3,445,386 Patented May 20, 1969

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3,445,386 DETERGENT COMPOSITIONS Ferdinand P. Otto, Woodbury, N.J., and Andreas Logothetis, Philadelphia, Pa., assignors to Mobil Gil Corporation, a corporation of New York
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U.S. Cl. 252—32.7
11 Claims

ABSTRACT OF THE DISCLOSURE

Lubricant compositions containing polypropenylsuccinimide amides, imidazolines, and imidazolidines, wherein polypropenyl group is derived from polypropene having a molecular weight of from about 500 to about 15 3000, possess improved detergency at high temperatures. The lubricant compositions can optionally contain alkaline earth metal salts of sulfonic acids and phosphosulfurized polyolefins and zinc dialkyl dithiophosphates. The succinimide products are also useful as fuel addi- 20 tives.

FIELD OF THE INVENTION

Recent interest in the use of detergents for such or- 25 ganic fluids as lubricating oils and fuels have lead to the employment of non-metallic compounds. The advantageous feature of these non-metallic detergents is that they do not leave ashy deposits in an engine as do the metallic detergents. Such detergents include alkyl-sub- 30 stituted organic compounds, some of them polymeric in nature, one particular class containing amide or imide groups. The optimum activity of many of these detergents appears to be at low or moderate temperatures only. However, if a lubricating oil containing these additives is used at a high temperature, the results are not as satisfactory as those obtained with metal detergents, such as calcium sulfonate, sulfurized calcium phenate, or metal salts of phosphosulfurized polyolefins.

DESCRIPTION OF PRIOR ART

The non-metallic compounds described in U.S. Patents Nos. 3,172,892, 3,219,666, 3,272,746 and 3,281,428 are directed broadly to polyalkenylsuccinic-type ashless additives, but the polyalkenyl group preferred and actu- 45 ally claimed is consistently the poly-C₄ derivatives. These derivatives have a utility only in low temperature lubrication. Desirable properties of these additives at high temperatures have not been described before.

SUMMARY OF INVENTION

It has now been discovered that polypropylene derivatives of succinimide amides, imidazolines, and imidazolidines, wherein the propylene group has a molecular weight ranging from about 500 to about 3000, prefer- 55 ably about 800 to 1400, are capable of performing as a detergent in lubricants for engines in which surface temperatures may reach about 400° F. or higher.

PREFERRED EMBODIMENTS

The succinimide compounds employed in accordance with this invention include succinimide-amides, succinimide-imidazolines, and succinimide-imidazolidines. Preferred of the polypropenylsuccinimide compounds is the polypropenylsuccinimde imidazoline. This preferred class of compounds provides a truly advantageous improvement over those of other alkylsuccinimide derivatives, in high temperature lubrication applications.

The succinimide compounds of this invention are pre- 70 pared by reacting a polypropene and maleic anhydride or acid together to form the corresponding polypropenyl2

succinic compound. Reacted with this resulting intermediate is an amide, or an amine imidazoline or imidazolidine, containing at least one nitrogen atom with a hydrogen atom. Such amine derivatives are prepared by reacting an alkylenepolyamine of the structure

$$NH_2$$
— $(RNH—)_n$ — R — NH_2

wherein R is alkylene having from 1 to 5 carbon atoms and n is from 0 to 10 with a monocarboxylic acid or an aldehyde or ketone. Suitable polyamines include methylenediamine, ethylenediamine, diethylenetriamine, dipropylenetriamine, triethylenetetraamine, tetraethylenepentamine, hexaethyleneheptamine, pentaethylenehexamine, and the like.

As disclosed in U.S. Patent No. 2,568,876, issued on Sept. 25, 1951, an amine may be reacted with a monocarboxylic acid to yield either the amide or the amine imidazoline, by removing either one or two moles of water, respectively, or mixtures of these, or to yield amine salts. For example, the following reaction may occur with an ethylenepolyamine:

wherein m is from 1 to 10 and R' may be hydrogen or a hydrocarbyl radical having in the range of from 1 to about 29 carbon atoms. Aliphatic, cycloaliphatic and aromatic carboxylic acids are included. Such acids as acetic acid, propionic acid, butyric acid, oleic acid, stearic, benzoic acid, and the like may be employed; monocarboxylic acids are preferred. The imidazolidine derivative is produced by reacting the amine with an aldehyde or ketone, containing from 1 to about 30 carbon atoms. Butyraldehyde is a preferred reactant.

The amides, imidazoline or imidazolidine compound may be prepared first and then reacted with the succinic reactant, or the corresponding amine and acid (or aldehyde or ketone) may be mixed with succinic reactant to produce the desired product in situ.

The polypropenylsuccinic acid or anhydride reactant may be reacted with nitrogen reactants at ratios ranging from about 0.5 to (n+1) moles of succinic reactant per mole of the nitrogen reactant and n is the number of RNH— groups in the alkylenepolyamine. A mole ratio of at least 2:1 is preferred.

It is entirely unexpected to find that the polypropylene derivative is considerably more stable and has more effective detergency properties than that of the neighboring polymers the polybutenyl or the polyisobutenyl analogs. The polypropylenesuccinimide imidazoline and imidazolidine products of this invention have far greater stability at high temperatures than hitherto supposed. These compounds also have such superior high temperature detergent properties that they are able to perform for long periods of time in motor lubricants without permitting the formation of undue deposits of sludge or lacquer. The compounds of this invention find important use in the mineral lubricating oils and in water emulsion systems, such as oil-in-water compositions. Other base media in-65 clude synthetic ester lubricants, polyglycol ether fluids, polyacetals, silicone fluids, and the like.

These polypropenylsuccinimide compounds may be used in the oil together with numerous additives, preferably overbased alkaline earth metal sulfonates, such as those disclosed in U.S. Patents Nos. 3,158,572 and 3,133,019 or alkaline earth metal phosphosulfurized polyolefins, such as those disclosed in U.S. Patent No. 3,213,019. Salts con3

taining metal content of from 5% to about 20% by mol concentration are most desirable. Calcium and barium salts are preferred. A further salt useful as a coadditive is the zinc dialkyl dithiophosphates having from 4 to about 20 carbon atoms in the alkyl radical. Excellent oil blends can be prepared from these additives with the polypropenylsuccinimide products and derivatives.

EXAMPLE 1

To a four-neck flash equipped with a mechanical stirrer, thermometer, condenser and inlet feed tube was added 2475 grams (3 moles) of polypropene having a molecular weight of 825 and 392 grams (4 moles) of maleic anhydride. The mixture was heated at 210° to 220° C. for 8 hours as 171 grams (2.5 moles) of chlorine gas was passed through. At the end of this period the reaction mixture was stripped under 5 mm. Hg vacuum for 2½ hours to 170° C. to remove unreacted maleic anhydride. The remaining liquid was filtered in a Buchner funnel using diatomaceous earth filter aid. A dark, viscous oil was obtained having the following analysis:

Analysis.—Acid No., 54.3 mg. KOH/g.; chlorine, 0.15%.

EXAMPLE 2

Into a reaction vessel similar to that of Example 1 were added 2000 grams of the product of Example 1 and 205.4 grams of 1-triethylenetriamine, 2-methyl-2-imidazoline (prepared by reacting one mole of tetraethylenepentamine and 1.2 moles of acetic anhydride) in 735 grams of a process mineral oil. The reaction mixture was heated slowly to 150° C. under a nitrogen gas blanket. The mixture was stripped for 3 hours under 30 mm. Hg vacuum. The mixture was then cooled to 120° C. before the vacuum was released. The dark brown, clear, viscous oil had the following analysis:

Analysis.—Acid No., 7.0 mg. KOH/g.; nitrogen, 2.2%.

EXAMPLE 3

Using the same equipment as in Example 1, a mixture of 5040 grams (4.5 moles) of polypropene having a molecular weight of 1120 and 588 grams (6 moles) of maleic anhydride was heated at about 210° to 220° C. for 8 hours as 470 grams (6.7 moles) of chlorine gas is passed through. The resulting reaction mixture was treated as in Example 1. The final product had the following analysis:

Analysis.—Acid No., 44.24 mg. KOH/g.; chlorine, 0.65%.

EXAMPLE 4

Using the same equipment as in Example 1, 4000 grams of the polypropenylsuccinic anhydride of Example 3 was mixed with 334.8 grams of 1-thiethylenetriamine, 2-methyl-2-imidazoline in 1445 grams of the process mineral oil. The reaction mixture was heated and sripped according to the conditions of Example 2. The final product had the following analysis:

Analysis.—Acid No., 12.8 mg. KOH/g.; nitrogen, 1.6%.

The compositions of this invention were tested in a lubricating oil blend consisting of a straight-grade solvent refined lubricating oil containing 1% by weight of an overbased calcium sulfonate (11.7% calcium), 2.5% by weight of a barium salt of a phosphosulfurized polypropylene (12% barium), and 0.75% by weight of a commercial zinc dialkyl dithiophosphate. To this blend was added 1.34% by weight of the detergent additive. The base stock is a blend of mineral oil having a 64.1 S.U.V. at 210° F.

The compositions of this invention represented by the product of Example 2 are compared in a high temperature engine test with a polybutenylsuccinimide imidazoline prepared in a manner similar to the above examples from polybutene having a molecular weight of about 800.

EVALUATION OF PRODUCT

The evaluation in the 1-H Caterpillar Engine Test is 75

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directed to the high temperature performance of the lubricant by rating the quantity of sludge, lacquer deposits and ring deposits in a single-cylinder Diesel engine. The engine is operated under a steady load and storage periodically for oil changes for 480 hours. The fuel consists of 70% of a coastal gas oil, 20% of a Kuwait 650° F. gas oil, and 10% kerosene. The engine conditions are as follows:

Speed, r.p.m.	1800 ± 10
Intake air temp., ° F.	170±5
Coolant out temp., ° F.	160 ± 5
Oil pressure, p.s.i.	30 ± 1
Top ring groove temp., ° F.	500-650

At the end of the test the engine is dismantled and the selected parts of the engine are inspected. The following results wereobtained:

Active ingredient	Hours	Piston rating	Lacquer demerits
Polybutene derivative	240 *480	95. 2	3. 2
Polypropene derivative (Example 2)	000	98. 8 97. 3	0. 2 0. 7

*Discontinued because of fail rating after 240 hrs.

From these results, it may be seen that the lacquer demerits using the polybutene analog is too high to be of acceptable use. Thus, under the high temperatures encountered in the engine this lubricant would be considered to have a fail rating under MIL-L-2104B specifications after only 240 hours of operation. On the other hand, the polypropene analog after 480 hours had considerably less lacquer demerits and the overall piston rating remained at a high level. The oil composition of this test represents a highly satisfactory formulation.

The polypropenylsuccinimide imidazoline reaction products, as described in the above examples, represent the most effective and therefore the most preferred products of this invention. The predominant component of the reaction products is a polypropenylsuccinimide imidazoline which contains an additional polypropenylsuccinyl radical attached to an inner nitrogen atom. As indicated previously, the mole ratio of the polypropenylsuccinic acid or anhydride to nitrogen reactant may range from about 0.5 to (n+1), while the preferred mole ratio is at least 2:1. The terminal nitrogen atom containing two hydrogen atoms, enters into the imide formation, and a second inner nitrogen atom forms a polypropenylsuccinyl monoamido group. For such preferred products of the 2:1 reaction, the alkylenepolyamine amide, imidazoline or imidazolidine must contain at least one nitrogen atom having two hydrogen atoms and a second nitrogen atom containing one hydrogen atom. The structure for the product of the examples, is believed to have the following structure:

wherein R" is the polypropenyl radical.

The invention is not considered limited in any respect by the aforementioned examples or illustrations except as limited by the following claims.

We claim:

1. An organic composition comprising a major amount of an organic fluid, selected from the group consisting of a lubricating oil and a normally liquid hydrocarbon fuel, and a minor amount sufficient to impart detergency thereto of an imide reaction product of:

 from 2 to (n+1) moles of a polypropenylsuccinic compound selected from the group consisting of polypropenylsuccinic acid and polypropenylsuccinic

acid anhydride, wherein the polypropenyl group is derived from a polypropene having a molecular weight of from about 500 to 3000, and

(2) one mole of an alkylene polyamine reactant selected from the group consisting of a monoamide, an amine imidazoline, and an amine imidazolidine having the structure

$$NH_2-(RNH-)_n-R-X$$

wherein R is alkylene having 1 to 5 carbon atoms, n is an integer of from 0 to 9, and X is selected from the group consisting of

and

wherein R' is selected from the group consisting of hydrogen and hydrocarbyl having from 1 to 29 carbon

- 2. The composition of claim 1 wherein R is ethylene. 3. The composition of claim 1 wherein there is also
- present an alkaline earth metal compound selected from the group consisting of an alkaline earth metal sulfonate and a salt of phosphosulfurized polyolefins, said com- 35 pound containing from 5 mole percent to 20 mole percent of metal.
- 4. The composition of claim 1 wherein there is also present a zinc dialkyl dithiophosphate having from 4 to about 20 carbon atoms in the alkyl group.
- 5. The composition of claim 1 wherein the alkylene polyamine reactant is prepared by reacting an alkylene polyamine and a monocarboxylic acid compound selected from the group consisting of monocarboxylic acid and a monocarboxylic acid anhydride and removing from the 45 reaction mixture from one to two moles of water of
- 6. The composition of claim 5 wherein two moles of the polypropenylsuccinic compound is reacted with one mole of the alkylene polyamine reactant, one carboxy 50 group of one mole of the polypropenylsuccinic compound becoming attached to an inner nitrogen atom of the said alkylene polyamine reactant to provide a polypropenylsuccinyl monoamido group, and the carboxy groups of the other mole of polypropenylsuccinic compound form. 55 44—63, 71; 252—33.4, 51.5; 260—309.6, 309.7, 326.3

ing an imide with a terminal nitrogen atom of the alkylene polyamine reactant.

7. The composition of claim 6 wherein the alkylene polyamine reactant is the reaction product of an ethylene polyamine and a monocarboxylic acid compound, in which a major component of the reaction product has the

$$\begin{array}{c} CH_2-CH_2\\ NH_2-(CH_2-CH_2-NH)_{m-1}-CH_2CH_2-N\\ \\ C\\ R' \end{array}$$

wherein R' is selected from the group consisting of 15 hydrogen and hydrocarbyl having from 1 to about 29 carbon atoms and m is an integer sufficient to provide at least one inner nitrogen atom and having a maximum of 10.

8. The composition of claim 7 wherein the alkylene 20 polyamine reactant is prepared by reactant tetraethylene pentamine with acetic anhydride.

9. The composition of claim 8 wherein the alkylene polyamine reactant is 1-triethylenetriamine, 2-methyl-2imidazoline.

10. The composition of claim 9 wherein one component of the reaction product has the structure

wherein R" is a propenyl radical having a molecular weight of from 500 to about 3000.

11. The composition of claim 1 wherein the polypropene has a molecular weight of from about 800 to about ⁴⁰ 1400.

References Cited

UNITED STATES PATENTS

2,568,876 9/1951 White et al. 3,185,704 5/1965 Kahn et al. 3,216,936 11/1965 Le Suer. 3,220,949 11/1965 Bell et al. 3,272,743 9/1966 Norman et al. 3,272,746 9/1966 Le Suer et al. 3,280,034 10/1966

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UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,445,386

May 20, 1969

Ferdinand P. Otto et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 51, "1-thiethylenetriamine" should read -- 1-triethylenetriamine --. Column 4, formula, that portion reading

Column 6, line 20, "reactant", second occurrence, should read -- reacting --; lines 28 to 36, the right-hand portion of the formula should appear as shown below:

Signed and sealed this 24th day of March 1970.

(SEAL) Attest:

EDWARD M.FLETCHER, JR. Attesting Officer

WILLIAM E. SCHUYLER, JR. Commissioner of Patents