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3,360,464 LUBRICATING OILS CONTAINING ALKYLATED PHENOXY ACID DERIVATIVES

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This invention relates to improved lubricating oil compositions and particularly to lubricating oil compositions containing novel detergents, and to the method of making them.

It is well recognized that mineral oils used as lubricants in modern engines tend to oxidize during use. The products of such oxidation are acids which can corrode the metal parts of the engine. The oxidation, moreover, results in the formation of heavy sludge, hard lacquers and thick adhesive deposits inside the engine, especially around the pistons and other moving parts. These substances seriously interfere with the efficient performance of the engine.

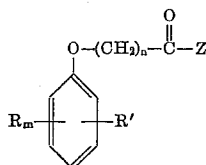
Agents are generally added to lubricants to prevent the sludge, lacquers and adhesive deposits from settling. These agents, known as detergents, keep the oxidation products suspended or dispersed in the oil thereby permitting the engine to operate freely. One group of highly effective detergents are complex metal salts. However, while such agents perform satisfactorily, these detergents may themselves deteriorate under extreme engine conditions, leaving ash-like deposits inside the engine. Some metallic detergents even contribute to the formation of acids in the lubricating oil. It would therefore be desirable to provide detergents which do not form deposits during use.

A major object of this invention is to provide novel lubricating oil compositions which possess detergent properties. A further object is to provide novel lubricating oil compositions which contain non-ash forming detergents. Another object is to provide novel non-metallic reaction products which may be added to lubricating oil for enhancing the detergent properties of the oils.

These and other objects I accomplish by adding to a major proportion of a lubricating oil a minor proportion of an ester, amide, alkanolamide, or imidazoline of a polyalkylphenoxymonocarboxylic acid compound. The acid compound is reacted with an alcohol, an amine, or an alkanolamine, to produce these novel products. The products are non-metallic, and yet they exhibit excellent detergent properties.

Broadly, the compounds of this invention are prepared from a polyalkylphenoxymonocarboxylic acid compound wherein the polyalkyl radical is a polyalkylene. The phenol precursor may be otherwise unsubstituted or it may have other ring substitution, besides the polyalkylene. This phenol, in the form of an alkali metal phenate, is reacted with a carboxylic compound to form the phenoxy acid compound or the metal salt of the phenoxy acid compound. The phenoxy acid compound, also termed ether acid compound, is reacted with the alcohol, amine, or alkanolamine to form the final product.

The exact structures of these novel detergent compounds are not known with certainty. However, it is believed the compounds have the following general formula:



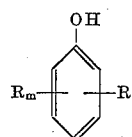
wherein R is an organic radical, such as alkyl, cycloalkyl, aralkyl, aryl and alkaryl, the alkyl radicals having from

1 to 20 carbon atoms; R' is a polyalkylene radical, including polyethylene, polypropylene, polybutylene, polyisobutylene, and polyamylene having a molecular weight of about 500 to 3,000, and preferably from about 750 to 1200; Z is alkoxy, amino, alkanolamino or heterocyclic amino having from 1 to about 20 carbon atoms; m is from 0 to 4; and n is an integer of from 1 to about 19. The products may, therefore, include esters, amides, or alkanolamides of polyalkylphenoxy monocarboxylic acids. The preferred products are those wherein m is 0, the hydrogen atoms of the polyalkylphenol nucleus being unsubstituted.

More precisely, the formation of the compounds within the scope of this invention involves the steps of (1) alkylating a phenol with a polyalkylene compound in a mol ratio of about 0.1 to about 10 moles of phenol to 1 mole of polyalkylene, but preferably using up to a 50% molar excess of phenol; (2) reacting the resulting polyalkylphenol as an alkali metal phenate, with a monocarboxylic compound having from 2 to about 20 carbon atoms and a phenol-reactive functional group to produce a phenoxy acid compound; and (3) reacting the phenoxy acid formed in step 2 with from about 0.5 to about 2.0 moles of an alcohol, an amine, or an alkanolamine per mole of the acid.

In the first step of my preferred reaction sequence, the polyalkylene compound and the phenol are mixed together with moderate heating. A catalyst suitable for such alkylation reactions, such as aluminum chloride, boron trifluoride etherate or phenolate, or the like, is added slowly into the reaction mixture, under agitation. The temperature is raised to a range of approximately from 70° to 125° C. and maintained for an extended period, the temperature increase being preferably performed gradually or in stages. When the reaction is complete, the mass is cooled slightly and the diluted mixture is washed free of unreacted materials with water. The wash water and solvent are removed by stripping, preferably under an inert atmosphere. This reaction and the products prepared thereby are described fully in copending patent application Ser. No. 418,524, filed Dec. 15, 1964.

The resulting polyalkylphenol has the formula



wherein R, R' and m have the above definition. This compound is first converted into an alkali metal phenate and then reacted with the desired carboxylic compound. The phenol is heated in the presence of an alkali metal alkoxide, such as sodium ethylate or sodium isopropylate to produce the metal phenate. Either the metal alkoxide or a mixture of alcohol and metal is first introduced into the reactor. The polyalkylphenol usually admixed with a liquid diluent, such as a process mineral oil, is then added. Excess alcohol is preferably removed from the reactor by stripping. The carboxylic compound is then added, preferably in excess of up to twice the stoichiometric requirement, and the resulting mixture is heated under reflux conditions to form the phenoxy carboxylic acid product. In certain cases the product is in the form of the metal salt. The reaction mixture should be therefore neutralized with an acid, such as hydrochloric acid, to convert the metal salt to the acid. Thereafter, the reaction mass is heated to remove water formed during the reaction; solids are filtered out of the liquid mass, still hot; and a final stripping action is performed.

In the third step, the refined polyalkylphenoxy carboxylic compound is reacted with an ester, an amine or an alkanolamine. The preferred mole ratio of reactants ranges 0.5 to 2.0 moles of the latter per mole of car-

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boxylic compound. The reaction may be catalyzed with small amounts of an acidic catalyst, such as paratoluene sulfonic acid. Heat is applied and water of reaction is taken off as distillate, preferably in an azeotropic mixture with an inert organic diluent which may be present in the reaction mass. The temperatures may range from 125° C. to 250° C. during the reaction and distillation steps. The resulting product is washed free of unreacted components with hot distilled water. Small quantities of antifoaming or demulsifying agents may be included, if desired. The remaining mixture is filtered while still hot, and thereafter the organic solvent is stripped off.

With respect to the polyalkylenes which may be used in this invention, those described in the above copending application are included. Polyalkylenes having a repeating alkyl unit of 3 to 5 carbon atoms, such as polypropylene, polybutene, and polyisobutylene may be used. The molecular weights may range from about 500 to 3,000, and preferably 750 to 1200. A preferred reactant is polypropylene, with a molecular weight of between 750 and 850. The phenol with which the polyalkylene is reacted initially may be phenol, an alkyl or cycloalkyl phenol, or a naphthol or other aromatic-substituted phenol.

The metal alkoxide may be any of the alkali metal alcoholates made from alcohols having from 1 to about 5 carbon atoms, and preferably from 2 to 3.

The carboxylate compound may have from 2 to about 20 carbon atoms. These include the lactones, such as propiolactone and butyrolactone, halocarboxylic acids, such as chloroacetic acid, and other similar carboxylic compounds having functional groups which will react with a metallic phenate to form the phenoxy acid or phenoxy acid salt. If the lactone reactant is employed, it is believed that the metal salt is produced. Therefore the product is acid-treated to convert it to the acid form. If the halocarboxylic acid is employed, the metal is displaced during the reaction as a metal halide. The carboxylate compound may be straight- or branched-chain or alicyclic.

In the third step, the alcohol, amine or alkanolamine reactant may be any aliphatic compound having from 1 to about 20 carbon atoms. My preferred reactants include the polyamines, such as diethylene triamine and tetraethylene pentamine, and the alkanolamines, such as diethanolamine and triethanolamine. In the case of the polyamine reactant, there is indication that instead of only the simple amide being formed, all or at least a portion of the product consists of an imidazoline substance. This, too, has proven to be a valuable lubricating oil detergent. Hence, the products of this invention include not only esters, amides, and alkanolamides, but also cyclicized products, such as an imidazoline product. As I have indicated heretofore, the exact structures of these specific final products are not known with certainty. It is believed, however, that the reaction of step III produces compounds having the above-disclosed general product formula.

The invention may be better illustrated by the following specific examples, although the examples are not intended as a limitation thereof.

Example I.—Alkylation of phenol

Into a four-necked flash equipped with a stirrer, condenser, addition funnel, and thermometer were added 4860 grams (6 moles) of polypropylene having a molecular weight of about 810 and 705 grams (7.5 moles) of phenol. The mixture was heated to 50° C. and 278 grams of boron trifluoride etherate were added gradually through the addition funnel. The temperature was raised to 80° C. and held for 20 hours, then to 100° C. for 4 hours.

The resulting reaction mass was quenched with 500 ml. of water to a temperature of 80° C. and diluted with 2500 ml. of toluene. The toluene solution was washed with hot water until the washings were neutral to litmus paper, and the washed solution was filtered. Residual water and some toluene were stripped off, under nitrogen,

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to 170° C. at atmospheric pressure, and the remaining toluene was removed at 175° C. and below 1 mm. Hg.

The product was analyzed for active hydrogen with the following results—Calcd, 1.10 mm. active hydrogen/gram sample. Found: 0.69 mm. active hydrogen/gram sample. Percent yield: 62.8 based on active hydrogen.

Example II.—Preparation of polypropylphenoxybutyric acid

Into a reactor similar to that used in Example I were added 1650 ml. of isopropyl alcohol and 29.1 grams (1.7 moles) of metallic sodium, and the mixture was heated to reflux until all of the sodium had dissolved. The resulting solution was cooled to room temperature and a mixture of 3450 grams of a process mineral oil and 2300 grams (1.7 moles) of the polypropylphenol was stirred in. Excess isopropyl alcohol was removed by stripping the reaction mixture under nitrogen to a temperature of 200° C.

The remaining mass was cooled to 150° C. Into this mixture were stirred 253 grams (2.94 moles) of butyrolactone and the reaction mass was heated to reflux for 5 hours at 175° C. Thereafter, the temperature was reduced to 106° C. and 230 ml. of concentrated hydrochloric acid was added. Water was distilled off at 180° C., under a nitrogen atmosphere. The remaining mass was cooled to 120° C., 250 grams of "Hyflo" (a diatomaceous earth filter-aid) were added and the mass was filtered through an electrically heated "Hyflo"-precoated Büchner funnel. The filtrate was then stripped under nitrogen, to 175° C. at 5 mm. Hg.

The acid number of the remaining product was 14.5 mgm. of KOH per gram of oil-containing product.

Example III.—Preparation of an amide with diethanolamine

A mixture of 278 grams (2.65 moles) of diethanolamine, 5117 grams (1.325 moles) of the polypropylphenoxybutyric acid product of Example II, containing about 60% of the process mineral oil, 1300 ml. of xylene, and 4 grams of paratoluene sulfonic acid was heated and stirred, under nitrogen, in a reaction flask equipped with a Dean-Stark take-off tube. During the heating, the temperature increased from 135° C. to 200° C. over a 12-hour period. The mass was then held at 225° C. for one hour.

The xylene solution, containing the reaction product, was washed with six one-liter portions of hot, distilled water; n-butyl alcohol was added to the water to break emulsion forming during the washing step. When the washings were neutral to litmus, 100 grams of "Hyflo" were added and the product was filtered as in Example II. The product was stripped under nitrogen to 175° C., at 5 to 6 mm. Hg.

The product was analyzed for nitrogen content and acid number with the following results:

Total nitrogen=0.32%.

Basic nitrogen=0.17%.

Acid number=0.25 mgm. KOH per gram of product.

Example IV.—Preparation of an amide with triethanolamine

Using procedures similar to that of Examples I to III, a polypropylphenol was prepared with an active hydrogen value of 0.70 mm. hydrogen per gram. This product was reacted with butyrolactone to form a polypropylphenoxybutyric acid in 60% of process mineral oil, with an acid number of 15 mgm. KOH per gram of oil-diluted product.

A mixture of 3200 grams (0.86 mole) of the polypropylphenoxybutyric acid, 1300 ml. of xylene, 262.4 grams (1.76 moles) of triethanolamine, and 8.5 grams of paratoluene sulfonic acid was refluxed for 3 hours at 150° C.; water was removed in a Dean-Stark take-off tube. Xylene was distilled off under nitrogen at 200° C. and atmos-

pheric pressure. The remaining reaction product was heated for 2 hours at 200° C. and for one hour at 225° C. The reaction mass was cooled to room temperature and dissolved in 2 liters of toluene. This solution was washed with 8 one-liter portions of hot, distilled water, until washings were neutral to litmus. The remaining solution was heated to 175° C. at 130 mm. Hg and then to 175° C. at 5 mm. Hg to remove the organic solvents.

The product was analyzed as in Example III.

Total nitrogen=0.31%.

Basic nitrogen=0.27%.

Acid number=0.76 mgm. KOH per gram of product.

Example V.—Preparation of a reaction product with diethylene triamine

In a reaction flask similar to that of Example III, a mixture of 3000 grams (0.697 mole) of a polypropylphenoxylbutyric acid containing 60% mineral oil (prepared in the same manner as in Example II, having an acid number of 13 mgm. KOH per gram of oil-diluted product), 139 grams (1.35 moles) of diethylene triamine, and 1200 ml. of xylene was heated to reflux for about 5 hours at 167° C. Water distillate was collected in a Dean-Stark take-off tube. An additional 2000 ml. of xylene were added and the resulting xylene solution was washed with 1500 ml. portions of hot, distilled water, until the washings were neutral to litmus. Xylene was distilled to 175° C. at 130 mm. Hg and then to 175° C. at 7 mm. Hg.

The product was analyzed, with the following results:

Total nitrogen=0.62%.

Basic nitrogen=0.30%.

Acid number=0.96 mgm. KOH per gram of product.

During the water removal in this example, the amount collected exceeded that amount expected for producing a simple amide. Infrared spectrum analysis indicated the presence of an imidazoline product.

ENGINE TESTS OF REACTION PRODUCTS

(1) *Caterpillar Engine Test.*—The ability of the reaction products, namely the esters, amides, and imidazolines of this invention, to perform as lubricating oil detergents has been shown by using oils blended with minor amounts of these products in the Caterpillar Engine Test.

The Caterpillar Engine Test measures the ability of an oil to prevent deposits on the piston. The grooves, lands, and skirts of the piston are examined for thickness, density and amount of deposits; the degree of lacquer formation is also determined. The amount and quality of deposits are reduced to numerical demerits. The total rating is the total number of demerits subtracted from 100, a rating of 100 signifying a perfectly clean piston. The lacquer demerits (Lac.) indicate the amount of lacquer formation below the top ring groove. The top groove packing (percent TGP) shows the percent of top groove volume behind the piston ring that is filled with carbon.

The test oil samples consist of a solvent-refined mineral oil, having an S.U.V. @ 210° F. of 64.1, blended with 7% by weight of the total blend of each of the products of Examples III, IV, and V, respectively and 1% of a zinc dithiophosphate antioxidant. The engines were run on a diesel fuel containing 1% sulfur. A single cylinder, 4-cycle Caterpillar engine is used under the following operating conditions:

Oil temperature, ° F.	150
Jacket temperature, ° F.	180
Speed, r.p.m.	1000
Brake load, H.P.	19.8

The duration of the test varied in each case. The results obtained are tabulated below:

Detergent	Duration, hours	Total Rating	Lac.	Percent TGP
Example III.....	120	85.7	9.9	12
Example IV.....	480	96.7	2.0	15
Example V.....	240	92.2	4.6	15

(2) *Low Temperature Deposit Test (Gasoline Engine).*—A lubricating oil blend containing 7% by weight of the total blend of Example III and 1% of a zinc dithiophosphate antioxidant was tested in a second engine. In this test the ability of the oil to prevent low-temperature deposits from forming is investigated. The one-cylinder CLR Oil Test Engine is operated on a specific fuel prepared for this test, CRC Designation RMF 215-59 containing about 0.21% sulfur. The engine is run at a low temperature for 3 hours and at a high temperature for 1 hour consecutively for a total duration of 120 hours. The following engine conditions are maintained:

	3-Hour Low Temp. Cycle	1-Hour High Temp. Cycle
Speed, r.p.m.	1,800	1,800
Fuel Flow, lb./hr.	4.7	4.7
Water Temperature, ° F.	120	200

Various parts of the engine are checked for total sludge or deposits, and particularly deposits around the piston skirt, oil rings, and oil screen. The results are rated according to the CRC Deposit Rating Scale.

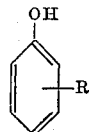
Engine Part	Rating
Piston	7.9
Sludge	47.0
Oil Ring Slot Clog	
Narrow	percent... 27
Wide	do... 2.0
Oil Screen Clog	do... 1.0

It will be seen from the data of these two engine tests that the products of this invention are effective lubricating oil detergents. From about 1% to 10%, by weight, of the total lubricating composition of the esters, amides, alkanol-amides, and imidazoline compounds may be employed. The oil compositions may also contain other addition agents such as pour point depressants, viscosity index improvers, and the like.

Although the present invention has been described herein by specific embodiments and illustrative examples, it is not intended that the scope of the present invention be limited thereby, except as indicated in the following claims.

I claim:

1. A lubricating oil composition comprising a major proportion of a lubricating oil and a minor proportion sufficient to provide detergent properties thereto of a compound prepared by (1) the reaction of an alkali metal salt of a polyalkylenephenol having the formula:



wherein R' is a polyalkylene radical selected from the group consisting of polypropylene, polybutene, and polyisobutylene having a molecular weight in the range of about 500 to 3000, with an aliphatic lactone having from 2 to about 20 carbon atoms, thereby forming a polyalkylenephenoxymonocarboxylic acid compound; and (2) the reaction of said acid compound with an alkanolamine having from 1 to about 20 carbon atoms.

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2. The composition of claim 1, wherein the aliphatic compound is selected from the group consisting of diethanolamine and triethanolamine.
3. The composition of claim 1, wherein the said polyalkylene radical is a polypropylene having a molecular weight in the range of 750 to 850.
4. The composition of claim 1, wherein the said compound is a polypropylphenoxybutyric acid-diethanolamine reaction product.
5. The composition of claim 1, wherein the said compound is a polypropylphenoxybutyric acid-triethanolamine reaction product.

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