the groups desirably have not more than 10 carbon atoms, particularly not more than 4 carbon atoms. A particularly preferred organic base is guanidine.

Other salts which may be used include the quaternary ammonium salts having the general formula:

$$\left[\begin{array}{c} R_1 \\ | \\ R_4{-}N{-}R_2 \\ | \\ R_3 \end{array}\right] X$$

wherein R_1, R_2, R_3 and R_4 are aliphatic hydrocarbon groups each containing preferably not more than 10 carbon atoms, particularly not more than 4 carbon atoms, and X is an anion, preferably carbonate, sulphate chloride or acetate.

Examples of compounds within the scope of this invention are catechol, hydroquinone, o-aminothiophenol, o-amino phenol, benzoxazole, mercaptobenzthiazole, 1,4,2,benzoxazine, phenothiazine, thianthrene, quinoxaline, resorcinol, pyrogallol, ethyl salicyclate, mono- or di-butyl salicylate, mono- or di-butyl phthalate, salicyl anilide, NN' di-t-butyl p-phenylene diamine, 2,3,dihydroxynaphthalene, and the corresponding naphthalene derivatives, and guanidine carbonate, guanidine sulphate and guanidine acetate, the last three being guanidine salts of oxy acids.

Thus this invention comprises a lubricant composition consisting essentially of an ester type lubricant of the type hereinbefore described and a minor and fractional proportion of an additive compound of the formula $Ar(R_1)R_2$ as defined above. The present invention also comprises adding a small percentage of a salt of a strong organic base, preferably an oil-insoluble salt of a strong organic base to a synthetic lubricating oil composition, particularly a composition comprising a blend of a complex-ester and a di-ester, heating the mixture to a temperature above 100° C. and filtering the reaction mixture.

The proportion of the material used depends somewhat on the thickening tendency of the lubricant and the improvement sought. Generally speaking, the amount used will be not greater than 7% by weight, preferably between .1% and 5%. Particularly useful compositions are those containing about 1% or 2% additive. The additive used must be soluble in the lubricant and must not itself be precipitated at any temperature likely to be encountered by the lubricant in service.

The following tables exemplify the efficacy of the addi-

tives used in this invention. In the first table a lubricant having the composition:

20 parts by weight complex ester from sebacic acid, 2-ethyl hexanol and polyglycol 200.
20 parts by weight dioctyl sebacate.
60 parts by weight dinonyl sebacate.
+3.7 parts by weight Acryloid 710 (poly methacrylate ester).

was used as the base oil.

TABLE 1

	Additive	−40° F. K.V., cs.	−40° F. K.V., cs., after −65° F. soaking	Percent increase
Batch A		5,635	7,780	38
Do	1% Catechol	5,985	6,160	2.9
Batch B		5,645	12,605	88
Do	1% Catechol	6,260	6,380	1.9
Batch C		5,435	Solid	
Do	1% Catechol	6,085	7,090	16.5
Do	½% Catechol	5,510	10,310	87
Do	8% o-aminophenol	5,805	6,345	12.5
Do	1% mercaptobenzthiazole.	6,095	10,380	70

In the second table the lubricant had the composition:

20% complex ester* sample D
20% DOS
60% DNS
+3.85% Acryloid 710
+1% purified phenothiazine

*From sebacic acid, 2-ethyl hexanol and Polyglycol 200.

TABLE 2

Additive	K. V., cs. at −40° F. Before soak	K. V., cs. at −40° F. After −65° F. soak (17 hours)
Nil	5,740	14,450
2% Catechol	7,180	7,060
2% Hydroquinone	7,360	7,340
2% Resorcinol	7,950	7,870
2% 2,3,dihydroxy naphthalene	7,510	7,400
1% N acyl p-amino phenol [1]	5,830	6,310
2% pyrogallol	7,860	7,470
1% pyrogallol	6,360	6,260
Complex Ester* Sample (e) in same blend:		
Nil	5,740	10,620
1% pyrogallol	6,610	6,920
2% ethyl salicylate	5,405	6,080
1.4% butyl salicylate	5,305	6,250
1% butyl phthalate	5,610	6,990
2% butyl phthalate	5,965	6,290
1% salicyl anilide	6,241	7,350
2% NN′ di-tert butyl p-phenylene diamine	6,245	9,125

*From sebacic acid, 2-ethyl hexanol and Polyglycol 200.

In the third table the lubricant had the following composition:

30% complex ester* sample E
20% DOS
50% DNS
+3.6% Acryloid 710
+1% purified phenol

*From sebacic acid, 2-ethyl hexanol and Polyglycol 200.

TABLE 3

Additive	K. V., cs. at −40° F. Before soak	K. V., cs. at −40° F. After −65° F. soak (17 hours)
Nil	6,780	solid
1% Catechol	7,655	9,005
2% Catechol	8,450	8,655
1% Resorcinol	7,890	8,910
2% Resorcinol	9,376	9,596

In the fourth table the lubricant had the following composition:

20% complex ester* sample D
20% DOS
50% DNS
+3.6% Acryloid 710
+1% purified phenol

*From sebacic acid, 2-ethyl hexanol and Polyglycol 200.

TABLE 4

Additive	K. V., cs. at −40° F. Before soak	K. V., cs. at −40° F. After −65° F. soak (17 hours)
Nil	5,740	14,450
2% Glycerol monostearate	6,950	36,000
1% Hexachlorobenzene	5,850	19,280

It will be seen that the aromatic nucleus seems essential and that other substituents such as halogens appear to result in ineffective compounds.

It will be seen that the additive used in the above example had a dramatic effect in reducing the low temperature thickening properties of three distinct batches of ester lubricant that had themselves diverse properties in this respect.

The treatment with the salt of the strong organic base is preferably carried out by heating the blend containing more than 0.1%, preferably between 0.2% and 2% by weight of the salt, with stirring, to a temperature above 100° C., preferably between 170° C. and 190° C., for a time between 5 and 120 minutes, preferably 10 and 60 minutes, and then filtering the reaction mixture.

The mixture usually precipitates a small amount of a dark coloured resinous material and the colour of the synthetic lubricating oil composition is improved.

The treatment does not appear to affect, significantly, the viscosity of the blend at 100° F. or the viscosity index.

The following example illustrates one embodiment of the present invention.

Example

A complex-ester di-ester blend was made up of 60% by volume of a complex ester and 40% by volume of dinonyl sebacate. The complex ester was prepared from nonyl alcohol, sebacic acid and polyglycol 200 (predominantly tetra-ethylene glycol) by forming the half-ester of the polyglycol and the acid in a first stage, and esterifying the acid product so formed with the monohydric alcohol in a second stage as described and claimed in our British specification No. 666,697. This blend was heated, with stirring, with 1% by weight of guanidine carbonate at 180° C. for 15 minutes. A small amount, comparable to the amount of added salt, of a dark brown resinous material precipitated and carbon dioxide was evolved. The reaction mixture was filtered.

The following table shows the effect of this treatment:

	Before treatment	After treatment
Initial viscosity at −40° F. (Centistokes)	11,500	11,770
Viscosity at −40° F. after 17 hours storage at −40° F. (Centistokes)	60,000	12,360
Colour T. R.	2½	13
Viscosity at 100° F. (Centistokes)	57.8	61.2

The present invention may, of course, be applied to synthetic lubricating oil compositions which contain added materials such as, for example, anti-oxidants, anti-wear agents and V.I. improvers.

What we claim is:

1. A process for improving the low temperature viscosity of a synthetic lubricating composition, said com-

position consisting essentially of a blend having a viscosity at 210° F. in the range of 1 to 20 cs. of a complex ester prepared from nonyl alcohol, sebacic acid, and a polyethylene glycol of a molecular weight of about 200, by forming a half ester of the polyglycol and the acid in the first stage, and esterifying the acid product so formed with the monohydric alcohol in a second stage and a di-ester consisting essentially of di-nonyl sebacate, said process comprising adding to said blend in the range of 0.1 to 2.0 weight percent of a guanidine salt of an oxy acid, heating said mixture above 100° C. and filtering said mixture.

2. A process for improving the low temperature viscosity of a synthetic lubricating composition, said composition comprising a blend of 60% of a complex ester prepared from nonyl alcohol, sebacic acid, and a polyethylene glycol of a molecular weight of about 200, by forming a half ester of the polyglycol and the acid in the first stage, and esterifying the acid product so formed with the monohydric alcohol in a second stage and 40% of a di-ester consisting essentially of di-nonyl sebacate, said process comprising adding to said blend in the range of 0.1 to 2.0 weight percent of guanidine carbonate, heating the mixture so obtained to a temperature of 180° C., maintaining said mixture at said temperature for fifteen minutes whereupon a small amount of a resinous material comparable to the added amount of carbonate is precipitated and carbon dioxide is evolved, and filtering said mixture to remove said precipitate.

3. A process comprising adding to a synthetic dicarboxylic acid ester lubricant having a viscosity at 210° F. in the range of 1 to 20 cs., in the range of 0.1 to 2.0 weight percent of a guanidine salt of an oxy acid, heating said mixture between about 100° C. and 190° C. for about 5 to 120 minutes, filtering it to remove precipitated resinous material, and recovering a synthetic lubricant improved in color and in resistance to thickening upon storage at low temperatures.

4. A synthetic lubricating composition improved in color and in resistance to thickening upon storage at low temperatures, formed by preparing a mixture consisting essentially of a synthetic dicarboxylic acid ester lubricant having a viscosity at 210° F. in the range of 1 to 20 cs. and in the range of 0.1 to 2.0 weight percent of a guanidine salt of an oxy acid, heating said blend between about 100° C. and 190° C. for about 5 to 120 minutes and filtering to remove precipitated resinous material.

5. A synthetic lubricant improved in color and in resistance to thickening upon storage at low temperatures, formed by reacting a lubricant consisting essentially of a blend of a complex ester prepared from nonyl alcohol, sebacic acid, and a polyethylene glycol of a molecular weight of about 200, by forming a half ester of the polyglycol and the acid in the first stage, and esterifying the acid product so formed with the monohydric alcohol in a second stage and a di-ester consisting essentially of di-nonyl sebacate within the range of 0.1 to 2.0 weight percent of a guanidine salt of an oxy acid, heating the mixture so obtained above 100° C. and filtering to remove precipitated resinous material.

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