United States Patent [19]

Miller et al.

[11] **3,927,104**

[45] **Dec. 16, 1975**

[54] POLYBUTENYL-ALKYLENE POLYAMINE-POLYALKANOL LUBRICANT ADDITIVE

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[22] Filed: **Dec. 18, 1974**

[21] Appl. No.: **533,910**

Related U.S. Application Data

[60] Division of Ser. No. 408,226, Oct. 19, 1973, which is a continuation-in-part of Ser. No. 155,286, June 21, 1971, abandoned.

[52] **U.S. Cl.** .... **260/584 B;** 260/584 C

[51] **Int. Cl.**[2] **C07C 87/20**

[58] **Field of Search** .... 260/583 P, 584 B, 584 C

[56] **References Cited**

UNITED STATES PATENTS

2,952,707	9/1960	Nikawitz	260/584 B
3,165,477	1/1965	Crowe et al.	260/584 B X
3,197,510	7/1965	Cyba	260/584 R

Primary Examiner—Allen B. Curtis
Attorney, Agent, or Firm—T. H. Whaley; C. G. Ries; J. J. O'Loughlin

[57] **ABSTRACT**

Polybutenyl-alkylene polyamine-polyalkanol ashless dispersant lubricant additive represented by the general formula:

$$R{-}\underset{}{\overset{X}{\overset{|}{N}}}{-}(R'{-}\overset{Y}{\overset{|}{N}})_x{-}(R''{-}O)_yH$$

in which R is a polybutenyl radical having a molecular weight from 900 to 10,000 and a mineral lubricating oil composition containing said polybutenyl-alkylene polyamine polyalkanol.

8 Claims, No Drawings

POLYBUTENYL-ALKYLENE POLYAMINE-POLYALKANOL LUBRICANT ADDITIVE

CROSS REFERENCE TO RELATED APPLICATIONS

This is a divisional application of application Ser. No. 408,226 filed on Oct. 19, 1973 which in turn is a continuation-in-part of application Ser. No. 155,286, filed on June 21, 1971, now abandoned.

BACKGROUND OF THE INVENTION

Straight mineral lubricating oils cannot meet the lubricating needs of modern internal combustion engines and it is customary to incorporate additives in the base oil giving a formulated lubricating composition having enhanced dispersant, detergent, corrosion inhibiting and antiwear properties. The problem of providing a satisfactory motor oil is compounded because these lubricants are subjected to a wide range of operating conditions. In particular, it is rather difficult to formulate a motor oil composition which will be effective under both continuous, high temperature, high speed operating conditions as well as under low-temperature stop and go driving conditions. This problem is further aggravated when the motor oil is intended for service in different type engines, i.e. diesel and gasoline engines, both of which put very severe but different stresses on the motor oil composition.

PRIOR ART

Motor oil compositions for internal combustion engines containing polyolefin-substituted polyamines have been disclosed in U.S. Pat. No. 3,275,554.

A copending patent application Ser. No. 208,978 filed Dec. 16, 1971 discloses a lubricating oil composition containing a polyisobutenyl-substituted N-aminoethylethanolamine as an ashless dispersant.

SUMMARY OF THE INVENTION

An oil-soluble ashless dispersant for a mineral lubricating oil composition comprising a polybutenyl-alkylene polyamine-polyalkanol is provided as well as a mineral lubricating oil composition containing same. The polybutenyl-alkylene polyamine-polyalkanol is represented by the general formula:

$$\mathrm{R{-}\overset{\overset{X}{|}}{N}{-}(R'{-}\overset{\overset{Y}{|}}{N})_x{-}(R''{-}O)_y{-}H}$$

in which R is a polybutenyl radical having a molecular weight from 900 to 10,000, X and Y represent H or $(R''{-}O)_yH$ at least one of X or Y being $(R''{-}O)_yH$, R' is a divalent hydrocarbyl radical having from 2 to 8 carbon atoms, R'' is a divalent hydrocarbyl radical having from 2 to 4 carbon atoms, x has a value from 1 to 6 and y has a value from 1 to 5. Alternatively, the polyisobutenyl radical "R" will consist of from about 70 to 700 carbon atoms.

A formulated mineral lubricating oil composition will generally contain the dispersant in a concentration ranging from about 0.1 to 10 weight percent with the preferred concentration being from about 0.2 to 5 percent.

The polybutenyl-alkylene polyamine-polyalkanol dispersant compound of the invention is broadly represented by the general formula:

$$\mathrm{R{-}\overset{\overset{X}{|}}{N}{-}(R'{-}\overset{\overset{Y}{|}}{N})_x{-}(R''{-}O)_y{-}H}$$

in which R is a polybutenyl radical having a molecular weight from 900 to 10,000, X and Y represent H or $(R''{-}O)_yH$ at least one of X or Y being $(R''{-}O)_yH$, R' is a divalent hydrocarbyl radical having from 2 to 4 carbon atoms, x has a value from 1 to 6 and y has a value from 1 to 5.

A preferred class of compounds are those in which R is a polybutenyl radical having a molecular weight from 1,000 to 5,000, with a more preferred class being those in which R is a polybutenyl radical of 1,200 to 2,500 moleweight.

The symbols X and Y represent hydrogen or the radical $(R''{-}O)_yH$ with at least one of X or Y being $(R''{-}O)_yH$. The dispersants of this invention thus can be represented by the formulas:

$$\mathrm{R{-}\overset{\overset{H}{|}}{N}{-}(R'{-}\overset{\overset{(R''-O)_y-H}{|}}{N})_x{-}(R''{-}O)_y{-}H}$$

and

$$\mathrm{R{-}\overset{\overset{(R''-O)_y-H}{|}}{N}{-}(R'{-}\overset{\overset{H}{|}}{N})_x{-}(R''{-}O)_y{-}H}$$

where R, R' . R'' x and y have the values noted above.

Highly effective compounds for lubricating oil compositions are those in which R' and R'' are divalent ethylene and propylene radicals and x and y are 1 or 2. Certain classes of these compounds are represented by the formulas:

$$\mathrm{R{-}\overset{\overset{H}{|}}{N}{-}(CH_2CH_2{-}\overset{\overset{(CH_2CH_2-O)-H}{|}}{N}){-}(CH_2CH_2{-}O){-}H}$$

and

$$\mathrm{R{-}\overset{\overset{(CH_2CH_2-O)-H}{|}}{N}{-}(CH_2CH_2{-}\overset{\overset{H}{|}}{N}){-}(CH_2CH_2{-}O){-}H}$$

in which R has the values noted hereinabove.

The compound of the invention contains at least two hydrooxyalkyl radicals per mole of the compound attached to the same or different nitrogen atoms in the compounds. It will be appreciated that a substantially larger number of hydrooxyalkyl groups can be present in the compounds hereinabove defined.

The prescribed polybutenyl-alkylene polyamine-polyalkanol can be prepared in two steps involving a reaction between a polybutenyl polymer and an alkylene polyamine in the first step to form an intermediate compound followed by a reaction with an alkylene oxide in the second step.

The polybutenyl component for the above reactions is a polymer of isobutylene which can be prepared by known polymerization methods. This polymer will have an average molecular weight ranging from 900 to 10,000. A preferred polybutenyl polymer is one having an average molecular weight ranging from 1,000 to 5,000 with the most preferred having a molecular weight from 1,200 to 2,500.

The alkylene polyamine component employed can be a straight or branched chain diamine or a polyalkylene polyamine of mixture thereof. Examples of suitable diamines include ethylene diamine, propylene diamine, 1,4-butane diamine, 1,4-pentane diamine and 1,6-hexane diamine. Examples of suitable polyalkylene polyamines include diethylene triamine, piperazine, triethylene tetramine, N-aminoethylpiperazine, tetraethylene pentamine and pentaethylene hexamine.

One method of reacting the polybutenyl polymer with the alkylene polyamine is to first prepare a halogen derivative, i.e. a chloride or bromide derivative of the polybutenyl polymer containing from 0.5 to 10 percent of the halogen according to known methods as set forth in U.S. Pat. No. 3,275,554 which disclosure is incorporated herein. This halogenated polybutenyl polymer is then reacted with the prescribed alkylene polyamine. In general, 1 to 2 moles of the alkylene polyamine is reacted with the halogenated polybutenyl polymer. This reaction is preferable conducted in the presence of an alkaline material to facilitate the reaction. However, the reaction can be conducted without employing alkaline material and in the absence of a solvent. The reaction is generally conducted at a temperature ranging from about 250° to 500°F.

The intermediate compound is then reacted with an alkylene oxide to form the dispersant of the invention. The preferred alkylene oxides for this reaction include ethylene oxide, propylene oxide and butylene oxide although higher alkylene oxides and alkyl substituted alkylene oxides are also suitable. This reaction is generally conducted by dissolving the intermediate compound in a hydrocarbon solvent and gradually adding the alkylene oxide reactant to the reaction mixture over a period of time. The reaction is conveniently conducted at room temperature although higher and lower temperatures generally ranging from about 0° to 100°C. can be employed. The ratio of alkylene oxide to alkylated alkylene polyamine is at least 2:1 and is generally in the range of 2:1 to 10:1 with the preferred range being 2:1 to 5:1. These ranges effect alkoxylation of the primary and secondary nitrogen atoms as well as for polyalkoxylation at these points. The reaction mixture is then filtered and the solvent stripped off under a vacuum.

The following table lists the dispersants which are prepared according to this invention:

N-polyisobutenyl-C_{90}-N',N' bis-2-hydroxyethyl-ethylenediamine.

N-polyisobutenyl-C_{100}-N',N'-bis-2-hydroxyethyl-ethylenediamine

N-polyisobutenyl-C_{70}-N',N'-bis-2-hydroxypropyl-diethylenetriamine.

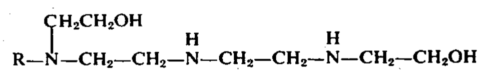
N-polyisobutenyl-C_{120}-N',N'-bis-2-hydroxypropyl-ethylenediamine

N-polyisobutenyl-C_{150}-N',N'-bis-2-hydroxyethyl trithylene tetramine

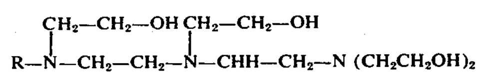
N-polyisobutenyl-C_{90}-N,N'-bis-2-hydroxyethyl-ethylenediamine

N-polyisobutenyl-C_{70}-N,hydroxypropyl, N'-hydroxyethyl-ehtylenediamine.

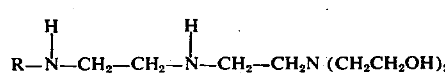
N-polyisobutenyl-C_{100}-N,N'-bis-2-hydroxyethyl-diethylenetriamine.



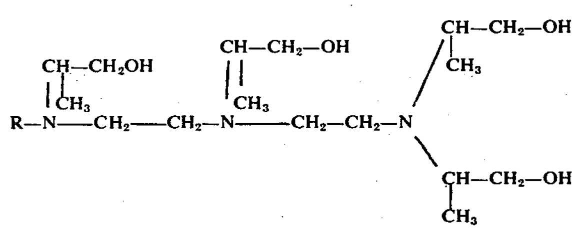
N-polybutene(C_{100})-N,N'' -bis-2-hydroxyethyl diethylenetriamine.



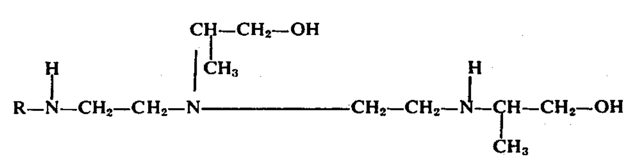
N-polyisobutenyl(C_{100})-N,N',N''-tetrakis-2-hydroxyethyl diethylenetriamine.



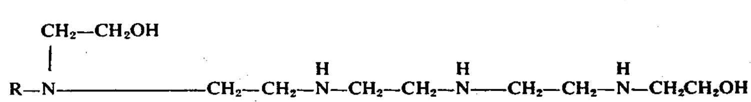
N-polyisobutenyl (C_{100})-N''bis-2-hydroxyethyl-diethylenetriamine



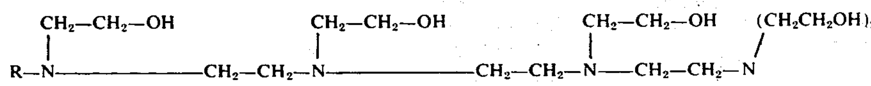
N-polyisobutenyl(C_{100})-N,N',N''-tetrakis-2-hydroxypropyl-diethylene triamine



N-polyisobutenyl(C_{100})-N',N''bis-2-hydroxypropyl-diethylenetriamine



N-polyisobutenyl(C_{100})-N,N'''-bis-2-hydroxyethyl-triethylenetetramine



N-polyisobutenyl(C_{100})-N,N',N'',N'''-pentakis-2-hydroxyethyl-triethylene tetramine.

The hydrocarbon mineral base oil employed in preparing the lubricating oil compositions of the invention can be a paraffinic base, naphthene base or mixed paraffin-naphthene base distillate or residual oil. Paraffin base distillate lubricating oil fractions are preferred for the formulation of the highest quality engine or motor oils. The lubricating oil base generally will have been subjected to solvent refining to improve its lubricity and viscosity temperature relationship as well as to solvent dewaxing to remove waxy components and to improve the pour of the oil. Generally, mineral lubricating oils having an SUS viscosity at 100°F between 50 and 1,000 may be used in the formulation of the improved lubricants of this invention with the preferred oils having a viscosity range from 70 to 300 SUS at 100°F. A blend of base oils can be employed to provide a suitable base oil for either a single or multigrade motor oil.

The following example illustrates a method for preparing the ashless dispersants of the invention.

EXAMPLE I

4,620 grams of chlorinated polybutene having a molecular weight of about 1300 and containing 2.76 percent of chlorine was mixed with 500 grams (4.3 moles) of hexamethylene diamine and 191 grams (1.8 moles) of sodium carbonate. The reaction mixture was cooled, diluted with four liters of hexane, filtered and the filtrate extracted with methanol. The hexane layer was stripped under vacuum at 200°F. yeilding an intermediate product containing 0.8 percent nitrogen. 2,340 grams of the above intermediate product was dissolved in 800 milliliters of toluene and 334 milliliters of isopropyl alcohol. 232 grams (4 moles) of propylene oxide was added dropwise to the solution of the intermediate product over a 30 min. period. The mixture was then heated to reflux for 4 hours, filtered and the solvents stripped off under vacuum at 200°F. The dispersant product contained 0.8 percent nitrogen.

The effectiveness of the dispersant of the invention was determined in the Caterpillar 1-H Diesel Engine Test. This is a standard industry test which is run on a 1Y73 single cylinder Caterpillar Diesel Lubricant Test Engine as described in FTMS 791a-346T. This test is used to qualify lubricants for MIL-L-2104B.

The engine is operated at a speed of 1,800 RPM and a fuel input of 4,950 BTU/min for a test duration of 480 hours. Performance is judged by examination of the power section of the engine for ring sticking, piston deposits and ring, piston and liner wear.

EXAMPLE II

The procedure of Example I is repeated using 2,000 grams of a chlorinated polybutene containing 2.76% chlorine, 209 g (1.6 mole) iminobispropylamine, and 85 g (0.80 mole) of sodium carbonate. The intermediate product contains 1.2% nitrogen.

117 grams of the above intermediate was dissolved in 150 ml of hexane, and together with 15.5 g (0.27 mole) of propylene oxide, charged to a reaction flask and heated at reflux for seven hours. The reaction mixture was filtered and solvent stripped under vacuum to 180°F. The dispersant product contained 0.97% nitrogen.

EXAMPLE III

Following the procedure of Example I, 3,500 g of a chlorinated polybutene containing 2.76% chlorine, 632 g (2.7 mole) of pentaethylenehexamine, and 140 g (1.3 mole) of sodium carbonate is reacted to give a product containing 2% nitrogen.

Reaction of 1500 g of the above intermediate in 1000 ml toluene and 350 ml isopropyl alcohol with 200 g (3.4 ml) of propylene oxide, gave a dispersant material containing 2% nitrogen.

CATERPILLAR 1-H TEST

The lubricating oil composition employed in this example was fully formulated motor oil composition containing an alkaline detergent, a zinc dithiophosphate and a pour depressant in a paraffinic mineral oil having an SUS viscosity at 100°F. of 535. The detergent of Example I was added to the fully formulated base oil in an amount to give 0.28% nitrogen in the finished oil.

The foregoing oil composition was tested in the Caterpillar 1-H Test for the full test duration of 480 hours. Inspection of the piston showed 5% TGF, and 100% light lacquer on the first land and no deposits below. These results demonstrate the effectiveness of the dispersant for controlling both carbonaceous and lacquer deposits in diesel engine operation.

The detergent of the invention was also treated for its effectiveness in motor oil compositions for a gasoline engine. The formulated oils were evaluated in laboratory bench tests (Bench Sludge I and Bench Sludge II tests) designed to discriminate between oils of differing light duty deposits control characteristics. The bench Sludge tests are a measure of the ability of a dispersant formulation to retain particulate foreign materials. The numbers obtained indicate the depth of sediment (in millimeters) obtained at the end of the test procedure. In general, the lower the values in the Bench Sludge I and II tests are, the more highly dispersant the formulations are.

The base oil employed was a paraffinic hydrocarbon oil having an SUS at 100°F of about 125. Three fully formulated oils were prepared containing an alkaline detergent, zinc dithiophosphate and a polymethacrylate pour depressant in addition to the dispersants described above. Lubricating oil A contained the dispersant of Example I to give a fully formulated oil containing 0.028 percent nitrogen. Lubricating oil B contained the dispersant of Example II to give a fully formulated oil containing 0.036 percent nitrogen. Lubricating oil C contained the dispersant of Example III to give a fully formulated oil containing 0.081% nitrogen. Lubricating oil D contained no ashless dispersant.

The results of the Bench Sludge Tests are given in Table I below.

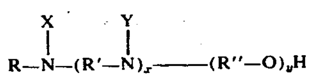
TABLE I

BENCH SLUDGE TESTS	Bench Sludge I (mm Sediment)	Bench Sludge II (mm Sediment)
1. Lubricating Oil A	0.1	0.5
2. Lubricating Oil B	0.3	0.7
3. Lubricating Oil C	0.1	0.4
4. Lubricating Oil D (no dispersant)	0.5	3.8

The foregoing tests show that the dispersant and the lubricating oil composition of the invention are highly effective for controlling deposits in four cycle gasoline engine type operation which this test simulates.

We claim:

1. An oil-soluble, ashless polybutenyl-alkylene polyamine-polyalkanol dispersant represented by the formula:



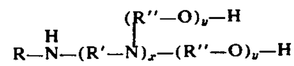
in which R is a polybutenyl radical having a molecular weight ranging from 900 to 10,000, X and Y are H or $(R''—O)_yH$ at least one of X or Y being $(R''O)_yH$, R' is a divalent hydrocarbyl radical having from 2 to 8 carbon atoms, R'' is a divalent hydrocarbyl radical having from 2 to 4 carbon atoms, x has a value from 1 to 6, and y has a value from 1 to 5.

2. A dispersant according to claim **1** in which said polybutenyl radical has a molecular weight ranging from 1,000 to 5,000.

3. A dispersant according to claim **1** in which said polybutenyl radical has a molecular weight ranging from about 1,200 to 2,500.

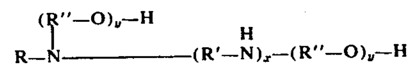
4. A dispersant according to claim **1** in which x and y each have a value of 1.

5. A dispersant according to claim **1** represented by the formula:



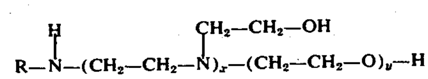
in which the symbols have the values given in Claim **1.**

6. A dispersant according to claim **1** represented by the formula:



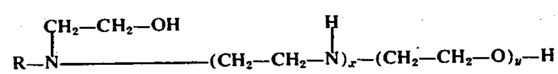
in which the symbols have the values given in claim **1.**

7. A dispersant according to claim **1** represented by the formula:



in which R, x and y have the values given in claim **1.**

8. A dispersant according to claim **1** represented by the formula:



in which R, x and y have the values given in claim **1.**

* * * * *