United States Patent Office

3,162,602
Patented Dec. 22, 1964

3,162,602

SUPER-POLYESTER LUBRICANT COMPOSITION

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No Drawing. Filed Feb. 28, 1961, Ser. No. 92,160
7 Claims. (Cl. 252—47)

This invention relates to a thermally stable lubricant additive and to lubricant compositions of improved viscosity characteristics containing said additive. More particularly, it pertains to a novel type of lubricant additive consisting of the linear polymeric superpolyester reaction product of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight between 4,000 and 50,000. It further pertains to synthetic ester base and aromatic base lubricating oil compositions containing said superpolyester.

Esters of a molecular weight less than 2000 are widely used as lubricating oils in engines which are subject to high temperatures such as combustion turbine engines, particularly those of the "turbo-jet" and "prop-jet" type. The reason for this is these synthetic ester oils are generally characterized by a higher viscosity index and a lower pour point than mineral oils of corresponding viscosity. In addition, the synthetic ester lubricating oils leave a lower percentage of carbonaceous residue than their mineral oil counterparts. Carbonaceous residue from engine oils is undesirable in that it accumulates and interferes with the operation of the engine. Further the synthetic ester lubricants generally have higher flash points than mineral oils of equivalent viscosity thereby lessening the danger of combustion of the oil at high engine temperature operation.

The synthetic ester lubricating oils can be broadly described as esters of hydrocarbyl carboxylic acids and hydrocarbyl alcohols. They are high molecular weight (e.g., between 300 and 2000) materials of lubricating oil characteristics derived from alcohols which are usually aliphatic alcohols containing from 1 to 4 or more hydroxyl radicals and carboxylic acids which are usually aliphatic carboxylic acids containing 1 to 4 or more carboxyl acid radicals.

Widely used synthetic ester lubricants are aliphatic esters of saturated aliphatic monocarboxylic and dicarboxylic acids containing 6–12 carbon atoms. From the standpoint of cost and availability the preferred carboxylic acids are caproic, heptoic, caprylic, pelargonic, adipic, sebacic and azelaic acids. The monohydric and polyhydric aliphatic alcohols used to form the esters usually contain at least 4 carbon atoms and up to 20 or more carbon atoms. C_4 to C_{18} saturated aliphatic alcohols are commonly used such as 2-ethylhexanol and 2,2-diethyl-1,3-propanediol. Ether alcohols such as 2-ethoxyethanol and monoethyl ether of diethylene glycol may also be employed in the formulation of the ester oils. Alcohols containing two or more hydroxyl radicals and an absence of hydrogen on the beta carbon atom such as trimethylolethane, pentaerythritol and trimethylolpropane have proven particularly effective in formulating stable high temperature ester lubricants.

Examples of simple esters of an aliphatic carboxylic acid and alcohol are the following: diisooctyl azelate, di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, di-2-ethylhexyl adipate, dilauryl azelate, di-sec-amyl sebacate, di-2-ethylhexyl C_{18}-alkenyl succinate, di-2-ethoxyethyl sebacate, di-2-(2′-methoxy) ethoxyethyl sebacate, di-2-butoxyethyl sebacate, di-2-(2′-ethoxy) butoxyethyl azelate, di-2-butoxyethyl azelate, di-2-(2′-butoxy) ethoxyethyl C_{12}-alkenylsuccinate, tetracaproate of pentaerythritol, triisooctanate of trimethylolpropane and nonyl caproate.

In addition to such esters, complex ester lubricants formed by the reaction of an aliphatic polycarboxylic acid, an aliphatic polyhydroxy compound and a monofunctional aliphatic alcohol or acid are employed as synthetic lubricants. Complex esters of this type are described in U.S. 2,628,974. Complex esters formed by the reaction of a mixture containing stoichiometric amounts of 1,3-hexanediol, sebacic acid, and 2-ethylhexanol and by the reaction of a mixture containing adipic acid, diethylene glycol, and 2-ethylhexanoic acid illustrate this class of synthetic complex ester lubricating oils. Further illustrations of the complex esters are the ester reaction products of sebacic acid, trimethylolpropane and pelargonic acid; sebacic acid, trimethylolpropane and 2-ethylhexanol; sebacic acid, trimethylolethane and hexanoic acid; and suberic acid, 1,3,5,7-octanetetraol and pentanoic acid.

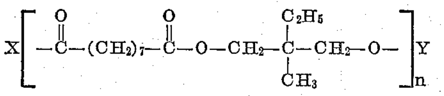
The sulfur analogs of the foregoing esters are also useful as synthetic lubricants. For example, simple thioesters are illustrated by di-2-ethylhexyl thiosebacate, di-n-octyl thioadipate and the dilaurate of 1,5-pentanedithiol; sulfur analogs of complex esters are exemplified by the reaction product of adipic acid, thioglycol and 2-ethylhexyl mercaptan.

Other types of synthetic lubricating oils which are included within the scope of the invention are the liquid aromatic compounds having lubricating oil properties which are not normally derived from petroleum refining. An example of liquid aromatics contemplated herein are the diaryl oxides such as diphenyl oxide.

Although the synthetic lubricants of the type described above are superior to comparative mineral oils in respect to thermal stability, viscosity characteristics, pour point and other properties they often require the addition of additives such as anti-oxidants (e.g., 0.1 to 5 wt. percent phenothiazine), thickeners (viscosity increasers) and viscosity index improvers in order to meet the rigid requirements of the high speed engine operations of today.

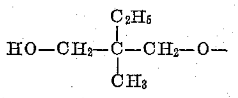
We have discovered, and this constitutes the invention and objects thereof, (1) a superpolyester lubricating oil additive which upon incorporation into a synthetic base lubricating oil imparts a higher viscosity and viscosity index to the lubricating oil and (2) remains outstandingly resistant to thermal decomposition. The lubricant additive which we have developed is the superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight between about 4000 and 50,000. It belongs to a class of compounds described as having a linear chain, two dimensional polymeric structure. By the term "a linear chain, two dimensional polymeric structure" it is intended to mean compounds which are theoretically visualized as consisting of long chains or threads in contrast to so-called three dimensional polymers in which molecular growth is visualized as having been effected by the reaction in three dimensions. In "High-Polymers" collected papers of W. H. Caruthers (Mark and Whitby), volume 1, page 15, linear polymers are considered characterized by a recurring structural unit, usually a bivalent radical. The polymeric superpolyester contemplated herein is considered to be a condensation or C polymer, that is, a polymeric molecule formed from monomeric compounds by a process of polyintermolecular condensations.

The superpolyester of the invention is a noncrystalline, highly ductile, soft plastic product exhibiting strong adhesive property and having excellent solubility in synthetic ester lubricating oils. The superpolyester can be characterized by the general formula:



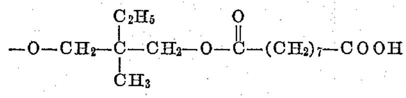
$$X\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_7-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-CH_2-O-\right]_nY$$

where n is an average integer between about 13 and 184 and X and Y are terminating members, X being selected from the group consisting of



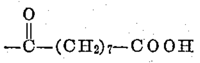
$$HO-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-CH_2-O-$$

and



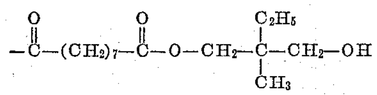
$$-O-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-CH_2-O-\overset{\overset{O}{\|}}{C}-(CH_2)_7-COOH$$

and Y being selected from the group consisting of



$$-\overset{\overset{O}{\|}}{C}-(CH_2)_7-COOH$$

and



$$-\overset{\overset{O}{\|}}{C}-(CH_2)_7-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-CH_2-OH$$

The superpolyester linear polymer of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol is prepared by contacting, preferably with agitation, azelaic acid and 2-methyl-2-ethyl-1,3-propanediol in a mole ratio of acid to alcohol between about 1.1:1 and 0.9:1, preferably between 0.9:1 and 1:1, at a temperature between about 150° C. and 300° C. for a period between 10 and 50 hrs. Advantageously, inert diluent forming azeotropes with water such as toluene and xylene may also be initially incorporated in the reaction mixture in order to facilitate the removal of the water by-product and the formation of the superpolyester product.

At the end of the reaction period the reaction mixture is then subjected to a fractional distillation in a manner to remove as overhead all products having a boiling point of below about 230° C. at 1 mm. Hg. The residue remaining after distillation is the superpolyester linear polymer of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol of a molecular weight between about 4000 and 50,000. It is to be noted that when we speak of molecular weight in relation to the superpolyester product of the invention we are referring to an average molecular weight since the polyester product recovered from the reaction mixture is constituted of molecules of the superpolyester of varying chain length.

When the superpolyester product contemplated herein is incorporated in a synthetic lubricating oil of a molecular weight less than 2000 the viscosity of the oil is increased and the resistance of the oil to change in viscosity with change in temperature is also increased. The superpolyester product, therefore, acts as a thickener and viscosity index improver in synthetic lubricating oils. The amount of superpolyester product that may be employed in the synthetic lubricating oil will be dependent on the effect desired. If the superpolyester product is only employed for thickening there is no limitation on the amount that may be incorporated into the synthetic oil. In other words, superpolyester product can be added until the desired viscosity for the synthetic oil is obtained. However, superpolyester concentrations outside the range of between 0.1 and 60 wt. percent are not normally anticipated. If the function of the superpolyester is to improve the viscosity index, the content of the superpolyester in synthetic oil is advantageously between about 0.1 and 20 wt. percent, preferably between 1 and 5 wt. percent At contents below about 0.1 wt. percent the beneficial effect of the superpolyester on viscosity index and viscosity of the synthetic oil is not significant.

One of the outstanding features of the linear polymeric product of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol is its excellent resistance to thermal decomposition in synthetic lubricating oil compositions. The significance of this is found in the fact that in order for a manufacturer to obtain government approval, a lubricating oil must meet certain rigid specifications. For example, lubricating oil specification "D.E.R.D./2487 Issue 3" of the British Ministry of Supply (Air Division) requires that the viscosity of an oil after being subjected to the British Thermal Stability Test for a period of 24 hrs. not change more than −10 to +20%. The British Thermal Stability Test consists in determining the percent change in the kinematic viscosity at 100° F. of an oil after heating the oil at a temperature of 538° F. for a period of four 6-hour increments. We have found that synthetic ester lubricating oil compositions containing superpolyesters closely homologous to our azelaic acid-propanediol polymeric ester, such as the superpolyester of sebacic acid and 2,2 diethyl-1,3-propanediol and the superpolyester of azelaic acid and 2,2 dimethyl-1,3-propanediol, fail to meet the Thermal Stability Test. In contrast synthetic ester oil compositions containing our superpolyester clearly meet said specification. The reason for this is the comparative homologous superpolyesters are significantly more thermally unstable than the superpolyester of the invention, and therefore, more readily decompose and transesterify with the synthetic ester base oil when subjected to an elevated temperature for a period of time. The degree change of viscosity in the British Thermal Stability Test is in essence a measurement of the degree of decomposition and transesterification in the synthetic ester oil composition.

The invention is further illustrated by the following examples:

Example I

This example illustrates the preparation of the superpolyester linear polymeric condensation product of azelaic acid and 2-methyl-2,2-ethyl-1,3-propanediol of an average molecular weight of about 5000.

In a liter 3-necked Pyrex flask equipped with a stirrer, thermometer, water separator and condenser there was added 188 grams of azelaic acid and 122 grams of 2-methyl-2-ethyl-1,3-propanediol, and 35 grams of xylene. The reaction mixture was heated to a temperature of 235° C. with stirring for a period of 22 hours. During the reaction period approximately 36 milliliters of water by-product were collected. At the end of the reaction period the reaction mixture was subjected to vacuum distillation at 250° C. at 1 mm. Hg for a period of 1 hour. The residue remaining after distillation was identified as the superpolyester reaction product of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight of about 5000.

Example II

The procedure of Example I was repeated except the reaction was conducted at a temperature of 246° C. and employing 124 grams of 2-methyl-2-ethyl-1,3-propanediol. About 36 mls. water were recovered during the reaction period. The superpolyester recovered was identified as the linear polymeric condensation product of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol of an average molecular weight of about 37,000.

Example III

The following table illustrates the thickening and viscosity index improving effect of the superpolyester of Example II on a synthetic ester lubricant marketed under the tradename Plexol 201J. Plexol 201J is di-2-ethylhexyl sebacate containing less than 0.5 wt. percent sebacic acid. The results were as follows:

Composition		Kinematic Viscosity (cs.) At 210° F./and 100° F.	Viscosity Index
Plexol 201J, Wt. Percent	Polyester of Example II, Wt. Percent		
100	0	3.3/12.7	145
96	4	5.1/20.9	176
92	8	7.4/32.3	164
88	12	10.7/50.4	162
84	16	15.3/76.7	150

Example IV

This example illustrates the outstanding thermal stability properties of the superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight of about 5000 in Plexol 201J.

The thermal stability of synthetic lubricating oil compositions containing the superpolyester thickening agent of Example I and comparative homologous superpolyesters were subjected to the British Thermal Stability Test. This test consists of initially determining the kinematic viscosity of the test oil at 100° F., then heating and maintaining the test oil at a temperature of 538° F. for a 24 hour period, and measuring the kinematic viscosity of the test oil at 100° F. at the end of the 6th, 12th, 18th and 24th hour of the 538° F. heating period. The British Thermal Stability Test results are reported as percent change in the 100° F. kinematic viscosity of the test oil after being subject to heating at a temperature of 538° F. at the end of the 6th, 12th, 18th and 24th hour period. The change in viscosity is a measure of the degree of thermal decomposition of the test oil composition. The greater the percent change in viscosity the greater the thermal decomposition.

The superpolyester of the invention and the comparative superpolyesters were essentially prepared by the method of Example I. They were designated as Polyester A—the superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight of about 5000; Polyester B, the superpolyester of sebacic acid and 2,2-diethyl-1,3-propanediol having an average molecular weight of about 5000; Polyester C, the superpolyester of sebacic acid and 2-methyl-2-propyl-1,3-propanediol having a molecular weight of about 6,000; and Polyester D, the superpolyester of azelaic acid and 2,2-dimethyl-1,3-propanediol having an average molecular weight of about 5000. The polyester of Example I is designated as Polyester A.

The British Thermal Stability Test results for Plexol 201J compositions containing the superpolyesters described above and a standard anti-oxidant, phenothiazine, are reported below:

Composition			Br. Therm. Stab. Test, % Visc. Change at 100° F. After—			
Polyester (Wt. percent)	Plexol 201J, Wt. percent	Phenothiazine, Wt. percent	6 hrs.	12 hrs.	18 hrs.	24 hrs.
A (9)	90	1	−0.3	−0.9	−1.9	−3
B (9)	90	1	−14.8	−23.6	−30.0	−50
C (12)	87	1	−2.4	−6.8	−17.5	−22.2
D (9)	91	1	−19.1	−30.8	−37.7	−41.2

As can be seen from the above the synthetic lubricant composition containing the superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol (Polyester A) is materially less prone to change in viscosity after being subjected to a high temperature than compositions containing comparative homologous superpolyesters (Polyesters B, C and D) thereby establishing its superior thermal stability.

All percentages hereinbefore and hereinafter recited are based on weight unless otherwise indicated.

We claim:

1. A synthetic lubricant composition comprising between about 80 and 99.9 wt. percent of di-2-ethylhexyl sebacate and between about 0.1 and 20 wt. percent of a linear polymeric superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight of between about 4000 and 50,000.

2. A composition in accordance with claim 1 wherein said superpolyester has a molecular weight of about 5000.

3. A composition in accordance with claim 1 wherein said superpolyester has a molecular weight of about 37,000.

4. A composition in accordance with claim 1 also comprising about 0.1 to 5 wt. percent phenothiazine.

5. A synthetic lubricant composition comprising between about 80 and 99.9 wt. percent of diphenyl oxide and between about 0.1 and 20 wt. percent of a linear polymeric superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol having an average molecular weight of between about 4000 and 50,000.

6. A lubricant composition consisting essentially of a linear polymeric superpolyester of azelaic acid and 2-methyl-2-ethyl-1,3-propanediol of an average molecular weight between about 4000 and 50,000 and a lubricant material selected from the group consisting of diphenyl oxide and a synthetic ester lubricating oil of a molecular weight of less than about 2000, said synthetic ester lubricating oil derived from an aliphatic alcohol containing from 1 to 4 hydroxyl radicals and an aliphatic carboxylic acid containing from 1 to 4 carboxyl acid radicals, and said superpolyester being present in said composition in an amount between about 0.1 and 60 wt. percent.

7. A composition in accordance with claim 6 wherein said superpolyester is present in an amount between about 0.1 and 20 wt. percent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,394,909	Gleason	Feb. 12, 1946
2,435,619	Young et al.	Feb. 10, 1948
2,902,463	Johnston et al.	Sept. 1, 1959
2,918,433	Buckmann	Dec. 22, 1959
2,945,008	Caldwell et al.	July 12, 1960
2,951,827	Siggel	Sept. 6, 1960
2,976,266	Lytton et al.	Mar. 21, 1961

FOREIGN PATENTS

847,629	Great Britain	Sept. 14, 1960