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URETHANE CONTAINING LUBRICANT

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This invention relates to a synthetic lubricant composition containing a urethane as anti-oxidant additive.

The lubricant composition of the invention comprises an ester type lubricating oil, an anti-oxidant of urethane selected from the group consisting of

$$R^y\left(O-\overset{\overset{X}{\|}}{C}-NH-R'\right)_y$$

where R^y is a saturated aliphtic hydrocarbon radical, y is an integer from 1 to 8 equalling the valence of the R^y radical, R' is a monovalent hydrocarbon radical and X is oxygen or sulfur.

The above described mono- and polyurethanes are advantageously present in the lubricating composition in a concentration between 0.1% and 5%, preferably between about 0.5% and 1.0%, of the lubricant composition. The novel lubricants of this invention are particularly effective in high temperature service with the urethane additive therein exhibiting excellent anti-oxidant properties at severe high temperatures.

The esters which constitute the major portion of the lubricant composition of this invention are broadly described as esters of hydrocarbyl carboxylic acids. They are high molecular weight 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 from 1 to 4 or more carboxylic acid radicals.

Widely used synthetic ester lubricants are aliphatic esters of saturated aliphatic mono- and dicarboxylic acids containing 6–12 carbon atoms. From the standpoint of cost and availability, the preferred carboxylic acids are caproic, heptoic, caprylic, nonylic, adipic, sebacic and azelaic. 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_6 to C_{18} saturated aliphatic alcohols are commonly used such as 2-ethyl hexanol and 2,2-diethyl-1,3-propanediol. Ether alcohols such as Cellosolve and Carbitol may also be used in the formation of the aliphatic diesters of organic dicarboxylic acids used as the lubricating base in compositions of this invention. Alcohols containing two or more hydroxyl radicals and no hydrogen substituted on the beta carbon atom such as trimethylolpropane and pentaerythritol have proven particularly effective in formulating stable high temperature ester lubricants.

Examples of alkyl esters of aliphtic carboxylic acids are the following: di-isoctyl azelate, di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, di-2-ethylhexyl adipate, dilauryl azelate, di-sec-amyl sebacate, di-2-ethylhexyl alkenyl-succinate, di-2-ethoxyethyl sebacate, di-2-(2'-methoxyethoxy) ethyl sebacate, di-2-(2'-ethylbutoxy) ethyl sebacate, di-2-butoxyethyl azelate, di-2-(2'-butoxyethoxy) ethyl alkenyl-succinate, pentaerythritol tetracaproate, trimethylolpropane tri-isooctanoate and nonyl caprate.

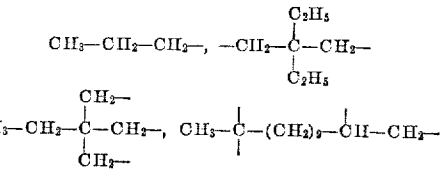
In addition to such esters, polyester lubricants formed by a reaction of an aliphatic dicarboxylic acid, a dihydroxy compound and a monofunctional compound, which is either an aliphatic monohydroxy alcohol or an aliphatic monocarboxylic acid, in specified mol ratios are also employed as the synthetic lubricating base in the composition of this invention; polyesters of this type are described in U.S. 2,628,974 on Polyester Synthetic Lubricants, which issued to R. T. Sanderson on February 17, 1953. Polyesters formed by the reaction of a mixture containing specified amounts of 2-ethyl-1,3-hexanediol, sebacic acid, and 2-ethylhexanol and by reaction of a mixture containing adipic acid, diethylene glycol and 2-ethylhexanoic acid illustrate this class of synthetic polyester lubricating bases.

The sulfur analogs of the above-described esters are also used in the formulation of the lubricating composition of this invention. Dithioesters are exemplified by di-2-ethylhexyl thiosebacate, di-n-octyl thioadipate and the dilaurate of 1,5-pentanedithiol; sulfur analogs of polyesters are examplified by the reaction product of adipic acid, thioglycol and 2-ethylhexyl mercaptan.

As heretofore stated the anti-oxidant additive ingredient of the novel composition is a urethane of the formula

$$R^y\left(O-\overset{\overset{X}{\|}}{C}-NH-R'\right)_y$$

R^y is a saturated mono or polyvalent aliphtic hydrocarbon radial of from 3 to 20 carbon atoms such as



R' is a monovalent hydrocarbon radical of 1 to 40 carbon atoms such as the alkyl, aryl, alkaryl and aralkyl radicals, e.g., phenyl, naphthyl, tolyl, xylyl, phenylpropyl, hexyl, isooctyl, decyl and nonadecyl.

Specific examples of the urethane additives contemplated herein are triphenylurethane of trimethylolpropane, 1,3-diphenylurethane of 2,2 diethyl-1,3-propanediol, triphenylthiourethane of trimethylolpropane, 1,3-diphenylthiourethane of 2,2- diethyl-1,3-propanediol and 1-hexylurethane of 1-isooctanol. These urethanes are normally prepared by reacting aliphatic alcohol with isocyanate or thioisocyanate at an elevated temperature e.g. between about 150 and 250° F. for a period of several hours. The reaction is usually conducted in the liquid phase, therefore, suitable inert liquid solvent such as benzene, toluene, heptane, propylether or triethylamine is employed when necessary. As heretofore stated advantageously between 0.1 and 5.0%, preferably between about 0.5 and 1.0% urethane additive is present in the novel composition. Additive concentrations above the maximum advantageous range value although providing some additional anti-oxidant protection do not warrent the increase amounts since this additional increase in protection is small in relation to the amounts employed. The reason for this is that the urethanes are normally insoluble in the synthetic ester base at percentages above about 5.0%. At concentrations below the minimum level of the advantageous range the anti-oxidant effect of the urethanes is not significant.

In a preferred embodiment of the novel composition phenothiazine is used in conjunction with the urethane additives contemplated herein in amounts between 0.2 to 1.5% of the lubricant with concentrations between 0.5 and 1.3% normally being employed. Phenothiazine is very widely used as an anti-oxidant in ester base lubricant. The combination of phenothiazine and a urethane as contemplated herein have been found to be a very satisfactory anti-oxidant combination, the combination having synergistic like anti-oxidant properties in many instances.

The finished lubricant compositions containing the urethane additive or the combination of a urethane and phenothiazine may also contain other well known additives such as viscosity index improvers and extreme pressure agents.

The effectiveness of the anti-oxidant additive contem-

plated by the invention was demonstrated in a modification of the oxidation test of MIL–L–7808B designed to evaluate lubricants at severe high temperature operating conditions. The modification involved the running of the oxidation test at 500° F. for 48 hours rather than at the usual conditions of 347° F. for 72 hours.

The following lubricant compositions were tested in the modified oxidation test, the results of which are reported in subsequent Tables I, II and III.

(1) Table I:
- (*a*) Lubricant A—100% di-2-ethylhexyl sebacate.
- (*b*) Lubricant B—99% di-2-ethyl sebacate and 1% triphenylurethane of trimethylolpropane.
- (*c*) Lubricant C—99% di-2-ethylhexyl sebacate and 1% phenothiazine.
- (*d*) Lubricant D—98% di-2-ethylhexyl sebacate, 1% triphenylurethane of trimethylolpropane and 1% phenothiazine.
- (*e*) Lubricant E—98.5% di-2-ethylhexyl sebacate, 0.5% triphenylthiourethane of trimethylolpropane and 1% phenothiazine.
- (*f*) Lubricant F—98.5% di-2-ethylhexyl sebacate, 1% phenothiazine and 0.5% diphenylurethane of 2,2 diethyl-1,3-propanediol.

(2) Table II:
- (*g*) Lubricant G—100% Ester T (tetraester of pentaerythritol and a mixture of n-caproic, n-heptoic, n-caprylic and n-nonylic acids).
- (*h*) Lubricant H—99% Ester T and 1% phenothiazine.
- (*i*) Lubricant I—99% Ester T, 0.5% triphenylurethane of trimethylolpropanol and 0.5% of phenothiazine.
- (*j*) Lubricant J—98.5% Ester T, 0.5% triphenylurethane of trimethylolpropane and 1% of phenothiazine.
- (*k*) Lubricant K—98.5% Ester T, 0.5% triphenylthiourethane of trimethylolpropane and 1% phenothiazine.

(3) Table III:
- (*l*) Lubricant L—100% of trioctanate of trimethylolpropane.
- (*m*) Lubricant M—99% trioctanate of trimethylolpropane and 1% phenothiazine.
- (*n*) Lubricant N—99% trioctanate of trimethylolpropane and 1% of triphenylurethane of trimethylolpropane.
- (*o*) Lubricant O—99% trioctanate of trimethylolpropane, 0.5% triphenylurethane of trimethylolpropane and 0.5% of phenothiazine.

The test data gained from the employment of the above compositions in the modified oxidation test are reported in following Tables I–III:

TABLE I

Anti-Oxidant Action of Polyurethanes and Phenothiazine in Di-2-Ethylhexyl Sebacate

Lubricant Comp.	A	B	C	D	E	F
Anti-oxidant wt. percent:						
Polyurethane	0	1	0	1	0.5	0.5
Phenothiazine	0	0	1	1	1	1
Properties of Unused Lube Comp.:						
Kin. Visc. (cs.) [1]—						
100° F.	12.7	12.8	14.0	13.8	13.3	13.6
210° F.	3.3	3.4	3.5	3.5	3.4	3.5
Appearance of Oil, Wt. Percent Sludge	0	0	0	0	0	0
Oxidation Test 500° F./48 hrs.:						
Used Lube Comp. Data—						
Percent Kin. Visc. Change:						
100° F.	[2]	10	[2]	20	75	30
210° F.	[2]	5	[2]	15	60	20
Appearance of Oil, Wt. Percent Sludge	100	50	100	33	50	50.0

[1] Cs.=centistokes.
[2] Unmeasurable—lube oxidized to sludge.

TABLE II

The Anti-Oxidant Action of Polyurethanes and Phenothiazine in Tetraesters of Pentaerythritol and Mixture of C_6–C_9 n-Monobasic Fatty Acids

Lubricant Comp.	G	H	I	J	K
Anti-oxidant wt. percent:					
Polyurethane	0	0	0.5	0.5	0.5
Phenothiazine	0	1	0.5	1	1
Properties of Unused Lube Comp.:					
Kin. Visc. (cs.)[1]—					
100° F.	29.0	29.1	29.0	30.2	29.3
210° F.	5.3	5.4	5.3	5.4	5.3
Neut. No.	0.1	0.1	0.01	0.01	0.03
Appearance of Oil, Wt. Percent Sludge	0	0	0	0	0
Oxidation Test 500° F./48 hrs.:					
Used Lube Comp. Data—					
Percent Kin. Visc. Change:					
100° F.	[2]	560	130	65	115.0
210° F.	[2]	290	85	55	80.0
Appearance of Oil. Wt. Percent Sludge	40	0	0	0	0

[1] Cs.=centistokes.
[2] Unmeasurable—lube oxidized to sludge.

TABLE III

The Anti-Oxidant Action of Polyurethanes and Phenothiazine in the Trioctanate of Trimethylolpropane

Lubricant Comp.	L	M	N	O
Anti-oxident wt. percent:				
Polyurethane	0	0	1	0.5
Phenothiazine	0	1	0	0.5
Properties of Unused Lube Comp.:				
Kin. Visc. (cs.) [1]—				
100° F.	17.9	18.1	18	18.9
210° F.	3.9	4.0	4.0	4.1
Appearance of Oil, Wt. percent Sludge	0	0	0	0
Oxidation Test 500° F./48 hrs.:				
Used Lube Comp. Data—				
Percent Kin. Visc. Change:				
100° F.	[2]	360	-----	50
210° F.	[2]	210	-----	35
Appearance of Oil, Wt. percent Sludge.	50	0	0	0

[1] Cs—centistokes.
[2] Unmeasurable—lube oxidized to sludge.

The data in the above tables clearly demonstrate the anti-oxidant action of the urethanes contemplated herein and the combination of the urethanes and phenothiazine.

All percentages heretofore and hereafter recited are based on weight unless otherwise stated.

We claim:

1. A lubricant composition comprising as the major component an ester formed from an acid selected from the group consisting of saturated aliphatic monocarboxylic acid and saturated aliphatic dicarboxylic acid of 6 to 12 carbon atoms and a saturated aliphatic alcohol of 6 to 18 carbon atoms containing 1 to 4 hydroxyl groups and as a minor component between 0.1 to 5.0 wt. percent of a urethane of the formula

$$R^y\left(O-\overset{\overset{X}{\|}}{C}-NH-R'\right)_y$$

wherein R^y is a saturated aliphatic hydrocarbon radical of from 3 to 20 carbon atoms, y is an integer from 1 to 8 and equals the valence of R^y, R' is a monovalent hydrocarbon radical selected from the group consisting of alkyl, aryl, alkaryl, and aralkyl of 1 to 40 carbon atoms and where X is selected from the group consisting of sulfur and oxygen.

2. A lubricant composition comprising di-2-ethylhexyl sebacate as the major component, and as minor components about 1 wt. percent phenothiazine and about 1 wt. percent triphenylurethane of trimethylolpropane.

3. A lubricant composition according to claim 1 also comprising between 0.2 and 1.5 wt. percent phenothiazine.

4. A lubricant composition according to claim 1 wherein said ester is di-2-ethylhexyl sebacate, and said polyurethane is triphenylurethane of trimethylolpropane.

5. A lubricant composition in accordance with claim 1 wherein said ester is di-2-ethylhexyl sebacate, said polyurethane is the triphenylurethane of trimethylolpropane, and wherein said composition also includes between 0.2 and 1.5 wt. percent phenothiazine.

6. A lubricant composition according to claim 1 wherein said ester is di-2-ethylhexyl sebacate, said polyurethane is triphenylthiourethane of trimethylolpropane wherein said composition also includes between 0.2 and 1.5 wt. percent phenothiazine.

7. A lubricant composition in accordance with claim 1 wherein said ester is di-2-ethylhexyl sebacate, said polyurethane is diphenylurethane of 2,2-diethyl-1,3-propanediol and where said composition also includes between a 0.2 and 1.5 wt. percent of phenothiazine.

8. A lubricant composition according to claim 1 wherein said ester is a tetraester of pentaerythritol and a mixture of C_6 to C_9 normal monobasic fatty acids, said polyurethane is the triphenylurethane of trimethylolpropane.

9. A lubricating composition according to claim 1 wherein said ester is a tetraester of pentaerythritol and a mixture of C_6 to C_9 normal monobasic fatty acids, said polyurethane is triphenylthiourethane of trimethylolpropane and wherein said composition also includes between 0.2 and 1.5 wt. percent phenothiazine.

10. A lubricating composition in accordance with claim 1 wherein said ester is a tetraester of pentaerythritol and a mixture of C_6 to C_9 normal monobasic fatty acids, said polyurethane is triphenylthiourethane of trimethylolpropane and wherein said composition also includes between 0.2 and 1.5 wt. percent phenothiazine.

11. A lubricant composition according to claim 1 wherein said ester is trioctanate of trimethylolpropane and said polyurethane is triphenylurethane of trimethylolpropane.

12. A lubricant composition according to claim 1 wherein said ester is trioctanate of trimethylolpropane and where said composition also includes between 0.2 and 1.5 wt. percent phenothiazine, said ester is triphenylurethane of trimethylolpropane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,160,880	Loane et al.	June 6, 1939
2,187,742	Johnson	Jan. 23, 1940
2,781,319	Barnum et al.	Feb. 12, 1957
2,815,327	Mehr et al.	Dec. 3, 1957

OTHER REFERENCES

Atkins et al.: "Development of Additives and Lubricating Oil Compositions," I. and E. Chem.. vol. 39, No. 4, April 1947, pp. 491–497.

Murphy et al.: "Mode of Action of Phenothiazine Type Antioxidants," I. and E. Chem., vol. 42, No. 12, December 1950, p. 2479.