LUBRICATING OIL DETERGENT COMPOSITION

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No Drawing. Filed Sept. 14, 1964, Ser. No. 396,417

7 Claims. (Cl. 252-46.7)

This invention relates to lubricating oil compositions, and more particularly to organophosphorus compounds useful as detergent additives for lubricating oil compositions and to a method for preparing the same. It is recognized that lubricating oils, especially the natural mineral oils, tend to decompose under the temperatures and pressures encountered in present-day internal combustion engines. Heavy sludges and lacquers may be deposited around the engine parts. Resinous materials may form, thereby thickening the lubricant considerably. The lubricity of the oil is thus greatly reduced, and the engine cannot operate efficiently. Moreover, the typical decomposition products are acidic, and corrosion of engine parts frequently occurs, resulting in loss of fuel and lubricant and in costly replacement or repair of such parts.

The presence of a detergent in the lubricating oil helps disperse decomposition products and prevent their interference with the operation of the engine. Preferably, the detergent is also chemically basic in order to neutralize the acids and to prevent corrosion. However, the detergent should not itself contribute to the formation of harmful agents. For example, although metallic detergents have been used because of their basicity, certain metallic detergents decompose to form deposits of ash, while others even help to increase acid formation in the oil.

One object of this invention is to provide novel lubricating oil compositions having a high detergent, another object is to provide a novel method for preparing non-metallic lubricating oil detergents. A further object is to furnish novel organic compounds having utility as lubricating oil detergents.

The aforementioned and other objects I accomplish by incorporating with a lubricating oil a minor amount of a reaction product prepared by the steps of reacting a phosphosulfurized polyolefin with a halogenating agent and reacting the product thereof with an amine. Preferably the products of this invention contain a significant amount of basic nitrogen.

In accordance with the present invention, a phosphosulfurized polyolefin is subjected to halogenation. The second step is the reaction between the halogenated product and an amine. During the reaction with the amine, the halogen atoms are substantially removed to form a hydroxaldehyde and the amino groups become bonded to the phosphorus. Although the mechanism of this reaction sequence is not precisely known, the structure of the final product is thought to be that of a phosphonamide or a thiposphonamide. For convenience in describing this invention, the product will hereinafter referred to simply as a phosphonamide.

In the first reaction step of this invention, a phosphosulfurized polyolefin is heated to the reaction temperature which is in the range of about 75° to 100° C., and preferably 80° to 90° C. A halogenating agent is then added, preferably over an extended period of time. Usually, the reaction mixture will commence to reflux at the beginning of this addition and will continue so until the end of the reaction. The reaction by-product is thereafter stripped off, preferably under inert atmosphere. The amounts of the two reactants in this first step are in proportion of about two moles of the halogenating agent per mole of the phosphosulfurized polyolefin.

The second step in this invention is the reaction with the amine in which the formation of the phosphonamide is believed to take place. This reaction is carried out in an inert organic solvent medium owing to the exothermic nature of the reaction. The reactants are preferably brought together in separate solvent solutions, the mixing again being performed gradually over a period of time. External cooling, such as an ice bath, may also be necessary. The initial reaction temperature is about room temperature, preferably in the range of 20° to 30° C. After all of the reactants have been introduced, the temperature is raised to reflux conditions, preferably in the range of about 100° to 200° C. for another extended period. Water-soluble substances, usually consisting of unreacted amine, are washed out of the reaction product. The organic solvent is thereafter distilled off in an inert atmosphere. An excess of the amine reactant is used, the preferred ratio being about two moles of amine per equivalent of halogen in the halogenated reactant.

The phosphosulfurized polyolefins which may be used to prepare the phosphonamides of this invention are derived from polypropylene, polybutene, and polyisobutylene, although polymers of higher olefins are also satisfactory. A typical phosphosulfurized polyolefin is a hydrolyzed phosphosulfurized polypropylene polyolefin having an acid number of 66.0; unhdrolyzed compounds may also be used. The preferred molecular weight of the polymer, prior to phosphosulfurization, is in the range of 500 to 1150 and preferably 700 to 900. The method of preparing the polyolefin is known to the art and involves, briefly, a relatively high temperature reaction ranging from about 90° to 325° C. between the polyolefin and about 7° to about 20° weight per cent of phosphorus sulfide. Suitable sulfides include phosphorus disulfide, phosphorus trioxide, and phosphorus pentasulfide.

The reaction is operated in an inert atmosphere, such as nitrogen. The product of this reaction may be hydrolzed by being treated with steam at about 150° to 160° C. for an extended period of time.

The halogenating agent to be reacted with the phosphosulfurized polyolefin may be any of the common halides. Such agents as chlorine gas, phosphorus pentachloride, phosphorus oxychloride, and thionyl chloride, are preferred as the most readily available.

Since it is theorized that the detergent is desirably basic in nature to counterbalance the acidic properties of the oil decomposition products, the amine to be reacted with the halogenated phosphosulfurized polyolefin should still retain some degree of basicity itself. Polyamines, such as diethylenetriamine and tetraethylenepentamine, pentaethylene hexamine, and diethylenimino-propylamine are preferred reactants.

The following specific examples serve to better illustrate the manner of obtaining the lubricating oil detergents of this invention without limiting the scope thereof.

Example 1—Halogenation of phosphosulfurized polypropylene

Into a reaction flask were added 1000 grams (about 1.176 moles) of hydrolzed, phosphosulfurized polypropylene and 490 grams (2.352 moles) of phosphorus pentachloride. The PCl₅ was added portionwise while the reaction mixture was held at a temperature between 80° and 90° C. After the first few additions of PCl₅ the reaction mixture began refluxing. Upon completing the addition of PCl₅ the mixture was agitated for 5 minutes at 90° C.

The reaction mass was then held under a nitrogen blanket at 200° C. and 50 mm. Hg and thereafter at 175° C. and 2 mm. Hg to remove by-products, consisting mainly of phosphorus oxychloride, and any unreacted material. The residual liquid was filtered through an electrically heated Buchner funnel that had been precoated with a "Hyflo" (a diatomaceous earth filter aid).
The liquid product was analyzed, with the following results:

- Chlorine: Present
- Phosphorus: 3.20
- Sulfur: 2.73
- Acid, No. 53 mgm. KOH/g. product.

Example II.—Preparation of phosphonamide

A solution of 51.6 grams (0.50 mole) of diethylene triamine in 100 ml of toluene was added to a reaction flask. As this solution was stirred, a second solution containing 200 grams (constituting 1 mole of chlorine per 2 moles of amine) of the chlorinated phosphosulfurized polypropylene of Example I and 300 ml of toluene was added drop-wise. The reaction temperature was maintained at about 25° C by applying an ice bath to the flask. When the reactants were completely mixed, the mixture was stirred at room temperature for an hour and thereafter refluxed for 6 hours at 114° C.

The final reaction mixture was then treated with successive washings of hot distilled water until the wash water was neutral to litmus. The toluene was removed by distillation at 150° C and 130 mm. Hg, and again at 8 mm. Hg, under a nitrogen blanket.

The product analysis was:

- Nitrogen: 2.40
- Basic Nitrogen: 1.36
- Chlorine: 0.33
- Acid No., 0 mgm. KOH/g. product.

Example III.—Engine test with phosphonamide-containing lubrication oil

A phosphonamide product was prepared substantially according to the methods of Examples I and II. It had the following analysis:

- Nitrogen: 2.50
- Basic nitrogen: 1.40
- Chlorine: 0.37

This product was added to a solvent refined mineral oil, designated as a straight grade oil having an S.U.V. @210° F. of 64.1, for the purpose of testing its detergent in the lubrication of an operating engine. The oil contained 3% by weight of the phosphonamide and 1% by weight of a typical zinc diethol phosphate antioxidant.

The engine tests on which the lubricating oil composition was evaluated were the LTD7 (L-43 engine) and the L-1 Caterpillar Test. These tests provide a means of evaluating detergent characteristics of a crankcase oil by operating an engine continuously for an extended period and then inspecting engine parts for deposits.

The LTD7 is a low temperature deposit test using the one-cylinder CLR Oil Test Engine (manufactured by Laboratory Equipment Corporation). The fuel is the gasoline specified for this test (CRC Designation RMF-216). The test engine is continuously operated for a specific period of time under cycling water jacket temperature, with the speed, air-fuel ratio, and fuel flow held constant. The engine is thoroughly cleaned and then subjected to a 3-hour low temperature cycle and a 1-hour high temperature cycle. In this example, the test lasted for 40 hours. The test oil performance is judged by visual examination of deposits. The operating conditions are as follows:

<table>
<thead>
<tr>
<th>3-Hour Low Temp. Cycle</th>
<th>1-Hour High Temp. Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed, r.p.m.</td>
<td>1,800</td>
</tr>
<tr>
<td>Post temperature, ° F</td>
<td>178</td>
</tr>
<tr>
<td>Air-fuel ratio</td>
<td>14.6</td>
</tr>
<tr>
<td>Fuel flow, lb/hr</td>
<td>4.7</td>
</tr>
<tr>
<td>Water temperature out, ° F</td>
<td>120</td>
</tr>
</tbody>
</table>

The Caterpillar test engine is a one-cylinder diesel engine (manufactured by Caterpillar Tractor Company). The fuel is a diesel fuel containing 1% sulfur. The test engine is cleaned and a two-hour break-in is conducted before the test run. During the test, the engine is operated for a specific period of time under a water jacket, with steady load conditions. Performance of the test oil is judged by visual examination of piston deposits, especially the top piston ring groove packing. The operating conditions are as follows:

- Duration, hours: 120
- Speed, r.p.m.: 1000
- Load, brake HP: 19.8
- Water temperature out, ° F: 180
- Oil temperature, ° F: 150

At the end of the test cycle, the piston, the piston grooves and rings, the oil passages, screens and sludge traps are checked for deposits.

The following data were obtained:

<table>
<thead>
<tr>
<th>Test I:</th>
<th>LTDT</th>
<th>L-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piston rating</td>
<td>7.7</td>
<td>99.1</td>
</tr>
<tr>
<td>Oil ring slot clogging percentage</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Oil screen clogging</td>
<td>do.</td>
<td>do.</td>
</tr>
<tr>
<td>Test II:</td>
<td>L-1</td>
<td>L-1</td>
</tr>
<tr>
<td>Piston rating</td>
<td>99.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Lacquer demerits</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Top groove packing percentage</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

In Test I, the type of deposits on the piston is rated, the highest rating being 10. The CRC sludge rating measures total deposits in the engine based on the thickness and area of deposits formed. The volume of clogging of the oil ring slot and the oil screen is rated in percentages, the cleanest rating being 0%. In Test II, the ring grooves and lands of the piston are inspected. The total piston rating is a standard scale of 0 to 100, a 100 rating being the cleanest. The lacquer demerit rating indicates deposits below the top ring groove; the top groove packing rating shows the volume of the groove filled with carbon, on a 0% to 100% scale. In these two ratings, the 0 rating indicates optimum conditions. The results of both of these tests indicate that the phosphonamide additives of this invention impart a high degree of detergency to lubricating oils.

The additives may be added to synthetic oils as well as mineral oils. The compositions of this invention may also contain minor amounts of other additives designed to improve the various characteristics of the predominant component, such as viscosity index improvers, antioxidants, pour-point depressants, and the like. The amount of the phosphonamide additive to be utilized may be any convenient amount, while generally the amount will be in the range of about 1% to 10% by weight, and more usually about 2% to 5%, of the total composition.

Although the invention has been described herein by means of certain specific embodiments and illustrative examples, it is not intended that it be limited in any way thereby, but only as indicated in the following claims.

What is claimed is:

1. A lubricating oil composition comprising a major proportion of a lubricating oil and a minor amount sufficient to impart detergency thereto of a reaction product obtained by initially halogenating a phosphosulfurized polyol with a halogenating agent from the group consisting of phosphorus trichloride, phosphorus oxychloride, phosphorus pentachloride and thionyl chloride and thereafter reacting, at an initial temperature of from about 20° C. to about 30° C. and then from about 100° C. to about 200° C. the resulting halogenated phosphosulfurized polyol with an amine selected from the group consisting of ethylene polyamines having up to 5 ethylene groups and diethylaminopropylamine.
2. The composition of claim 1, wherein the phosphosulfurized polyolefin is prepared from a polyolefin selected from the group consisting of polypropylene, polybutene and polyisobutylene.

3. The composition of claim 2, wherein the phosphosulfurized polyolefin is a hydrolyzed phosphosulfurized polyolefin.

4. A lubricating oil composition comprising a major proportion of a lubricating oil and a minor amount sufficient to impart detergency thereto of a reaction product obtained by chlorinating phosphosulfurized polypropylene with a chlorinating agent selected from the group consisting of phosphorus trichloride, phosphorus oxychloride, phosphorus pentachloride and thionyl chloride and then reacting at an initial temperature of from about 20° C. to about 30° C. and then from about 100° C. to about 200° C., the said chlorinated phosphosulfurized polypropylene with a polyamine selected from the group consisting of ethylene polyamines having up to 5 ethylene groups and diethylaminopropylamine.

5. A lubricating oil composition comprising a major proportion of a lubricating oil and a minor amount sufficient to impart detergency thereto of a reaction product obtained by chlorinating phosphosulfurized polypropylene with phosphorus pentachloride and by thereafter reacting at an initial temperature of from about 20° C. to about 30° C. and then from about 100° C. to about 200° C., the resulting chlorinated phosphosulfurized polypropylene with diethylene triamine.

6. The composition of claim 1 wherein the reaction mixture in the halogenation reaction and the amine reaction steps is subsequently maintained in a reflux state.

7. The composition of claim 1 wherein the said amine is selected from the group consisting of diethylene triamine, tetraethylene pentamine, pentaethylene hexamine and diethylaminopropylamine.

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