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3,275,555

SYNTHETIC LUBRICANT CONTAINING  
OXETANE POLYMERS

Francis Henry Waight, Eastham, Wirral, Alexander C. B. MacPhail, Little Sutton, Wirral, and Derek Southern, Heswall, Wirral, England, assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware  
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16 Claims. (Cl. 252—54.6)

This invention relates to synthetic ester lubricants and more particularly to synthetic ester lubricants useful for lubrication over wide temperature ranges required in the lubrication of moving parts of combustion turbines such as in gas turbine engines and the like.

The most effective lubricating bases developed for uses mentioned above are the ester types, particularly the diesters of aliphatic dicarboxylic acids and branched-chain aliphatic alcohols in the viscosity range of from about 2 to about 10 cs. at 210° F., preferably between 3 and 5 cs. at 210° F. Ester bases of this type have been fully described in such publications as the Industrial and Engineering Chemistry, 1947, 39, page 484 and 1950, 42, page 2421, and 1953, 45, page 1766 as well as ASTM Special Technical Publication No. 77 on Symposium on Synthetic Lubricants, and Gunderson's text entitled, "Synthetic lubricants," chapter 5, pages 151-245. The art also discloses that stabilization of these synthetic ester bases with various types of organic nitrogen containing compounds such as phenyl- $\alpha$ -naphthylamine and phenothiazine has been quite satisfactory. However, the problem of imparting load-bearing properties to such lubricants has not been solved successfully and has become more urgent as demands on turbo engines become more pressing.

It has now been discovered that load and extreme pressure properties can be imparted to ester base lubricants by addition thereto of a minor amount of from about 0.5% to about 10%, preferably between about 1% and 5% by weight of a polymeric oxetane having at least one halogen atom in each oxetane unit and which halogen is at least one carbon atom removed from the oxygen atom in each of the oxetane units.

The ester base which comprises the major portion of the lubricant consists of a diester of an aliphatic dicarboxylic acid containing from 6 to 20 carbon atoms in the molecule and a branched-chain aliphatic monohydric alcohols containing from 6 to 12 carbon atoms in the molecule, or a blend of such esters and their free acids.

Examples of the dicarboxylic esters of the present invention are dinonyl sebacate, di(2-ethyl hexyl) sebacate, di-iso-octyl azelate, di(3, 5, 5-tri-methylhexyl) adipate and the like. Mixtures of these esters are mixtures of the esters and the free acid may also be used. Such mixtures include: di-octyl sebacate and di-octyl azelate, di(2-ethyl hexyl) sebacate and sebacic acid (90%, 10%).

The viscosity of the above exemplified esters ranges between 3 and 4.7 cs. at 210° F. In order to increase their viscosity range to 5-10 cs. at 210° F. which is desirable when temperature above 350° F. and higher are encountered, it is advantageous to blend with the ester base a minor amount of from 1% to 20% of an oxygen-containing polymeric thickener selected from the group consisting of (1) a polymer of an ester of a C<sub>8-18</sub> alkyl acrylate, (2) a hetero or block polymer of dissimilar alkylene oxides and (3) a complex ester corresponding to the general formula:



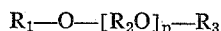
or a mixture of compounds corresponding to any or all of these esters, where R is a residue from a monohydric

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aliphatic alcohol, D is a residue from a dibasic acid, G is a residue from a glycol HOR<sub>4</sub>OH which is either a simple glycol wherein R<sub>4</sub> is a branched or unbranched alkylene radical or is a polyoxyalkylene glycol formed by the polymerization of ethylene or propylene oxides or a mixture of these compounds, in which case R<sub>4</sub> is a divalent polyether radical and n is a number from 1 to 6.

Preferably R in above cases is a residue from a branched-chain alcohol, e.g. 2-ethyl hexyl alcohol, 2,2,4-trimethyl pentan-1-ol and D is a residue from an aliphatic acid, e.g. sebacic acid, adipic acid, azelaic acid, glutaric acid. Polymers of class (1) can be exemplified by esters of acrylic or methacrylic acid and C<sub>8-18</sub> alkanols and mixtures thereof such as octyl, lauryl or stearyl methacrylate polymers in the molecular weight range of from 1,000 to 45,000 preferably between 10,000 and 20,000 of which preferred are lauryl and/or stearyl methacrylate having a molecular weight of from 5,000 to 15,000 as determined by the light scattering method.

The thickeners of class (2) are the polyoxyalkylene glycols and their mono- and di-ethers or esters having the general formula:



wherein R<sub>1</sub> and R<sub>3</sub> each represent a hydrogen atom, a non-aromatic hydrocarbon radical or an acyl group, R<sub>2</sub> represents an alkylene radical and n represents an integer.

In the polyoxyalkylene chain  $-(R_2O)_n-$ , the radical R<sub>2</sub> may be any alkylene radical, preferably an alkylene radical with 2 to 8 carbon atoms. Still more preferred in the compositions of the invention are the polyoxyalkylene fluids in which the alkylene radical is an ethylene or propylene radical.

In the polyoxyalkylene chain  $-(R_2O)_n-$ , there may be present alkylene radicals with different numbers of carbon atoms. They may for instance consist of both oxyethylene and oxypropylene radicals. In case the polyoxyalkylene chain contains different alkylene radicals, these may be randomly distributed throughout the molecule or may be arranged in regularly recurring units or blocks, each consisting of one or a plurality of similar oxyalkylene radicals. For the compositions of the invention preference is given to polyoxyalkylene liquids in which the polyoxyalkylene chain consists of blocks of (for instance 1 to 8) oxyethylene radicals alternating with blocks of (for instance 1 to 8) oxypropylene radicals.

In those cases where the radicals represented in the above general formula by R<sub>1</sub> and/or R<sub>3</sub> are hydrocarbon radicals, the radicals may be saturated or unsaturated, straight chained or branched, or similar or dissimilar, non-aromatic hydrocarbon radicals. For the compositions of the invention preference is given to the polyoxyalkylene liquids in which the radical R<sub>1</sub> is a hydrogen atom and the radical R<sub>3</sub> is an alkyl group such as a propyl, butyl, pentyl or decyl group.

In those cases where the radicals R<sub>1</sub> and/or R<sub>3</sub> are acyl radicals, the radicals may be derived from any carboxylic acid. Preference is given to the alkane or alkene monocarboxylic acids such as acetic acid, propionic acid, butyric acid, lauric acid, stearic acid and oleic acid.

The molecular weight of the compounds which may be employed in the invention may vary over a wide range. Compounds of the type falling within the scope of this invention generally have molecular weights from 350 up to 10,000 the polyoxyalkylene liquids possessing a molecular weight between 800 and 6,000 being preferred.

The physical properties of the polyoxyalkylene liquids such as their viscosity and their viscosity index depend upon the length of the polyoxyalkylene chain, the nature of the oxyalkylene chain and the nature of the terminal groups. It will be clear that apart from the obvious requirement of compatibility with the ester oils, the

polyoxyalkylene liquids should have a viscosity which is higher than the viscosity of the ester oils in order to act as a thickener for these oils. Moreover, they should have a high viscosity index so as to ensure that the viscosity index of the finished composition is not lower or not appreciably lower than the viscosity index of the ester oils.

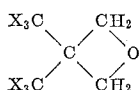
Suitable heterocyclic polyalkylene fluids are heterocyclic copolymers of ethylene oxide and propylene oxide in the viscosity range of 380–700 at 100° F. SUS and prepared by the methods described in U.S. Patents 2,425,755 and 2,425,845. Specific examples of such copolymers are: (A) copolymer of ethylene oxide and 1,2-propylene oxide having a viscosity at 100° F. SUS of 385, VI of 144 and PP, ° F., of –40; (B) copolymer of ethylene oxide and 1,2-propylene oxide having a viscosity at 100° F. SUS of 525 and (C) copolymer of ethylene oxide and 1,2-propylene oxide having a viscosity at 100° F. SUS of 625. By block copolymers of ethylene oxide and propylene is meant that first one of the oxides, e.g. propylene oxide is polymerized and thereafter this polymer is treated with a dissimilar alkylene oxide compound as described in U.S. Patent 2,677,700.

The ether and ester derivatives of these polymers are preferably alcohols and fatty acids of from 1 to about 10 carbon atoms. Still more preferably are the esters and ethers of aliphatic monohydric alcohols and saturated aliphatic monocarboxylic acids having from 1 to 4 carbon atoms.

The thickener of class (3) can be exemplified by neopentyl glycol, 2-methyl 2-n-propyl propan-1,3 diol. Suitable monocarboxylic acids are those containing from 4 to 9 carbon atoms.

The novel load and extreme pressure agent of the present invention is a halogen-containing polymeric oxetane having at least 2 and not more than 20 repeating units, each of said units having at least one halogen atom (X=Cl or Br) which is not on the carbons adjacent to the oxygen atom of the oxetane units and which halogen is preferably attached to the number 3 position of the oxetane units through a radical  $\text{CH}_2\text{X}$ ,  $\text{CHX}_2$  and  $\text{CX}_3$  and the carbons adjacent to the oxygen can have attached substituent groups such as alkyl radicals, e.g.  $\text{C}_1\text{--C}_4$  alkyl radicals.

A preferred class of oxetanes is that represented by the formula:



wherein one X is Cl or Br and the others are chosen from H, Cl or Br. The preferred compound of this class is 3,3-bis(chloromethyl)oxetane. Polymers of the re-

chosen so as to yield a polymer which is not appreciably volatile at 200° C.

The preparation of substituted oxetane polymers suitable for the purpose of the present invention is illustrated by the following examples.

#### Example 1

245 g. of 3,3-bis(chloromethyl)oxetane were placed in a flask fitted with a double surface air condenser. The system was sealed from the atmosphere by leading a tube from the top of the condenser so that it dipped beneath the surface of a mercury reservoir. Nitrogen was blown through the system before heat was applied. The monomer was refluxed at 210° C. for 11 days. During this period the color of the reaction mixture changed to amber. At no time was air allowed to get into the system. Unreacted monomer (83 g.) was distilled from the reaction mixture. The polymer residue (162 g., i.e. 66% w. yield), was an amber, viscous liquid and was poured into 80% aq. industrial methylated spirits (I.M.S.); the two liquids were immiscible. The mixture was stirred and when the layers had completely separated the I.M.S. was decanted from the polymer. The final traces of water and alcohol were removed from the polymer by distillation at 10–15 mm. Hg. The polymer so prepared had an average molecular weight of 450 and a chlorine content of 44.9% w.

#### Example 2

175 g. of 3,3'-bis(chloromethyl) oxetane were refluxed in a nitrogen atmosphere as in Example 1 for 10 days. The product was then fractionally distilled as follows:

| Fraction | Boiling range, ° C.           | Weight, g. | Cl content, percent w. |
|----------|-------------------------------|------------|------------------------|
| A. ....  | <84/15 mm. Hg. ....           | 67         | -----                  |
| B. ....  | 120-180/0.1 mm. Hg. ....      | 41         | 45.4                   |
| C. ....  | 180/0.1 mm. Hg-270/5 Hg. .... | 31         | 45.4                   |
| D. ....  | >270/5 Hg. ....               | 36         | 45.3                   |

Fraction A consisted of unreacted monomer. Fractions B, C and D were predominantly the dimer, trimer and tetramer respectively.

#### Example 3

The polymer as described in Example 1 was further washed with a silver nitrate/alcohol mixture to remove free chloride ions.

The invention is further illustrated by examples (Nos. 4–10) of lubricant compositions in accordance with the present invention summarized in Table I. For the purpose of comparison, compositions not containing the polymer of the present invention are also included in Table I, described as Examples 11–13.

TABLE I

| Composition                                      | Examples |       |       |       |       |       |       |       |       |       |
|--|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|  | 4        | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    |
| Di(2-ethyl hexyl) sebacate, percent w. ....      | 97       | 97    | ----- | ----- | ----- | ----- | ----- | 97    | 97    | ----- |
| Diisooctyl azelate, percent w. ....              | -----    | ----- | 94    | 94    | 94    | 94    | 94    | ----- | ----- | 94    |
| Azelate acid, percent w. ....                    | -----    | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  | ----- | 0.02  |
| Adipic acid, percent w. ....                     | 0.02     | ----- | ----- | ----- | ----- | ----- | ----- | ----- | 0.02  | ----- |
| 3,7 diethyl phenothiazine, percent w. ....       | -----    | ----- | 1.5   | 1.5   | 1.5   | 1.5   | 1.5   | ----- | ----- | ----- |
| Phenyl- $\alpha$ -naphthylamine, percent w. .... | -----    | ----- | 1.5   | 1.5   | 1.5   | 1.5   | 1.5   | ----- | ----- | ----- |
| 5 Methyl benzotriazole, p.p.m. ....              | -----    | ----- | 25    | 25    | 25    | 25    | 25    | ----- | ----- | ----- |
| Silicone MS 200/12, 500, p.p.m. ....             | -----    | ----- | 5     | 5     | 5     | 5     | 5     | ----- | ----- | ----- |
| 3% of the Polymer of Example. ....               | 1        | 1     | 2B    | 2C    | 2D    | 3     | 1     | ----- | ----- | ----- |

quired degree of polymerization can readily be obtained by heating the monomer (preferably in the absence of air) at a temperature sufficient to induce polymerization. An acceptable rate of polymerization is obtained at temperatures of about 200° C. The configuration of the polymer is not known with certainty but it is thought that cyclization occurs with the formation of large rings containing ether linkages. The degree of polymerization is

In addition to the halogen containing oxetane polymer other additives may be incorporated into the lubricant of the present invention if desired. Thus, antioxidants such as phenothiazine or its derivatives or naphthylamines may be used. Rust inhibitors may be incorporated, for example, the metal salts of petroleum sulfonates and in particular lead corrosion can be inhibited by the use of certain dibasic carboxylic acids, for example, azelaic acid.

Small amounts of antifoaming agents may be incorporated. If further load carrying capacity is required organic phosphate or phosphite esters, for example, tricresyl phosphate, may be added. Other suitable extreme pressure additives are the chlorinated di and polyphenyls.

The compositions of Examples 4-13 were tested on an I.A.E. 3/4 inch gear lubricant testing machine as described by Mansion in the Journal of the Institute of Petroleum, 1952, 38, 633, using B.S.S. EN34 steel gears. Results, expressed in lb., are given in Table II.

TABLE II

| Speed, r.p.m.----- | 2,000 |     | 6,000 |     |
|--------------------|-------|-----|-------|-----|
|                    | 60    | 110 | 60    | 110 |
| Temp., ° C-----    |       |     |       |     |
| Example No.:       |       |     |       |     |
| 11-----            | 55    | 60  | 30    | 35  |
| 5-----             | 90    | 75  | 40    | 45  |
| 12-----            | 55    | 60  | 30    | 35  |
| 4-----             | 105   | 85  | 55    | 45  |
| 13-----            | 70    | 60  | 40    | 30  |
| 6-----             | 90    | 80  | 45    | 45  |
| 7-----             | 80    | 85  | 45    | 35  |
| 8-----             | 75    | 80  | 30    | 40  |
| 9-----             | 90    | 85  | 40    | 45  |

Table II shows that the lubricant compositions of the present invention gave improved performance over compositions which did not contain the polymer of the present invention.

The compositions of Examples 6-10 also comply with the United States Military Specification MIL-L-7808D. For example, in the MIL-L-7808D Oxidation/Corrosion test at 175° C., the following results were obtained with Example 9.

|                           | Volatility Loss, Percent w. | Acidity Increase | Viscosity Increase, Percent | Metal wt. change, mg./cm. <sup>2</sup> |      |       |      |       |
|---------------------------|-----------------------------|------------------|-----------------------------|--|------|-------|------|-------|
|                           |                             |                  |                             | Cu                                     | Mg   | Ag    | Al   | Fe    |
| Example 9-----            | 0.6                         | 1.5              | 12.2                        | -0.37                                  | Nil  | +0.12 | Nil  | -0.02 |
| Specification limits----- |                             | 2.0              | -5 to +15                   | ±0.4                                   | ±0.2 | ±0.2  | ±0.2 | ±0.2  |

In the MIL-L-7808D Oven Storage Lead Corrosion Test, Example 10 yielded a weight loss of 34 mg. Pb/in.<sup>2</sup> after 45 days at 85° C. The specification limit is 150 mg./in.<sup>2</sup>.

We claim as our invention:

1. A synthetic lubricating composition comprising a major amount of a dibasic ester of an aliphatic dicarboxylic acid and a branched chain aliphatic alcohol and from 0.5 to 10% of a polymeric halogen-containing oxetane having from 2 to 20 oxetane units each of which contains at least one halogen which is on carbons other than the carbons adjacent to the oxygen atom of each unit.

2. A synthetic lubricating composition comprising a major amount of a dibasic ester of an aliphatic dicarboxylic acid and a branched chain aliphatic alcohol in the viscosity range of from about 2 to about 10 cs. at 210° F. and from about 0.5% to about 10% of a polymeric chlorine containing oxetane having from 2 to 20 oxetane units, the chlorine being present on carbons other than the carbons adjacent to the oxygen atom in the oxetane units.

3. A synthetic lubricating composition comprising a major amount of di-2-ethylhexyl sebacate and from 0.5% to 10% of a polymer of chlorinated oxetane having from 2 to 20 of such units in the polymer, the chlorine being present on carbons other than the carbons adjacent to the oxygen atom in the oxetane units.

4. A synthetic lubricating composition comprising a major amount of di-2-ethylhexyl sebacate and from 0.5% to 10% of a polymer of 3,3'-bis(chloromethyl) oxetane having from 2 to 20 of such units in the polymer.

5. The composition of claim 1 containing a minor amount of a polymeric thickener selected from the class consisting of polymeric C<sub>8-18</sub> alkyl acrylate, polyoxyalkylene fluid and an ester of a polyol and a monocarboxylic acid.

6. The composition of claim 2 containing a minor amount of a polymeric thickener selected from the class consisting of polymeric C<sub>8-18</sub> alkyl acrylate, polyoxyalkylene fluid and an ester of a polyol and a monocarboxylic acid.

7. The composition of claim 3 containing a minor amount of a polymeric thickener selected from the class consisting of polymeric C<sub>8-18</sub> alkyl acrylate, polyoxyalkylene fluid and an ester of a polyol and a monocarboxylic acid.

8. The composition of claim 4 containing a minor amount of a polymeric thickener selected from the class consisting of polymeric C<sub>8-18</sub> alkyl acrylate, polyoxyalkylene fluid and an ester of a polyol and a monocarboxylic acid.

9. A synthetic lubricating composition comprising a major amount of di(2-ethyl hexyl) sebacate, from about 0.5% to about 10% of a polymer of 3,3-bis(chloromethyl)oxetane having from 2 to 4 units and a minor amount of a polymer of lauryl methacrylate.

10. A synthetic lubricating composition comprising a major amount of diisooctyl azelate from about 0.5% to about 10% of a polymer of 3,3-bis(chloromethyl)oxetane having from 2 to 4 units and a minor amount of a polymer of lauryl methacrylate.

11. A synthetic lubricating composition comprising a major amount of di(2-ethyl hexyl) sebacate, from about 0.5% to about 10% of a polymer of 3,3-bis(chloromethyl)oxetane having from 2 to 4 units and a minor amount of a polymer copolymer of ethylene oxide and 1,2-propylene oxide in the viscosity range at 100° F. SUS of 380 to 700.

12. A synthetic lubricating composition comprising a major amount of diisooctyl azelate from about 0.5% to about 10% of a polymer of 3,3-bis(chloromethyl)oxetane having from 2 to 4 units and a minor amount of a polymer of copolymer of ethylene oxide and 1,2-propylene oxide in the viscosity range at 100° F. SUS of 380 to 700.

13. The composition of claim 9 containing a small amount of an organic amine antioxidant.

14. The composition of claim 10 containing a small amount of an organic amine antioxidant.

15. The composition of claim 11 containing a small amount of an organic amine antioxidant.

16. The composition of claim 12 containing a small amount of an organic amine antioxidant.

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DANIEL E. WYMAN, Primary Examiner.

C. O. THOMAS, W. H. CANNON, Assistant Examiners.