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LUBRICATING OIL COMPOSITION

Helen I. Thayer, Pittsburgh, Pa., assignor to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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This invention relates to lubricating oil compositions having improved detergency characteristics. More particularly, the invention relates to lubricating compositions containing detergent amounts of certain amine salts of borylated partially esterifier thiophosphates.

Uncompounded hydrocarbon lubricating oils are frequently objectionable because they fail to prevent formation of rust and because they tend to deposit sludge, carbonaceous materials or varnish on the engine parts. As is known in the art, the function of a detergent additive in lubricating oils used in internal combustion engines is to impart such properties to the oil as to enable it to keep sludge, carbonaceous materials or varnish in suspension or dispersion in the oil. The use of detergent additives tends to prevent or retard sticking of piston rings, formation of varnish-like coatings on the pistons, cylinder walls and moving parts, and the settling out of sludge in the crankcase.

I have found that the detergent characteristics of hydrocarbon lubricating oils can be improved by the addition of the reaction product of (*a*) an oil-soluble primary, secondary or tertiary alkyl (cyclic or open-chain), alkenyl or alkylol, mono- or diamine whose alkyl or alkenyl substituent or substituents contain 6 to 22 (preferably 8 to 18 carbon atoms each, such as 3-octadecenylaminopropylamine or tertiaryoctylamine, and (*b*) an anhydride prepared by reacting a partially esterified thiophosphoric acid containing 1 to 2 organic substituents per molecule and whose organic substituents are hydrocarbon radicals containing 6 to 22 carbon atoms each, such as O,O'-diisooctylphenyl dithiophosphate with boric acid, boric oxide or an anhydride of boric oxide and an aliphatic monocarboxylic acid, preferably a C_{1-8} unsubstituted acid, in the ratio of about 0.5 to about 6 moles of partially esterified thiophosphoric acid per mole of borylating agent, and wherein the amine to anhydride equivalent ratio is in the range of about 1:2 to 2:1. The hydrocarbon substituents of the partially esterified thiophosphoric acid can be alkyl (cyclic or open-chain), alkenyl, aryl, alkaryl or aralkyl. Normally the detergent characteristics of the oil will be improved by the use of about 0.1 to 20 percent of the above-indicated reaction products. However, other proportions can be used.

The amine derivatives incorporated in the lubricating oils of this invention can be prepared in any suitable manner. I prefer, however, to prepare the anhydride of the partially esterified thiophosphate and the borylating agent and thereafter prepare the amine derivative by adding that quantity of amine to the borylated thiophosphote ester that will result in an acid to amine equivalent ratio of 1:2 to 2:1. The reaction between the amine and the borylated thiophosphate will procede spontaneously but mild heating may be desirable to facilitate the reaction. It is to be understood that the method of preparing these reaction products forms no part of this invention. However, it may be mentioned that the preferred method of preparing these reaction products is disclosed in the copending application of Helen I. Thayer, Serial No. 819,566, filed of even date herewith. Briefly, the aforementioned application discloses that reaction products of the kind described herein can be formed by the reaction of a partially esterified thiophosphoric acid of the kind described above with

a borylating agent such as boric acid, boric oxide or an anhydride of boric oxide and an aliphatic monocarboxylic acid, in the range of about 0.5 to about 6 moles of thiophosphoric acid ester per mole of borylating agent by refluxing the reactants in a solvent at the boiling point of the solvent for a period of about 0.5 to about 20 hours. This anhydride product is recovered and reacted with a suitable amine in the proportion of 0.5 to 2 equivalents of anhydride per equivalent of amine, preferably at a temperature of about 40° to 60° C. for about one-half hour or more. After the reaction is complete, if a solvent was used it is removed and the product is recovered.

Examples of the reaction products included in this invention are the amine reaction products of 1 or 2 equivalents of the anhydrides formed from boric oxide and ethyl lauryl dithiophosphate (0.5 to 1 molar ratio); boric acid and di(2-ethylhexyl) dithiophosphate (1:1 molar ratio); anhydride of boric oxide and acetic acid and di(2-ethylhexyl) dithiophosphate (0.25 to 1 molar ratio); boric oxide and dioctyl dithiophosphate (1:1 molar ratio); boric oxide and di-p-isooctylphenyl dithiophosphate (0.5 to 1 molar ratio); boric acid and dicyelohexyl dithiophosphate (1:1 molar ratio); boric oxide and monooctyl dithiophosphate (1:1 molar ratio); boric oxide and dibenzyl dithiophosphate (0.5 to 1 molar ratio); boric oxide and di-sperm oil alcohol ester of dithiophosphoric acid (0.5 to 1 molar ratio); boric oxide and diphenyl dithiophosphate (0.5 to 1 molar ratio); and 1 or 2 equivalents of amines such as any of the following: 2-ethylhexylamine, cyclohexylamine, dicyclohexylamine, trioctylamine, octylamine, decylamine, dodecylamine, N-octadecenyl ethylene diamine, 1,1,3,3-tetramethylbutylamine, and those mono- and diamines where the respective nitrogen substituents are mixed alkyl and alkenyl groups obtained from naturally occurring fats and oils, e.g., tallow, soybean oil, coconut oil and the like. In such instances the aliphatic N-substituents will be monovalent straight chain hydrocarbon radicals containing an even number of carbon atoms from 8 to 22. Examples of such mixtures are: 3-"tallow"-aminopropylamine, 3-"soya"-aminopropylamine, 3-"coco"-aminopropylamine, cocoamine, etc.

The amine reaction products of the borylated partially esterified thiophosphates disclosed herein are useful when incorporated in mineral oils in minor proportions sufficient to confer detergent properties on the composition. For example, satisfactory results will be obtained by the use of about 0.1 to 20 percent of the additive based on the weight of the lubricating oil. Especially effective results normally will be obtained with the use of about 0.5 to about 10 percent by weight in the lubricating oil disclosed herein and this constitutes the preferred range of proportions.

The amine reaction products of the borylated partially esterified thiophosphates disclosed herein may be incorporated in lubricating oils in any suitable manner. Thus, the compounds may be added per se directly to the lubricating oils or in the form of concentrates. Suitable concentrates containing the addition agents of this invention comprise, for example, lubricating oil solutions or dispersions containing about 10 to about 75 percent by weight and preferably 25 to 50 percent by weight active ingredients.

The following examples illustrate various methods of preparing my additives and improved compositions containing the same:

EXAMPLE 1

Borylated 0,0'-di(p-isooctylphenyl) dithiophosphoric acid was prepared by heating 126 grams (0.25 mole) of di-(p-isooctylphenyl) dithiophosphoric acid with 15 grams (0.22 mole) of boric oxide in the presence of benzene.

Heating was continued for 17 hours at temperatures of 80° to 100° C. and the solution was filtered to remove the unreacted boric oxide. The amine reaction product was prepared by adding 88 grams (0.44 equivalent) of the commercial 3-"tallow"-aminopropylamine which is a mixture of alkyl- and alkenylaminopropylamines having from 14 to 18 carbon atoms, whose amino substituents are mixed groups derived from tallow fatty acids, predominantly 3-octadecenyl groups, to 151 grams (0.22 equivalent) of borylated phosphate ester in benzene. The solution was heated to 30° to 60° C. for 40 minutes. The benzene was removed by distillation at its boiling point and the product recovered. The analysis was as follows:

	Percent
Boron	0.53
Phosphorus	3.53
Sulfur	3.88

A lubricating oil composition was prepared by adding 3 percent of this product to a commercial lubricating oil, a typical sample of which had the following inspection.

Properties:	
Gravity, ° API	28.1
Viscosity, SUV, sec.—	
100	450
130	208
210	61.3
Viscosity index	100
Flash, P-M, ° F	560
Pour, ° F	+5
Color, ASTM Union	3+
Carbon residue, Conradson, percent	0.06
Neutralization value, ASTM D 974, total acid No.	0.06

EXAMPLE 2

In another preparation of the O,O'-di(p-isooctylphenyl) dithiophosphoric acid compound was synthesized as follows:

A charge of 1 mole (206.3 grams) of p-isooctylphenol was added to a flask equipped with a stirrer and a reflux condenser. The phenol was heated to 115° C. and phosphorus pentasulfide (P_4S_{10}) in the amount of 55.5 grams (0.125 mole) was added slowly enough to keep the temperature in the range of 130° to 145° C. The solution was stirred vigorously for 3 hours. The crude product was filtered hot through glass wool. One-tenth of an equivalent (61.7 grams) of crude diisooctylphenyl dithiophosphoric acid in 125 milliliters of benzene and 7 grams (0.1 mole) of boric oxide were heated under reflux at the boiling point of benzene for 22.5 hours. The solution was then cooled, filtered and the solvent removed by distillation at its boiling point. The product analysis was as follows:

Sulfur	percent	5.79
Boron	do	1.22
Neutral equivalent		415

Neutral equivalent is defined as that amount of material in grams which will furnish one mole of hydrogen ion or will react with one equivalent (56.10 grams) of potassium hydroxide.

A charge of 26.6 grams (0.064 equivalent) of this product was dissolved in 50 milliliters of hexane and placed in a flask equipped with a stirrer. The amine, 25.6 grams (0.13 equivalent) of 3- "tallow" -aminopropylamine as defined above, was dissolved in 25 milliliters of hexane and added to the product of the above-described reaction with vigorous stirring. After the reaction was complete, the solution was cooled, filtered and the solvent removed under vacuum. An oil solution of the product gave an alkaline test. The product analysis was as follows:

	Percent
Sulfur	2.95
Boron	0.62

A lubricating oil composition was prepared by adding 1 percent of this product to the commercial lubricating oil of Example 1.

EXAMPLE 3

The same compound was prepared using the method of Example 2 except that the solvent used was benzene and the duration of the borylation step was 17 hours. The analysis of the compound after neutralization with amine was as follows:

	Percent
Boron	0.46
Phosphorus	3.30
Sulfur	4.01

A lubricating oil composition was prepared by adding 3 percent of this product to the commercial lubricating oil of Example 1.

EXAMPLE 4

The O,O'-di(p-isooctylphenyl) dithiophosphoric acid compound was prepared and borylated using the same molar proportions of the same reactants as in Example 2 except that the reaction was not conducted in steps. In this preparation both the acid and the amine were combined at one time and no solvent was used. The analysis of the product was as follows:

	Percent
Boron	0.48
Phosphorus	3.14
Sulfur	5.04

A lubricating oil composition was prepared by adding 3 percent of this product to the commercial oil of Example 1.

The detergent lubricating oil compositions described in the foregoing specific embodiments are illustrative only, and the invention is not limited thereto. Satisfactory results can be obtained by the substitution in the foregoing examples of other amines disclosed herein and other borylated partially esterified thiophosphates disclosed herein in the same or equivalent proportions.

The usefulness of the reaction products of the amines and borylated partially esterified thiophosphates has been demonstrated by means of a detergency bench-test procedure. This test apparatus and procedure evaluate the resistance of oil to oxidation and high temperature deterioration by splashing the test oil against a heated metal panel mounted on the test apparatus. The weight and character of the panel deposit is used in evaluating the utility of the test oil in automobile engines. The emphasis has been placed on the detergency or deposit preventing characteristics of the test oil oxidized by air during the test in addition to qualitative observations of the oxidation stability.

The apparatus consists of a reservoir mounted on legs. An oil leveling tube is welded under the bottom of the unit and an oil splasher (consisting of a series of stainless steel wires mounted on a shaft to form a cylindrical brush) is rotatably mounted in the unit. Heat to the oil reservoir is supplied by a strip heater attached to the bottom of the oil reservoir. In operation, test oil is thrown against the underside of an electrically heated test panel positioned in the center of the oil reservoir cover. In a typical test, 225 milliliters of test oil is poured into the oil reservoir and pre-heated to about 150° to 165° F. The oil level device is filled and positioned to maintain the oil at the initial oil level. The test panel is polished and tared, and the heater control thermocouple is inserted in the panel positioned on the oil reservoir cover. During

operation air is drawn through the system at a rate of about 10 liters per hour. The splasher is turned on after the test panel reaches a temperature of 500° F. At this point the oil reservoir heater is turned off and the splasher speed is adjusted to 1000 r.p.m. The test is continued for a period of 8 hours.

At the end of the test the panel is removed and allowed to drain and cool. The oil temperature is checked and the apparatus disconnected from the air system and drained. The discharge oil is observed for color, odor, sludge or other evidences of deterioration. After cooling the test panel is washed free from oil, allowed to dry and is weighed. The weight gain of the panel in milligrams is recorded. The visual rating is obtained by scoring the appearance of the deposit against the scale which encompasses varying degrees of deposit from rough black coke to very light lacquer. Experience has shown good reproducibility can be obtained both in test panel appearance and in weight changes.

The unusual effectiveness of the reaction products of the amines and the borylated partially esterified thiophosphates is demonstrated by the data presented in Table I below:

Table I

	Deposit weight in milligrams
Untreated lubricating oil	111
Lubricating oil composition of Example 1	15.5
Lubricating oil composition of Example 2	6.1

These data show that the amine salts of borylated dithiophosphates of the kind included by this invention significantly decreased the amount of sludge deposited from the oil and that these additives have effective detergent properties. Thus, the addition of only 1 percent of the composition to the lubricating oil decreased the deposits from more than 100 milligrams to about 6 milligrams. The slight increase in the weight of the deposits when 3 percent of the compound of Example 1 was employed was probably due to slight differences in the composition of the reaction product prepared by the method of Example 1.

It is also contemplated that the addition agents whose use is covered by this invention also possess bearing corrosion inhibiting properties.

The lubricating compositions of my invention can contain minor amounts of addition salts other than amine salts of bolyrated partially esterified thiophosphates. Thus, for example, it is particularly advantageous in many instances to add an anti-foam agent to the lubricating composition. Other addition agents normally added to lubricating oils for a specific purpose, such as an antioxidant, pour point depressant, corrosion inhibitor, viscosity index improver, oiliness and extreme pressure agent and the like, can be employed without adversely affecting the improved detergent characteristics of the lubricating compositions of this invention.

While my invention is described with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments may be variously practiced within the scope of the claims hereinafter made.

I claim:

1. A lubricating composition comprising a major amount of a hydrocarbon lubricating oil and a minor amount, sufficient to improve the detergent characteristics of said oil, of a reaction product of (*a*) a member selected from the group consisting of primary, secondary and tertiary alkyl, alkenyl and alkylol, mono- and diamines whose substituents each contain 6 to 22 carbon atoms, and (*b*) an anhydride prepared by reacting a partially esterified thiophosphoric acid containing 1 to 2 organic substituents per molecule, whose substituents are selected from a group consisting of alkyl, cycloalkyl, alkenyl, aryl, alkaryl, and aralkyl hydrocarbon radicals containing 6 to 22 carbon atoms each, with a borylating agent selected from the group consisting of boric acid, boric oxide, and an anhydride of boric oxide and an aliphatic monocarboxylic acid, in the ratio of about 0.5 to about 6 moles of partially esterified thiophosphoric acid per mole of borylating agent, and wherein the amine to anhydride equivalent ratio is in the range of about 1:2 to 2:1.

2. The lubricating composition of claim 1 where said minor amount is about 0.1 to 20 percent by weight of said oil.

3. The lubricating composition of claim 1 where said minor amount is about 0.5 to 10 percent by weight of said oil.

4. The lubricating composition of claim 1 where said amine is 3-"tallow"-aminopropylamine, said partially esterified thiophosphoric acid is O,O'-di(p-isooctylphenyl) dithiophosphoric acid, said borylating agent is boric oxide, and the molar ratio of partially esterified thiophosphoric acid to borylating agent is about 1:1, and the anhydride to amine equivalent ratio is about 1:2.

5. The lubricating composition of claim 1 where said amine is 3-"tallow"-aminopropylamine, said partially esterified thiophosphoric acid is O,O'-di(p-isooctylphenyl) dithiophosphoric acid, said borylating agent is boric acid, and the molar ratio of borylating agent to partially esterified dithiophosphoric acid is about 1:1, and the anhydride to amine equivalent ratio is about 1:2.

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