United States Patent Office 3,185,645 Patented May 25, 1965

3,185,645

OXIDATION INHIBITED LUBRICANTS

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No Drawing. Filed Sept. 28, 1962, Ser. No. 227,042
5 Claims. (Cl. 252—46.7)

This invention pertains to lubricating oil compositions having incorporated therein metal-free detergents. These particular detergents are also effective as oxidation inhibitors.

Present day internal combustion engines operate at high speeds and high compression ratios. When used in the so-called city stop-and-go driving, which includes the greater part of the driving conditions for a large percentage of today's automobiles, the internal combustion engines do not reach the most efficient operating temperature. Under city driving conditions, large amounts of partial oxidation products are formed, and reach the crankcase of the engine by blowing past the piston rings. Most of the partial oxidation products are oil-insoluble, tending to form deposits on the various operating parts of the engine, such as the pistons, piston rings, etc. For the purpose of preventing the deposition of these products on the various engine parts, it is necessary to incorporate detergents in the lubricating oil compositions, thus keeping these polymeric products dispersed in a condition unfavorable for deposition on metals.

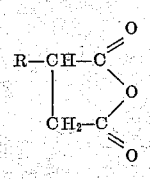
For the most part, the detergents which are added to crankcase oils to reduce this formation of sludges and varnishes are metal organic compounds, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. Although these metal-containing organic compounds have some effectiveness as detergents for dispersing the precursors of the deposits within the oil itself rather than permitting them to form as deposits on the engine parts, they have the disadvantage of forming ash deposits in the engine. These ash deposits lower engine performance by fouling spark plugs and valves, and contributing to pre-ignition.

It is a particular object of this invention to provide lubricating oil compositions having incorporated therein metal-free detergents which are also effective as oxidation inhibitors. Thus, these new additives inhibit the oxidation of lubricating oil compositions and also disperse the undesirable polymeric products which are formed.

Therefore, in accordance with this invention, it has been found that lubricating oil compositions particularly useful for heavy duty service are obtained by incorporating therein a product obtained by reacting an alkenyl succinic anhydride, a dihydrocarbyl dithiophosphoric acid, and a polyalkylene polyamine.

By the use of lubricating oil compositions containing the reaction products described herein, diesel and gasoline engine products remain remarkably free of deposits and varnish even under severe operating conditions.

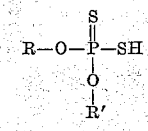
The alkenyl succinic anhydride reactants herein are of the formula



wherein R is a hydrocarbon radical having from 10 to 200 carbon atoms therein, preferably from 50 to 200 carbon

atoms. Examples of alkenyl radicals include n-decenyl, n-hexadecenyl, propylene tetramer, butylene trimer, propylene polymers containing from 50 to 200 carbon atoms, and polymers of mixtures of 1-butene and isobutene having from 50 to 200 carbon atoms.

The dihydrocarbyl dithiophosphoric acids which are reactants herein can be represented by the formula



wherein R and R′ represent hydrocarbon radicals each having from 1 to 25 carbon atoms, preferably from 4 to 20 carbon atoms. The R and R′ combined can have a total of from 6 to 50 carbon atoms, preferably from 10 to 40 carbon atoms.

The R and R′ radicals are exemplified as follows: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, secamyl, hexyl, isohexyl, n-octyl, n-decyl, n-dodecyl, tetradecyl, octadecyl, cyclohexyl, phenyl, amylphenyl, decylphenyl, dodecylphenyl, hexadecylphenyl, etc.

Examples of dihydrocarbyl dithiophosphoric acids include dimethyldithiophosphoric acid, methylethyldithiophosphoric acid, diethyldithiophosphoric acid, di-n-propyl dithiophosphoric acid, di-isopropyldithiophosphoric acid, di-n-butyldithiophosphoric acid, diisobutyldithiophosphoric acid, n-butyl-n-amyldithiophosphoric acid, di-secamyldithiophosphoric acid, methyl-n-hexyldithiophosphoric acid, isobutyl-n-hexyldithiophosphoric acid, di-n-octyldithiophosphoric acid, methylcyclohexyl dithiophosphoric acid, methylcyclohexyldithiophosphoric acid, dicyclohexyldithiophosphoric acid, methylphenyldithiophosphoric acid, diphenyldithiophosphoric acid, di-(amylphenyl)dithiophosphoric acid, di-(hexadecylphenyl)dithiophosphoric acid, etc.

The polyalkylene polyamines, which contribute the imide and the basic nitrogen atoms of the reaction products herein, are derived from polymers of ethylene or propylene, such as polyethylene polyamine, and polypropylene polyamines. Such polyalkylene polyamines may be represented by the formula

$$NH_2R(NHR)_xNH_2$$

wherein the R represents the divalent radical ethylene or propylene, and x is a number having a value from 1 to 10 or more. Examples of these polyalkylene polyamines include diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, dipropylene triamine, dipropylene tetramine, tetrapropylene pentamine, pentapropylene hexamine, di(trimethylene)triamine, tri(trimethylene) tetramine, tetra-(trimethylene)-pentamine and penta-(trimethylene)hexamine.

There is no one particular reaction mechanism which is used to produce reaction products which are useful herein in lubricating oil compositions as oxidation inhibitors and detergents according to this invention. An alkenyl succinic anhydride, a polyalkylene polyamine, and a dihydrocarbyl dithiophosphoric acid can be mixed together in the desired amounts and reacted; or a polyalkylene polyamine may be reacted with a dihydrocarbyl dithiophosphoric acid, and the resulting product then reacted with an alkenyl succinic anhydride, or the alkenyl succinic anhydride may be reacted with the dithiophosphoric acid, followed by the reaction with the polyalkylene polyamine.

The mol ratio of dithiophosphoric acid to polyamine can vary from $(X-1):1$ to 1:1, wherein X represents the number of titratable amine groups in the polyalkylene

polyamine. Preferably this mol ratio is $(X-1.22):1$, more preferably, 1:1.

The mol ratio of polyalkylene polyamine to anhydride can range from 0.5:1 to 1:1. Preferably, the polyamine-anhydride mol ratio is in the range of 0.8:1 to 1:1.

When the initial reactants are an anhydride and a dithiophosphoric acid, the mol ratio of anhydride to dithiophosphoric acid can vary from 0.5:1 to 1:1. Preferably, the mol ratio of anhydride to dithiophosphoric acid is 1:1.

In the reaction herein to form the desired reaction products, the reaction temperature can vary from 70° F. to 400° F., preferably from 210° F. to 310° F. In the reaction of polyalkylene polyamine and the dithiophosphoric acid, the preferred reaction temperature is from 70° F. to about 200° F., followed by a temperature sufficient to evolve H_2S in the reaction with the alkenyl succinic anhydride.

No theory is postulated herein as to the structure of the reaction products herein. It is recognized, however, that the final reaction temperature is a temperature sufficient to evolve hydrogen sulfide from the reaction mixture.

Lubricating oils which can be used as base oils to form lubricating oil compositions include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base lubricating oils, other hydrocarbon lubricants, e.g., lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and the mixtures thereof), alkylene oxide-type polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohols, e.g., ethyl alcohol, dicarboxylic acid esters (such as those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic aid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethyl hexyl alcohol, dodecyl alcohol, etc.), liquid esters of acids of phosphorus, alkyl benzenes (e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc.), and dialkyl benzenes (e.g., n-nonyl 2-ethyl hexyl benzene); polphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, polymers of silicon (e.g., tetraethyl silicate, tetraisopropyl silicates, tetra (4-methyl-2-tetraethyl)silicate, hexyl (4-methyl-2-pentoxy)disiloxane, poly(methyl)siloxane, poly(methyl-phenyl)siloxane, etc. Synthetic oils of the alkylene oxide-type polymers which may be used include those exemplified by the alkylene oxide polymers.

The products described herein can be used in oils in amounts of 0.1% to 40% by weight, preferably 0.1% to 15%; more preferably 1% to 10%.

The following examples illustrate the formation of the reaction product useful herein as oxidation inhibitors and detergents.

EXAMPLE I

72 grams (0.38 mol) of tetraethylene pentamine was charged to a reaction vessel with continued agitation, and blanketed with nitrogen To this tetraethylene pentamine there was added 409 grams (0.38 mol) of a 50% lubricating oil solution of di(alkylphenyl)dithiophosphoric acid in which the alkyl radicals were derived from propylene polymers having an average of 13 carbon atoms. The temperatures of the reaction vessel rose from 80° F. to 155° F. The reaction mixture was heated to 200° F., after which there was added 1005 grams (0.47 mol) of a 48% lubricating oil solution of polyisobutenyl succinic anhydride which had been preheated to 200° F. The alkenyl radical of the isobutenyl succinic anhydride contained an average of 66 carbon atoms. The reaction mixture was heated at temperatures in the range of 305–315° F. for 2 hours while a solid stream of nitrogen was blown through the mixture.

Upon analysis, it was found that the resulting lubricating oil composition contained the following:

Table I

	Weight percent	
Basic nitrogen	0.83,	0.83
Nitrogen	1.71,	1.72
Phosphorus	0.84,	0.84
Sulfur	1.16,	1.15
Acid No., mgs. KOH/gram	14.91,	13.08

EXAMPLE II

A mixture of 103 grams (1 mol) of diethylene triamine was reacted at ambient temperature with 270 grams (1 mol) of isobutyl-n-hexyl dithiophosphoric acid. This reaction product was heated with 322 grams of n-hexadecenyl succinic anhydride to 325° F. until the water of reaction had been removed.

EXAMPLE III

818 grams (0.76 mol) of a di(alkylphenyl)dithiophosphoric acid (wherein the alkyl group was derived from a polypropylene having an average of 13 carbon atoms) was rapidly added with agitation to 144 grams (0.76 mol) of tetraethylene pentamine wherein the reaction vessel was blanketed with nitrogen. The temperature rose from ambient temperatures to 110° F., after which the mixture was heated to 200° F., after which there was added 1980 grams (0.93 mol) of a polyisobutenyl succinic anhydride wherein the polyisobutenyl radical had a molecular weight of about 1,000, preheated to 200° F. The reaction mixture was heated to 310° F. for a period of 2 hours. Hydrogen sulfide was evolved during the entire 2 hour reaction period.

The following analytical results were obtained on the reaction product.

	Wt. percent
Phosphorus	0.85
Nitrogen	1.72
Basic nitrogen	0.92
Sulfur	1.43
Acid No.	17.1

EXAMPLE IV

113 grams (0.38 mol) of a mixed dialkyl dithiophosphoric acid, wherein one of the alkyl radicals contained 4 carbon atoms and the second alkyl radical contained 6 carbon atoms, was added to 72 grams of tetraethylene pentamine (0.38 mol) in a reaction vessel blanketed with nitrogen. The reaction mixture was heated to 200° F., after which 990 grams (0.46 mol) of the same polyisobutenyl succinic anhydride described in the example hereinabove, preheated to 200° F. was added with agitation. The temperature was raised to 305–310° F. and maintained for a period of about 2 hours under a blanket of nitrogen. Upon analysis, it was found that the reaction mixture contained 1.09% by weight of phosphorus, and 1.77% by weight of sulfur. The dialkyl dithiophosphoric acid itself originally contained 11.2% phosphorus and 23.4% sulfur.

Table II hereinbelow presents data obtained with lubricating oil compositions containing the reaction product of Example III hereinabove.

The test was made in a Caterpillar L–1 engine according to the Supplement I conditions (for a period of the hours noted) as described in the Coordinating Research Council Handbook, January 1946.

The "PD Nos." refer to the piston discoloration rating. After the engine test, the three piston lands are examined visually. To a piston land which is completely black is assigned a PD No. of 800; to one which is completely clean, a PD No. of 0; to those intermediate between those completely black and completely clean are assigned PD Nos. intermediate in proportion to the extent and degree of darkening.

The "GD" Nos. refer to the percentage deposit in the piston ring grooves; that is, a 0 evaluation being a clean groove, and a 100 evaluation being a groove full of deposits.

The base oil was a Mid-Continent SAE 30 base oil.

Dithiophosphate A was the zinc salt of a mixed dialkyl dithiophosphoric acid wherein one of the alkyl radicals contained 4 carbon atoms and the other alkyl radical contained 6 carbon atoms.

Dithiophosphate B was a zinc dialkylphenyldithiophosphate wherein the alkyl radical was derived from a polypropylene having an average of 13 carbon atoms.

Table II

Additive:			
1. Reaction product of Example III, wt. percent	0.0	0.0	2.75
2. Dithiophosphate:			
(A) mM./kg. [1]	0.0	12	10
(B) mM./kg. [1]	0.0		2

Test results	120 hours	120 hours	Hours	
			60	120
Top GD No.	39	21	0	0
PD Nos., Land	800, 800, 800	695, 245, 235	0, 0, 0	1, 0, 0

[1] Millimols of zinc per kilogram of finished lube oil.

Table III hereinbelow presents oxidation test results for lubricating oil compositions described herein. The oxidation test measures the time (hours) for the agitated oil sample to take up 1 liter of oxygen per 100 grams of oil sample at 340° F.

The base oil was a California paraffinic base oil having a viscosity of 500 SSU at 100° F.

Each of the compositions described in Table III contained the same amount of total phosphorus, that is, 24.4 mM./kg.

Table III

Composition:	Oxidation Test, hours
(1) Base oil	0.25
(2) Base oil+6.81 wt. percent [1] Prod. of Ex. IV hereinabove	8.9
(3) Base oil+8.6 wt. percent [1] Prod. of Ex. III hereinabove	10.7
(4) Base oil+3% Succinimide [2]+12 mM./kg. dithiophosphate A	3.1
(5) Base oil+3% Succinimide [2]+12 mM./kg. dithiophosphate B	4.5

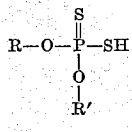
[1] Equivalent to 3.0% by weight of succinimide ([2]).
[2] The alkenyl succinimide of tetraethylene pentamine, wherein the alkenyl radical contained 66 carbon atoms.

I claim:

1. A composition of matter comprising a major proportion of an oil of lubricating viscosity and from 0.1% to 40% by weight of a product obtained by reacting (1) an alkenyl succinic anhydride having from 50 to 200 carbon atoms in said alkenyl radical, (2) a polyalkylene polyamine of the formula

$$NH_2R(NHR)_xNH_2$$

wherein R is a divalent radical selected from the group consisting of ethylene and propylene and x is a number having a value from 1 to 10, and (3) a dihydrocarbyl dithiophosphoric acid of the formula



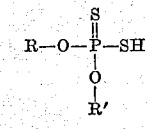
wherein R and R' are hydrocarbon radicals each having from 4 to 20 carbon atoms with a combined total of 10 to 40 carbon atoms, wherein the mole ratio of said

dithiophosphoric acid of said polyamine is from $(X-1):1$ to 1:1, wherein X is the number of titratable amine groups in said polyamine, wherein the mole ratio of said polyalkylene polyamine to said anhydride is from 0.5:1 to 1:1, said reaction being at temperatures of 210° F. to 400° F. sufficient to cause evolution of hydrogen sulfide.

2. A composition of matter comprising a major proportion of an oil of lubricating viscosity and from 0.1% to 40% by weight of a product obtained by reacting (1) a polyalkylene polyamine of the formula

$$NH_2R(NHR)_xNH_2$$

wherein R is a divalent radical selected from the group consisting of ethylene and propylene and x is a number having a value from 1 to 10, and a dihydrocarbyl dithiophosphoric acid of the formula



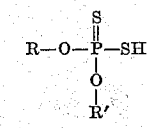
wherein R and R' are hydrocarbon radicals each having from 4 to 20 carbon atoms with a combined total of 10 to 40 carbon atoms, said reaction being at temperatures from 70° F. to 200° F. followed by (2) reacting the product of (1) with an alkenyl succinic anhydride at temperatures of 210° F. to 400° F. sufficient for evolution of hydrogen sulfide wherein said alkenyl group contains from 50 to 200 carbon atoms, wherein the mole ratio of said dithiophosphoric acid to said polyamine is from $(X-1):1$ to 1:1, wherein X is the number of titratable amine groups in said polyamine, wherein the mole ratio of said polyamine to said anhydride is from 0.5:1 to 1:1.

3. The composition of matter of claim 2 wherein said polyamine is tetraethylene pentamine.

4. A composition of matter comprising a major proportion of an oil of lubricating viscosity and from 1% to 10% by weight of a product obtained by reacting (1) an alkenyl succinic anhydride having from 50 to 200 carbon atoms in said alkenyl radical, (2) a polyalkylene polyamine of the formula

$$NH_2R(NHR)_xNH_2$$

wherein R is a divalent radical selected from the group consisting of ethylene and propylene and x is a number having a value from 1 to 10, and (3) a dihydrocarbyl dithiophosphoric acid of the formula



wherein R and R' are hydrocarbon radicals each having from 4 to 20 carbon atoms with a combined total of 10 to 40 carbon atoms, wherein the mol ratio of said dithiophosphoric acid of said polyamine is from $(X-1):1$ to 1:1, wherein X is the number of titratable amine groups in said polyamine, wherein the mol ratio of said polyalkylene polyamine to said anhydride is from 0.5:1 to 1:1, said reaction being at temperatures from 210° F. to 400° F. sufficient to cause evolution of hydrogen sulfide.

5. The composition of matter of claim 4 wherein said polyamine is tetraethylene pentamine.

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