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EXTREME PRESSURE LUBRICANT ADDITIVES

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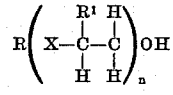
No Drawing. Continuation of abandoned application Ser. No. 826,284, May 20, 1969. This application May 7, 1971, Ser. No. 141,386

Int. Cl. C10m 1/26, 1/24

U.S. Cl. 252—37 9 Claims

ABSTRACT OF THE DISCLOSURE

Extreme pressure lubricant additives comprising the reaction product of (a) a lead compound which if it contains an anion, the anion is removed by distillation and (b) an organic mono carboxylic acid of from 8 to 20 carbon atoms which can be a branched chain fatty acid, unsaturated acid, cyclic acid, or its glyceride in an amount less than about 50% of the stoichiometric equivalent of said lead compound and (c) an alcohol of the formula:



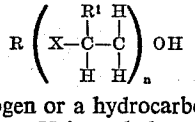
wherein R is hydrogen or a hydrocarbon radical of from 1 to 8 carbon atoms inclusive, X is a chalcogen, n is an integer of from 1 to 3 inclusive, and R^1 is hydrogen or can be taken together with R to form a heterocyclic ring when n is 1, which ring can be substituted.

This application is a continuation of Ser. No. 826,284 filed May 20, 1969, now abandoned.

This invention relates to lubricant additives and more particularly to lubricant compositions of the extreme pressure type suitable for the lubrication of hypoid gears found in automotive differentials. More particularly this invention relates to lubricant additives comprising the reaction product of a lead compound, an organic monocarboxylic acid and an alcohol which additive can be blended with a lubricating oil to form an EP or extreme pressure lubricant.

Hypoid type gears employed in automotive differentials impose an axial component of sliding upon the radial sliding of ordinary gear teeth causing a sliding velocity and total temperature which is much greater than that of ordinary gears. The compositions which are employed as lubricants for these gears are called EP lubricants or extreme pressure lubricants. It is the primary object of this invention to provide compositions suitable for use as EP lubricants and particularly hypoid gear type lubricants.

The lubricant additives of the invention comprise the reaction product of: (a) a reactive lead compound which if it contains an anion, the anion is removed by distillation during the reaction, (b) an organic monocarboxylic acid of from 8 to 20 carbon atoms and/or its glyceride and (c) an alcohol of the formula:



wherein R is hydrogen or a hydrocarbon radical of from 1 to 8 carbon atoms, X is a chalcogen, n is an integer of from 1 to 3 inclusive, and R^1 is hydrogen or can be taken together with R to form a heterocyclic ring when n is 1 which ring can be substituted. The acid to include its glyceride should be present in an amount less than about 50% of the stoichiometric equivalent of lead compound and preferably from about 25 to 40%. The

alcohol should be present in an amount from about 25% to about 75% and preferably from about 30 to about 45% of the stoichiometric equivalent of the lead.

Lead compounds which can be employed are those which react at a temperature between about 100° C. and about 200° C. Exemplary of suitable lead compounds are litharge (lead oxide), lead carbonate and the lead salts of carboxylic acids having from 1 to 4 carbon atoms, inclusive, such as lead formate, lead propionate and lead butanoate, including the corresponding basic lead salts.

The organic monocarboxylic acid employed can be a branched chain aliphatic acid, unsaturated acid or naphthenic acid. Exemplary of suitable branched chain aliphatic acids are 2-ethylhexoic and neodecanoic acid. Exemplary of suitable unsaturated acids are oleic acid, elaidic acid, cinnamic acid, erucic acid, brassidic acid, behenic acid, linolenic acid, fish oil acids, tall oil, linseed oil acids, tung oil acids and soy bean oil acids.

Cyclic carboxylic acids such as naphthenic acids can also be used.

The glycerides of the aforesaid acids can be employed in lieu of the acid, such as for example fish oil, linseed oil, tung oil, and soy bean oil. The alcohol can be monohydric or polyhydric and can contain an ether or thioether group or furan ring. In the aforesaid formula, the chalcogen represented by X can be sulfur or oxygen. The hydrocarbon radical represented by R can be alkyl, phenyl, alkaryl or aralkyl. Representative alkyl are methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl or tertiary butyl. Representative of alkaryl are methyl phenyl, ethylphenyl and t-butyl phenyl. Representative of aralkyl are benzyl and phenylethyl. Exemplary of suitable monohydric alcohols are tetrahydrofurfuryl alcohol (2-tetrahydrofuryl alcohol), 2-furyl methanol furfuryl alcohol, 2-(methylthio)-ethanol, 2-phenoxy-ethanol, diethylene glycol monohexyl ether, diethylene glycol monomethyl ether, 2-thienyl-methanol, 5-methylfurfuryl alcohol, isobutoxy-ethanol, 2-methoxy-ethanol and butoxytriglycol. Exemplary of suitable polyhydric alcohols are diethylene glycol (dihydroxydiethyl ether), thiodiethyleneglycol [bis(2-hydroxyethyl) sulfide] ethylene glycol monoethyl ether (2-ethoxyethanol) and ethylene glycol monomethyl ether (2-methoxyethanol).

The lubricating oil employed can be any of the non-high-performance oils such as are used in automotive engines and transmissions.

The compositions of the invention can be prepared by first blending the lead compound, carboxylic acid and/or glyceride and preferably a lubricating oil solvent and alcohol at room temperature and then the reactants can be heated to a temperature between about 100° C. and about 200° C. for a period between about ½ and about 2 hours until the reaction is complete. The product can be filtered hot to remove any small amounts of solid materials. Prior to filtration, a mineral oil may be added as a diluent to reduce viscosity and speed up filtration.

The following examples will serve to illustrate the invention and its preferred embodiments.

EXAMPLE 1

Fifty grams of light cold pressed fish oil (A.V., 8; I.V., 180; Saponification number, 190), 16.7 grams of vegetable fatty acids (A.V., 170; I.V., 145; unsaponified, 10%), and 150 grams of crude motor oil (containing no additives, etc.) were added to a 500 ml. three-neck flask, equipped with a Dean-Stark tube and condenser, agitator and thermometer. Agitation was begun and a slurry of 93.5 grams PbO (litharge) in 33.3 grams of tetrahydrofurfuryl alcohol was added to the flask. The reactants were

then heated to a temperature of about 140° C., and maintained at this temperature until all of the lead oxide had reacted, about 1½ hours. When the reaction was complete the reaction mass was cooled and filtered, to yield 323 grams (94% of theory) of an oil soluble lead composition containing 24.6% lead and having an acid value (A.V.) of —96.3.

EXAMPLE 2

In order to test the composition of Example 1 as an extreme pressure lubricant, three parts by weight of said composition were blended with 97 parts of motor oil and the composition compared with a blank of motor oil and a commercial product composed of 90 parts lubricating oil, 3 parts lead naphthenate and 7 parts sulfurized sperm oil. The compositions were then subjected to the Timken extreme high pressure test which is conducted as follows. A hardened steel ring is rotated against a steel test block while lubricant is fed to the point of contact of the two test members. The ring is rotated at a mandrel speed of 800 r.p.m. for 10 minutes. Pressures between the ring and the test block were regulated by applying weights and the beam load, or maximum weight in pounds which does not cause scarring of the test bearing, recorded. The machine which is manufactured by the Timken Roller Bearing Company of Canton, Ohio, also permits the determination of pressure which is reported in Table I below. From the results reported in Table I it can be seen that the composition of the invention can withstand a greater load without scarring, than can the commercial product and is considerably better than the control and formulations containing 97 parts motor oil and 3 parts lead naphthenate, and 97 parts motor oil and 3 parts of the composition of Example 1, respectively.

TABLE I

Test Lubricant Compositions and Timken Test Results

	1	2	3	4	5
Motor oil [1]	100	97	97	90	90
Pb naphthenate		3		3	
Composition of Example 1			3		3
Sulfurized sperm oil				7	7
Test results [2]:					
Beam load	5	5	10	45	60
P.s.i.	1,500	2,000	3,000	12,000	14,000

[1] Texaco 586 URSA P 50 oil.
[2] All test run at 800 r.p.m. for 10 minutes.

EXAMPLE 3

To a 250 ml. flask were added 17 parts by weight of naphthenic acid (220 acid value), 10 parts of tetrahydrofurfuryl alcohol and 49 parts of a mineral oil in which 26 parts of litharge had previously been slurried. The reactants were mixed thoroughly at about room temperature and then a small amount of acetic acid was added (about 3 parts) to convert at least a part of the litharge to a basic lead acetate. These ingredients were then heated to 200° C. with vigorous agitation using a Dean-Stark type of water trap on the flask. After about 45 minutes at 200° C., most of the acetic acid that had been added along with some water had been collected in the trap. The batch was filtered hot and upon cooling remained a clear, dark colored liquid. It analyzed 19.6% Pb and had a negative acid value of 67. This corresponds to the presence of naphthenic acid in the amount of 35.4% of the stoichiometric equivalent of the lead present and of tetrahydrofurfuryl alcohol in the amount of 52% of the stoichiometric equivalent of the lead present in the filtered product. When tested in accordance with the procedure of Example 2, the composition is found to have excellent load carrying ability.

EXAMPLES 4–9

In accordance with the procedure of Example 1, compositions were prepared employing several different blends of carboxylic acids and when tested the results are in general agreement with those of composition 5 given in Table I. The percentage of each ingredient are listed below in Table II.

TABLE II

	4	5	6	7	8	9 [1]
Black fish oil						16.7
Resin grade fish oil	61	53.3	48	53.3		50
Cold pressed fish oil [2]					53.3	
Vegetable fatty acids [2]	5.7	13.3	18.7		13.3	
Soya fatty acids [3]				13.3		
Tetrahydrofurfuryl alcohol	33.3	33.3	33.3	33.3	33.3	33.3
Litharge	93.5	93.5	93.5	93.5	93.5	93.5
Crude motor oil [2]	150	150	150	150	150	150
A.V. of product	−89.2	−76.2	−74.8	−73.5	−84.0	−69.7
Percent of lead in product	23.9	23.5	22.5	23.3	22.5	23.6

[1] Composition 9 was prepared using a commercial blend of 25% by weight fish oil and 75% by weight resin grade fish oil, the blend had an A.V.=34.6, I.V.=Sap. V.=188.
[2] As identified in Example 1.
[3] Commercial soya fatty acids; A.V.=198, I.V.=120, Sap. V.=199.

The preferred compositions are those in which the source of carboxylic acid is a blend of resin grade fish oil or light cold pressed fish oil with vegetable fatty acids, soya fatty acids and the like, or mixtures of such fatty acids and glycerides. It is only required that the carboxylic acid or its equivalent as glycerides be present in an amount less than 50% of the stoichiometric equivalent of the lead compound. Preferably the carboxylic acid equivalent is from about 25% to about 40% and the alcohol is present in an amount from about 25 to about 75% of the stoichiometric equivalent of the lead. The other alcohols and lead compounds mentioned herein can be employed with the same general results as that of composition 5, Table I.

The compositions of the invention can be employed with the conventional additives such as antioxidants, rust inhibitors, detergents, pour-point depressants, viscosity index improvers and foam inhibitors. Exemplary of suitable antioxidants are the zinc, barium and calcium thiophosphates and compounds such as di-t-butyl-p-cresol, 2-napthol and phenyl-1-napthylamine. Generally from about 0.5 to about 1.0% is sufficient. Exemplary of suitable rust inhibitors are the organic phosphites, polyhydric alcohols and sodium and calcium sulfonates. Exemplary of suitable detergents are the barium and calcium sulfonates, and phenoxides and generally constitute from about 2 to about 20% by weight of the composition. Exemplary of suitable pour-point depressants are the polymethacrylates or polymers formed by the condensation of wax with naphthalene or phenols. Generally from about 1.0% or less is employed. Exemplary of suitable viscosity index improvers are the polyisobutylenes, polymethacrylates and polyalkylstyrenes having a molecular weight from about 5,000 to about 20,000. Exemplary of suitable foam inhibitors are the methylsilicone polymers having a viscosity of from about 300–1,000 cst. at 100° F.

Although the compositions of the invention are particularly well suited for use in the lubrication of hypoid gears,

they can be used to advantage in many other applications where temperatures and pressures are severe.

I claim:

1. An alkaline composition of matter suitable as an additive to extreme pressure lubricants comprising the reaction product produced by heating at from 100° C. to 200° C. for at least 30 minutes a hydrocarbon oil and a mixture of reactants comprising:

(a) a lead compound selected from the group consisting of lead oxide, lead carbonate and lead salts of carboxylic acids having 1 to 4 carbon atoms;

(b) a carboxylic compound selected from the class consisting of a branched chain, saturated aliphatic hydrocarbyl monocarboxylic acid of 8–20 carbon atoms, an unsaturated fatty acid, a naphthenic acid and a glyceride of an unsaturated fatty acid, said carboxylic component being present in an amount of about 25 to less than 50 percent of the equivalent weight of said lead compound; and

(c) an alcohol of the formula

$$R(X-\underset{\displaystyle R^1}{\underset{|}{C}}H-CH_2)_nOH$$

wherein R is hydrogen or a hydrocarbon radical of 1 to 8 carbon atoms inclusive, X is a chalcogen, n is an integer of from 1 to 3 inclusive, and R^1 is hydrogen or an aliphatic divalent moiety which forms with R a furan ring when n is 1, the total number of carbon atoms in R plus R^1 being from 1 to 5 carbon atoms, which ring can have substituted thereon a group selected from the class consisting of methylol, ethylol, methyl, ethyl and halogen, said alcohol being initially present in an amount equal to 25 to 75 percent of the equivalent weight of said lead compound and reacting with (a) and (b).

2. The composition of matter of claim 1 wherein the total number of carbon atoms in $R+R^1$ is from 3 to 5.

3. A composition of claim 1 wherein the acid is present in an amount from about 25% to about 40% of the stoichiometric equivalent of lead compound.

4. The composition of claim 1 dissolved in a lubricating oil in an amount from about 0.5% to about 85% by weight of the resulting solution.

5. A composition of claim 1 wherein the acid is a mixture of fish oils and vegetable fatty acids.

6. A composition of claim 1 wherein the lead compound is litharge.

7. A composition of claim 1 wherein the alcohol is tetrahydrofurfuryl alcohol.

8. A composition of claim 1 wherein the lead compound is $Pb(OH)_2$.

9. A composition of claim 1 wherein the lead compound is $PbCO_3$.

References Cited

UNITED STATES PATENTS

2,417,428	3/1947	McLennan	252—35
1,967,656	7/1934	Bertsch	252—364
2,625,510	1/1953	Moore	252—37
2,895,914	7/1959	Kern et al.	252—37
2,594,822	4/1952	Stross et al.	252—25
2,122,940	7/1938	Hodson	252—38

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