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POLYISOBUTYLENE NITROGEN OXIDE REACTION PRODUCTS AS LUBRICATING OIL DETERGENTS

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ABSTRACT OF THE DISCLOSURE

Lubricating oil detergents are prepared by reacting an oil soluble branched long-chain aliphatic hydrocarbon olefin with nitrogen oxides, optionally treating the product with nitric acid or an amine, and then using the complex reaction product as the detergent.

BACKGROUND OF THE INVENTION

Field of the invention

Ashless lubricating oil detergents have become relatively commonplace in today's lubricating oils. By ashless is intended the absence of any metal ion. For the most part, the ashless lubricating oil detergents have had a relatively long aliphatic hydrocarbon chain bonded to a polyamine, either directly or through a carboxyl functionally, e.g., succinyl. The ashless detergents have found much favor because they avoid the possibility of metal deposition in the engine and provide good dispersion of deposit-forming materials. Continuing efforts have been made to improve on the dispersive and detergent qualities of the ashless detergents and on finding more economic ways to prepare the detergents.

Description of the prior art

The reaction of olefins with various nitrogen oxides and nitric acid have been repeatedly reported in both the patent and scientific literature. See, for example, U.S. Pat. Nos. 2,478,243, and 2,811,560. Also see articles by Bachmann J. Org. Chem. 21 465–7 (1956), Levy et al., J. Chem. Soc. 1946 1093–1104; J. Chem. Soc. 1948 52–60, and Brown, J. Am. Chem. Soc. 79 2480–8 (1957). These references have, for the most part, been concerned with the reaction of the nitrogen oxides with relatively low molecular weight olefins.

More recently, U.S. Pat. No. 3,328,463 describes the reaction of nitrogen tetroxide with a relatively high molecular weight olefin to obtain a product which is then treated with hydroxylic base followed by further treatment with an amine and boric acid to obtain a lubricating oil additive.

SUMMARY OF THE INVENTION

Lubricating oil compositions are provided having an effective amount as a detergent of the reaction product of an oil soluble aliphatic hydrocarbon olefin and nitric acid or a nitrogen oxide. Optionally, the reaction product may be treated with an amine in a non-aqueous system and the resulting product isolated and unincorporated amine removed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The lubricating oil compositions of this invention contain as a detergent additive the reaction product of nitric acid or a nitrogen oxide and an oil soluble aliphatic hydrocarbon olefin. The product will generally be of at least 400 and not more than 3,000, generally, of from about 600 to 2,800 average molecular weight. The product will

have from about 0.5 to 3 weight percent nitrogen, more usually of from about 0.6 to 2.5 weight percent nitrogen.

The product will be substantially free of aromatic and aliphatic unsaturation, generally, having not more than about one site of olefinic unsaturation. The product will be a mixture of compound having various functionalities, the nitro group being the predominant functionality present. Other groups which may be present are hydroxyl, nitroso, nitrate, nitrite and oxocarbonyl, e.g. ketonic. The various amounts of these functionalities and their relative proportions are unknown.

The hydrocarbon portion of the molecule will generally be a long branched-chain aliphatic hydrocarbon group having at least 25 carbon atoms and usually not exceeding about 220 carbon atoms, more usually 50 to 200 carbon atoms.

The reaction product is prepared by contacting nitric acid or a nitrogen oxide with an aliphatic hydrocarbon olefin at mild temperatures for a time sufficient to incorporate at least ⅓ of the theoretical nitrogen, assuming that there should be 2 nitrogen atoms introduced per hydrocarbon olefin. The hydrocarbon olefin will generally be of from about 25 to 220 carbon atoms, more usually of from about 50 to about 200 carbon atoms. The olefin is conveniently prepared by the polymerization of low molecular weight olefins of from about 2 to 6 carbon atoms, preferably, of from about 3 to 4 carbon atoms, e.g., propylene and isobutylene. The polyolefins should be oil soluble.

Illustrative polyoelnfins include polypropylene, polyisobutylene, copolymers of ethylene and isobutylene (cationic catalyzed polymer of 4-methyl-1-pentene), etc.

The nitrogen oxide which is employed may be nitric oxide (NO), nitrogen trioxide (N_2O_3), or dinitrogen tetraoxide (N_2O_4). The nitric acid will be 70 or higher weight percent, fuming nitric acid or nitric acid-sulfuric acid combinations.

The reaction between the olefin and nitric acid or nitrogen oxide is ordinarily carried out at temperatures from about —10° to 50° C., more usually of from about 10° to 45° C. Usually, the reaction will be carried out at ambient temperatures; during the course of the reaction, the temperature may rise, ordinarily not to exceed about 50° C.

Atmospheric or super-atmospheric pressures may be used, preferably, atmospheric pressure for convenience. To enhance the concentration of the nitric acid or nitrogen oxide in the olefin or olefin solution, mild super-atmospheric pressures may be used, ordinarily not exceeding 2 atmospheres.

The time for the reaction will vary widely depending on the reactants, the temperature, and the degree of conversion desired. The reaction is carried out until at least ⅓ of the stoichiometric nitrogen has been introduced into the olefin. By stoichiometric nitrogen is intended that there be 2 nitrogen atoms per hydrocarbon molecule. The nitrogen percent will vary with the molecular weight of the hydrocarbon olefin employed. The reaction time may vary from 0.5 hr. to 80 hrs., more usually of from about 1 hr. to 60 hrs.

When using gaseous nitrogen oxides, the reaction can usually be followed by color changes. It is found that when adding the gaseous nitrogen oxides, the reaction mixture will become quite colored. When no further color change occurs, this is taken as an indication that no further nitrogen oxide is being reacted. With the gaseous nitrogen oxides, the reaction is relatively slow, usually requiring at least about 10 hrs. and generally not exceeding 80 hrs., more usually in the range of about 15 to 60 hrs.

In contrast to the nitrogen oxides, the reaction with ni-

tric acid is relatively rapid, usually requiring from about 0.5 hr. to 6 hrs., more usually from about 1 to 3 hrs.

The nitrogen content of the product will generally vary from about 0.5 to 3 weight per cent, more usually of from about 0.8 to 2.8 weight per cent.

Usually, an inert hydrocarbon solvent will be employed, particularly with the nitrogen oxide reactants. Either unreactive aliphatic or aromatic hydrocarbons may be used, usually of from about 6 to 12 carbon atoms. Illustrative solvents are heptane, benzene, tert.-butyl benzene, decane, etc. The concentration of the olefin in the solvent may range from about 5 to 80 weight percent, more usually of from about 10 to 60 weight percent.

In isolating the reaction product, all volatile materials are stripped and the residue isolated. The residue may then be added directly to a lubricating oil or, as indicated previously, modified by treatment with an amine.

The amine treatment will generally employ from about 0.9 to 10 moles of amine per mole of reaction product, more usually from about 1 to 5 moles per mole of reaction product. The treatment is carried out at elevated temperatures and, generally, for from about 0.5 to 24 hrs., more usually for from about 1 to 6 hrs. An inert solvent may be used, conveniently a hydrocarbon solvent. The same hydrocarbon solvents which were described above may also be employed for this reaction. Similar concentrations of the reaction product may be used as employed for the olefin in the nitrogen oxide-olefin reaction.

Any amine may be used, either primary, secondary or tertiary as well as ammonia. Both mono- and polyamines may be used, the polyamines being preferred. The amines will ordinarily be of from about 1 to 20 carbon atoms, more usually of from about 3 to 16 carbon atoms. There may be from 1 to 6 amine nitrogen groups. The amines may be aliphatic, aromatic, alicyclic or heterocyclic.

Illustrative amines include pyridine, triethylamine, tripropylamine, morpholine, aniline, ethylene diamine, hexamethylene diamine, diethylene triamine, tetraethylene pentamine, ammonia, etc.

The alkylene polyamines will generally have alkylene groups of from 2 to 3 carbon atoms and have from 2 to 6 nitrogen atoms.

When the reaction is complete, the unreacted amine is readily removed by any convenient procedure. A simple procedure requires diluting the reaction mixture with an aliphatic hydrocarbon, if an aliphatic hydrocarbon has not been initially used or is present in insufficient amount, and extracting the mixture with a polar solvent, such as ethanol. The polar and nonpolar phases are readily separated by the addition of a small amount of water. The nonpolar phase may then be isolated, dried and the volatile materials removed. The resulting product is then ready for use.

The lubricating compositions of this invention may employ any hydrocarbon lubricating oil of lubricating viscosity. The lubricating oils may be derived from natural or synthetic sources. Lubricating oils generally have viscosities of from about 35 to 50,000 Saybolt Universal seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin base, naphthenic base, asphaltic base and mixed base oils.

Illustrative synthetic oils are hydrocarbon oils obtained by the polymerization of various olefins, generally of from 2 to 8 carbon atoms and alkylated aromatic hydrocarbons.

The nitric acid or nitrogen oxide-olefin reaction product will generally be present in the oil for use in an engine in at least 1 weight percent and, generally up to an amount not exceeding 20 weight percent, more usually of from about 3 to 15 weight percent. As concentrates, the reaction product may be present in up to 80 weight percent, usually from 10 to 70 weight percent.

The reaction products may be used by themselves or, preferably, in combination with polyisobutenyl succinimides of alkylene polyamines. The polyisobutenyl succinimides may be either the mono- or bis-succinimide. The polyisobutenyl group will be of from about 50 to 150 carbon atoms and the alkylene polyamine will have alkylene groups of from 2 to 3 carbon atoms and from 4 to 5 amine nitrogen atoms.

When the olefin-nitrogen oxide reaction product is used in combination with the succinimide, the total weight percent of the two will be in the range indicated above. That is, the olefin-nitrogen oxide product and succinimide will each be present in from 0.5 to 15 weight percent for a total weight percent of from 1 to 20.

Other additives may also be included in the oils, such as pour point depressants, oiliness agents, antioxidants, rust inhibitors, extreme pressure agents, corrosion inhibitors, etc. These additives will range in total amount of from about 0.1 to 10 weight percent, more usually of from about 0.5 to 5 weight percent. The individual additives may vary from about 0.01 to 5 weight percent.

A preferred aspect is to employ in the lubricating oil from about 1 to 50 mm./kg. of a dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are of from about 4 to 36 carbon atoms. Usually, the hydrocarbyl groups will be alkyl or alkaryl groups. The remaining valence of the phosphorodithioate will be satisfied by zinc, by polyalkyleneoxy (alkylene of from 2 to 3 carbon atoms) or a third hydrocarbyl group. The carbon containing groups will be of from 2 to 30 carbon atoms. (Hydrocarbyl is an organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic or aromatic or combinations thereof.)

The hydrocarbyl groups will generally be free of aliphatic unsaturation.

EXAMPLES

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE I

Into a reaction vessel was introduced 2,000 g. of polyisobutenylene (approximately 1,000 av. mol. wt.) as a 70 weight percent solution in benzene. Nitrogen oxide was bubbled through the mixture with stirring for 40 hrs. During this time, the reaction turned yellow, then greenish blue. The final product was a reddish color. The benzene was then stripped in vacuo, the temperature being raised to 80° C. The residue weighed 1,861 g. Analysis: N, 1.45%; 1.48%.

EXAMPLE II

Into a reaction vessel was introduced 200 g. of the reaction product of Example I and 28 g. of alkylene polyamine having the average composition of triethylene tetramine and the mixture heated to 50° C. and maintained at that temperature for about 15 min. At this time, half of the mixture was removed and the residue heated at 170° C. for 3 hrs. Each of the materials was extracted by diluting the mixture with an equal volume of hexane, extracting with an equal volume of 95 percent ethanol and adding a small amount of water to induce separation of the phases. The nonpolar phase was isolated, dried and stripped of all volatile materials. The product heated at 50° C. was analyzed: N, 1.31%; 1.27%. The product heated at 170° C. was analyzed: N, 1.21%; 1.26%.

EXAMPLE III

Into a reaction flask was introduced 200 g. of the product prepared in Example I and 28 g. of ethylene diamine. The product was heated at 50° C. and maintained at that temperature for about 15 min., an aliquot removed and the residue heated at 110° C. for 3 hrs. The workup of the 2 products was carried out as described in Example II. Analysis of the product heated at 50° C.: N, 1.45%; 1.38%.

When the above preparation was repeated using twice the amount of materials but being carried out in the same

way, the final product (heated at 110° C.) analyzed as follows. N, 1.20%; 1.20%.

EXAMPLE IV

Into a reaction vessel was introduced 601.4 g. of the product prepared in Example I, 84.2 g. of ethylene diamine and 136 g. of benzene. The mixture was refluxed for ½ hr. and then worked up as described in Example II. Analysis: N, 1.28%; 1.29.

EXAMPLE V

Into a reaction vessel was introduced 2,000 g. of polyisobutylene (molecular weight approximately 900; viscosity at 210° F., 1,245 SUS; supplied by Chevron Chemical Co. as OPB–24) and 1,000 g. of benzene and nitrogen oxide bubbled through the mixture with stirring fo 12 hrs. at a rapid rate. After 1 hr. the reaction had turned blue, but by 8 hrs. had turned green. While the initial temperature was room temperature, the reaction temperature during the course of the reaction rose to 45° C. At the end of 12 hrs., the benzene was stripped and the residue isolated and analyzed: N, 1.27%; 1.28%.

Approximately 100 ml. of the above product was heated at 250° C. for 1.5 hrs. Analysis: N, 0.82%. The product was then extracted as described in Example II.

EXAMPLE VI

Into a reaction vessel was introduced 700 g. of polyisobutylene (same as Example V) and 700 g. of benzene. The mixture was stirred and nitrogen trioxide introduced slowly. The nitrogen trioxide was introduced on and off for a period of about 90 hrs., a total of 114 g. having been introduced. The benzene was stripped and the product isolated. Analysis: N, 2.49%; 2.50%.

EXAMPLE VII

Into a reaction flask was introduced 2,000 g. of polyisobutylene (same as Example V) and 1,000 g. of benzene and nitric oxide bubbled through the mixture for 15 hrs. At the end of this time, the nitrogen oxide addition was stopped, the benzene stripped and the product isolated. Analysis: N, 1.39%; 1.34%.

EXAMPLE VIII

Into a reaction flask was introduced 190 g. of the product of Example VII and 20 g. of pyridine, and the mixture heated at 50° C. for ½ hr. followed by raising the temperature to 150° C. and maintaining that temperature for 1 hr. At the end of this time, the reaction mixture was then extracted twice by the method described in Example II. The product was isolated and analyzed: N, 1.01%; .99%.

The procedure described above was repeated except that 25 g. of triethylamine were used in place of the pyridine. The final product was analyzed: N, 1.0%; 1.0%.

EXAMPLE IX

Into a reaction flask was introduced 1,000 g. of a 78 weight percent solution in benzene of the product of Example VII and 105 g. of pyridine and the product heated at 50° C. for ½ hr. and then at 150° C. for 1 hr. The reaction mixture was then extracted twice as described in Example II and all volatiles stripped in vacuo at a temperature of 80° C. Analysis: N, 1.03%; 1.07%.

EXAMPLE X

Into a reaction vessel was introduced 1,000 g. of polyisobutylene (approximately 3,060 average molecular weight, supplied by Chevron Chemical Co. as OPB–128) and 500 g. of benzene. Nitric oxide was bubbled through the reaction mixture for 19 hrs. At the end of this time, all volatile materials were stripped in vacuo at 80° C. Analysis: N, 0.92%; 0.92%.

EXAMPLE XI

Into a reaction flask equipped with a fritted glass inlet and a cold-finger type condenser (CO_2/acetone) was charged 150 cc. of dry ether which was cooled at −15° C. To the mixture was added 10 g. of dinitrogen tetroxide, by sweeping it in with an oxygen stream through a drying tower charged with phosphorus pentoxide on helices. When the reaction mixture had warmed to 0° C. and while maintaining an oxygen stream, 100 g. (0.10 moles) of polyisobutylene in 100 ml. of ether was added. The temperature was maintained between 0 to 5° C. At the end of the addition, the mixture was stirred for 30 minutes at 5° C.

To the reaction mixture was then added dropwise 30.3 g. (0.33 mole) of triethylamine and the mixture allowed to stand while cooled in a dry ice/acetone bath overnight. The next morning 18 g. of acetic acid and 50 cc. of water were added to neutralize the excess amine. The mixture was transferred to a separatory funnel and the aqueous layer removed; the organic layer was washed with bicarbonate of soda solution and then dried over magnesium sulfate.

EXAMPLE XII

Into a reaction flask was charged 200 ml. dry ether and the ether cooled to −15° C. In an oxygen containing atmosphere, 85.7 g. of N_2O_4 (2.2 equiv. wt. NO_2) was distilled into the ether. When the solution had warmed to −5° C., 800 g. of polyisobutylene (approximately 800 average molecular weight) in 240 ml. ether was added dropwise. After stirring the mixture for one hour at 0° C. the temperature was allowed to rise to room temperature. The product was then purified by reprecipitation from pentane solution with methanol. Volatile materials were then removed in vacuo. Analysis: C, 80.21%; H, 12.92%; N, 2.43%.

In order to demonstrate the effectiveness of the compositions of this invention as lubricating oil detergents, exemplary compounds were tested in the 1–G Caterpillar Test (MIL–L–45199A conditions). The oil used was a Mid-Continent SAE–30 oil and 12 mm./kg. of zinc di(alkylphenyl)phosphorodithioate (the alkyl groups were polypropylene of from about 12 to 15 carbon atoms) was included. The test was carried out for 60 hrs. The following table indicates the results:

TABLE I

	Wt. percent	Grooves	Lands	Underhead
Example:				
I	5.65	68–1–0–0	210–40–40	7.1
IV	5.65	19–1–0–0	40–5–5	6.3
V	6.0	51–6–0–0	65–5–30	4.7
IX	5.9	42–10–0–0	225–10–15	5.0
XII	5.15	55–12–0–0	190–35–15	7.5

NOTE.—Data in the column headed "Grooves" indicate the percentage of each groove on the piston of the Caterpillar engine which is filled with deposits. Ratings are on a basis of 0 (clean) to 100 (completely filled). Data which are in the column headed "Lands" indicate the degree of piston land discoloration. These are on a rating of 0 (completely clean) to 800 (completely black). Intermediate values are based on the amount and darkness of the land discoloration. Data in the column headed "Underhead" are demerit ratings related to the degree of darkening of the underhead. A rating of 0 indicates a completely black underhead, while a rating of 10 indicates a completely clean underhead.

It is evident from the above results that quite surprisingly these simple compositions, which, for the most part, are free of basic nitrogen, are extremely effective as ashless detergents in lubricating oils under the severe conditions of the Caterpillar 1–G Test. Furthermore, the simple and economic way in which they can be prepared permits their combination with the alkenyl succinimide detergents to provide a combination having the best properties for the least cost.

Also, the compositions of this invention are soluble in lubricating oils and compatible with other additives commonly added to lubricating oils, as exemplified by the zinc phosphorodithioate.

Finally, the compositions of this invention can be used as emulsifiers to propare water-in-oil emulsions. The emul-

sifiers can be used to prepare soluble oils, as dipersants for pesticides, etc.

What is claimed is:

1. A lubricating oil composition having an oil of lubricating viscosity and from 1 to 80 weight percent of the total composition of the detergent reaction product of an oil-soluble olefin of from 25 to 220 carbon atoms and a nitrogen oxide selected from the group consisting of nitric oxide, nitrogen trioxide, and dinitrogen tetroxide, wherein said olefin and said nitrogen oxide are contacted at a temperature in the range of −10° to 50° C. and for a time sufficient to introduce at least ⅓ of the theoretical nitrogen, but not more than the theoretical amount of 2 nitrogen atoms per olefin.

2. A lubricating oil composition according to claim 1, wherein the said olefin is polyisobutylene and said nitrogen oxide is nitric oxide.

3. A lubricating oil composition according to claim 1, wherein the reaction product of olefin and nitric oxide is treated with from 0.9 to 10 moles of amine per mole of reaction product, followed by removal of unreacted amine.

4. A lubricating oil composition according to claim 3, wherein the nitrogen content of the reaction product is in the range of 0.5 to 3 weight percent.

5. A lubricating oil composition according to claim 1, wherein the nitrogen content of the reaction product is in the range of 0.5 to 3 weight percent.

6. A lubricating oil composition according to claim 1, wherein said nitrogen oxide is dinitrogen tetroxide.

7. A lubricating oil composition according to claim 6, wherein said olefin is polyisobutylene.

8. A lubricating oil composition according to claim 6, wherein the reaction product of olefin and dinitrogen tetroxide is treated with from 0.9 to 10 moles of amine per mole of reaction product, followed by removal of unreacted amine.

9. A lubricating oil composition having a total content of from 1 to 20 weight percent of the combination of the reaction product according to claim 1 and polyisobutenyl succinimide of an alkylene polyamine, wherein said polyisobutenyl group has from 50 to 150 carbon atoms and the alkylene polyamine has alkylene groups of from 2 to 3 carbon atoms and from 4 to 5 amine nitrogen atoms.

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