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3,185,647

## LUBRICANT COMPOSITION

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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 corrosion 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. This phenomenon is noticed more in engines having greater wear during the break-in period. 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, and to reduce break-in wear, it is necessary to incorporate detergents and wear-reducing agents in the lubricating oil compositions, thus keeping these polymeric products dispersed in a condition unfavorable for deposition on metals.

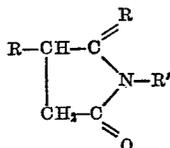
A great number of the detergents which are added to crankcase oils to reduce this formation of sludges and varnishes are metal organic compounds, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. Although these metal-containing organic compounds have 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 corrosion inhibitors. Thus, these new additives disperse the undesirable polymeric products which are formed, and also inhibit corrosion to metal wearing surfaces.

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 (1) reacting an N-alkyl alkenyl succinimide with phosphorus pentasulfide, followed by (2) reacting the product of (1) with a polyalkylene polyamine.

By the use of lubricating oil compositions containing the reaction products described herein, diesel and gasoline engine parts remain remarkably free of deposits and varnish, even under severe operating conditions. In addition, these lubricating oils reduce break-in wear.

The N-alkylalkenyl succinimide reactant is of the formula



wherein R, the alkenyl radical, is a hydrocarbon radical having from 30 to 200 carbon atoms therein, preferably from 50 to 200 carbon atoms, and R' is an alkyl radical having from 1 to 20 carbon atoms therein.

5 Examples of alkenyl radicals include propylene polymers containing from 30 to 200 carbon atoms, and polymers of mixtures of 1-butene and isobutene having from 30 to 200 carbon atoms.

10 Examples of alkyl radicals include propyl, butyl, amyl, isoamyl, hexyl, isohexyl, octyl, isooctyl, 2-ethylhexyl, decyl, etc.

The polyalkylene polyamines are derived from polymers of ethylene or propylene, such as polyethylene polyamines, and polypropylene polyamines. Such poly-  
15 alkylene polyamines may be represented by the formula



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

Other polyalkylene polyamines can be exemplified by the aminoalkyl piperazines, for example,  $\beta$  aminoethyl piperazine.

30 The mol ratio of phosphorus pentasulfide to N-alkyl succinimide can vary from 5:1 to 1:20; preferably 1:1 to 1:4.

With regard to the polyalkylene polyamine, the mol ratio of polyalkylene polyamine to the N-alkyl alkenyl succinimide can range from 0.5:1 to 1:1; preferably 0.8  
35 to 1.

In the reaction herein between the N-alkyl alkenyl succinimide and the  $\text{P}_2\text{S}_5$ , the reaction temperature can vary from 70° F. to 400° F., preferably from 175° F.  
40 to 250° F.

In the reaction between the  $\text{P}_2\text{S}_5$ -succinimide product and polyalkylene polyamine, the reaction temperature is from 250° F. to about 450° F., preferably 280° F. to  
45 350° F.

Lubricating oils which can be used as base oils to form lubricating oil compositions of the above-described additives 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.,  
50 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  
55 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 acid, 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, tetra-  
60 decyl benzene, etc., and dialkyl benzenes (e.g. n-nonyl 2-ethyl hexyl benzene); polyphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, compounds of silicon (e.g., tetraethyl silicate, tetraisopropyl silicates, tetra (4-methyl- 2-tetraethyl) silicate, hexyl (4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxane, poly(methylphenyl)  
70 siloxane, etc. Synthetic oils of the alkylene oxide-type polymers which may be used include those exemplified by the alkylene oxide polymers.

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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 corrosion inhibitors and detergents in lubricating oil compositions.

EXAMPLE I

A mixture of 51 grams (0.23 mol) of phosphorus pentasulfide, 500 grams of an oil solution of N-butyl polyisobutenyl succinimide (0.21 mol), wherein the polyisobutenyl radical contained an average of approximately 66 carbon atoms, and 500 grams of xylene was heated at reflux temperatures for a period of 5 hours under a blanket of nitrogen. The xylene was distilled off under reduced pressure (310° F. bottoms temperature at 4 mm.). For convenience the product is called Product A.

A mixture of 250.12 grams of Product A and 16.0 grams of tetraethylene pentamine was heated to 150° F., using a blanket of nitrogen over the reaction mixture. The mixture was slowly heated to 350° F. at an absolute pressure of 4 mm. Hg, and heated at that temperature and pressure for 2 hours.

The reaction product contained:

	Wt. percent
Phosphorus -----	2.54
Sulfur -----	3.21
Nitrogen -----	2.64

EXAMPLE II

A mixture of 137.6 grams (0.62 mol) of phosphorus pentasulfide, 2700 grams (1.24 mol) of an oil solution of N-butyl polyisobutenyl succinimide, and 2700 grams of xylene was heated at reflux temperature for 5 hours. The xylene was removed by heating the mixture at 310° F. at an absolute pressure of 4 mm. Hg. The remaining product was dissolved in hexane and filtered, and the hexane was removed.

A mixture of 2600 grams of the above product and 166 grams of tetraethylene pentamine was heated to 150° F., followed by heating at 350° F., at an absolute pressure of 4 mm. Hg for 2 hours

The reaction product contained:

	Wt. percent
Phosphorus -----	1.30
Sulfur -----	1.26
Nitrogen -----	2.60

EXAMPLE III

A mixture of 184 grams (0.83 mol) phosphorus pentasulfide, 1600 grams (0.73 mols) of an oil solution of N-butyl polyisobutenyl succinimide, and 1200 ml. benzene was heated at reflux temperature under a blanket of nitrogen for 30 minutes. The reaction mixture was filtered, and the benzene was removed by distillation.

A mixture of 200 grams of the above product and 12.8 grams of tetraethylene pentamine was heated to 150° F., then to 350° F. at an absolute pressure of 4 mm. Hg.

The final product contained:

	Wt. percent
Phosphorus -----	1.06
Sulfur -----	0.88
Nitrogen -----	2.65

Table I hereinbelow presents further data on the effectiveness of the reaction products described herein as lubricating oil additives. The data of Table I were obtained after 60 hours of operating under the severe conditions of a Caterpillar 1-H engine test used to qualify oils under the Mil 2104B procedure. This military specification procedure is so severe that the engine will not even operate with a base oil un compounded. Even a base oil with the normal commercial additives under this procedure does not provided sufficient lubrication; that is, the engine itself eventually sticks.

The base oil used in obtaining data for Table I con-

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sisted of a California paraffinic base oil having a viscosity of 500 SSU at 100° F., and having incorporated therein 15 mM./kg. (i.e., 15 millimols of metal per kilogram of the finished lubricating oil composition) of a basic sulfurized calcium phenate, and 12 mM./kg of a zinc dialkyl dithiophosphate.

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 No." refers to the percentage deposit in the top piston ring groove; that is, a 0 evaluation being a clean groove, and a 100 evaluation being a groove full of deposits.

Table I

Composition	Hrs.	PD Nos.	GD No.	Break-in-Wear, mgs. loss
1. Base Oil + 4% wt. Product of Example I	60	245-140-110-5	8	199
	120	305-190-135-5	13	336
2. Base oil + 4% wt. Product of Example II	60	200- 65-145-0	6	296
	120	215-120-140-0	11	487

Table II hereinbelow presents data showing the effectiveness of the compounds described herein as lubricating oil additives by testing a lubricating oil composition in an L-38 Test, using a 1 cylinder CLR engine in a test period of 40 hours.

The base oil consisted of a California paraffinic base oil having a viscosity of 500 SSU at 100° F., 14 mM./kg. of a zinc dialkyl dithiophosphate, and 4 mM./kg. of a zinc di(alkylphenyl) dithiophosphate.

Table II

Composition: (1) Base oil + 6.25% of product of Example II	Bearing weight loss (milligrams) 310
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Table III hereinbelow presents data obtained with lubricating oil compositions containing the reaction product of Example II 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." and "GD Nos." are defined hereinabove.

The base oil was a Mid-Continent SAE 30 oil containing 10 mM./kg. of a zinc dialkyl dithiophosphate, and 2 mM./kg. of a zinc di(alkylphenyl) dithiophosphate.

Table III

Composition	Hours	GD Nos.	PD Nos.	
			Land	Skirt
1. Base Oil + 2% Product of Example III	60	1	5-0-0	0
	120	1	5-0-0	0

In addition to the additives described hereinabove, the lubricating oils herein may contain other corrosion inhibitors, oxidation inhibitors, thickening agents, viscosity index improving agents, rust inhibitors, etc.

We claim:

1. A lubricating oil composition comprising a major proportion of a lubricating oil having incorporated therein from 0.1% to 40% of a product obtained by (1) reacting an N-alkyl alkenyl succinimide having from 30 to

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200 carbon atoms in said alkenyl group and from 1 to 20 carbon atoms in said alkyl radical with phosphorus pentasulfide at temperatures from 70° F. to 400° F. wherein the phosphorus pentasulfide-succinimide mol ratio is from 5:1 to 1:20 followed by (2) reacting the product of (1) with a polyalkylene polyamide at temperatures from 250° F. to 450° F. wherein the mol ratio of polyamine to succinimide is from 0.5:1 to 1:1, said polyalkylene polyamine being of the formula



wherein R is selected from the group consisting of ethylene and propylene and  $x$  is a number from 1 to 10.

2. The lubricating oil composition of claim 1 wherein said polyamine is tetraethylene pentamine.

3. The lubricating oil composition of claim 1 wherein said succinimide is reacted with said phosphorus pentasulfide at temperatures from 175° F. to 250° F., and said

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phosphorus pentasulfide-succinimide product is reacted with said polyalkylene polyamide at temperatures from 280° F. to 350° F.

4. The lubricating oil composition of claim 3 wherein said product is present in amounts from 0.1 to 15% by weight.

5. The lubricating oil composition of claim 4 wherein said phosphorus pentasulfide-succinimide mole ratio is from 1:1 to 1:4.

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## References Cited by the Examiner

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DANIEL E. WYMAN, *Primary Examiner.*

## UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

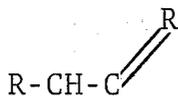
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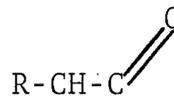
Robert G. Anderson et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 67 to 72, for that portion of the formula reading



read



column 3, line 73, for "provided" read -- provide --; column 5, line 6 and column 6, line 2, for "polyamide", each occurrence, read -- polyamine --.

Signed and sealed this 19th day of October 1965.

(SEAL)

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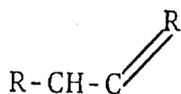
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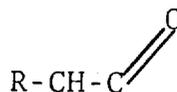
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