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MALEIC ANHYDRIDE COPOLYMER SUCCINIMIDES OF LONG CHAIN HYDROCARBON AMINES

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U.S. Cl. 252—32.7 **10 Claims**

ABSTRACT OF THE DISCLOSURE

Compositions comprising the reaction product of olefin-maleic anhydride copolymers of from about 4 to 20 units with alkylene polyamines having at least 1 relatively long chain aliphatic hydrocarbon bonded to nitrogen either directly or through a nonoxocarbonyl group. The products find use as detergents in lubricating oils. The lubricating oils can optionally contain dihydrocarbyl phosphorodithioates.

BACKGROUND OF THE INVENTION

Field of the invention

Lubricating oils used in internal combustion engines are compounded with a variety of materials to prolong the useful lifetime of the oil and enhance the oil's capability as a lubricant. An important adjunct to a lubricating oil is the addition of detergents and dispersants. These additives prevent the deposition of deposit forming materials which are formed in the oil on surfaces in the engine, particularly on moving parts such as the piston. Otherwise, the deposits can lead to ring and piston sticking, greatly reducing the efficiency of the engine. Not only must a successful lubricating oil detergent prevent the deposition of materials in the oil, but it must be compatible with the other additives present in the oil, must itself not enhance the formation of deposit forming materials, and. preferably, aid in the removal of deposits, should deposits form.

Description of the prior art

In the last 10 years, a major breakthrough in the use of lubricating oil detergents has been the ashless detergent. Primarily, these detergents have been alkenyl succinimides of alkylene polyamines, illustrations of which are found in the following U.S. Patents Nos. 3,194,812, 3,219,666 and 3,306,852. Other detergents have been reported which require a direct bond between an aliphatic carbon and the amine nitrogen, rather than a succinimide bond, e.g., U.S. Patent No. 3,275,554.

Maleic anhydride olefin copolymers have found wide use as reactants in the formation of the wide variety of products for use in lubricating oils, e.g., U.S. Patents Nos. 2,737,496 and 3,130,161.

SUMMARY OF THE INVENTION

The invention concerns the reaction product of an olefin-maleic anhydride altering copolymer with a substituted alkylene polyamine. There will be an average of at least 6 recurring units in the copolymer. The olefin of the copolymer will have an average of at least 6 carbon atoms. The substituent on the alkylene polyamine will be a long branched chain aliphatic hydrocarbon of at least 25 carbon atoms bonded to nitrogen either directyl through an aliphatic carbon atom or through a nonoxocarbonyl group. The compositions find use in internal combustion engines, both the relatively hot diesel engine and the more variable temperature automobile engine.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions which find use in this invention are the reaction products of a relatively low molecular weight alternating copolymer (olefins of at least 6 carbon atoms with maleic anhydride) with an alkylene polyamine having at least 2 nitrogen atoms bonded to a relatively long chain aliphatic hydrocarbon, either through a single bond or a nonoxocarbonyl. The reaction takes place at elevated temperatures and normally in an inert hydrocarbonaceous solvent.

The average molecular weight of the reaction product will generally be at least 3,000 and not greater than 15,000, more usually in the range of about 4,500 to 13,000.

The percent nitrogen will be at least about 1.5 and generally not in excess of about 5.0 weight percent. Usually, the percent nitrogen will be in the range of about 1.5 to 4.0. None of the nitrogen need be present as basic nitrogen. That is, all the nitrogen present may be bonded to nonoxocarbonyl. The amount of basic nitrogen will generally be in the range of about 0 to 2 weight percent, more usually in the range of about 0.2 to 1.5 weight percent.

The polymer will have on the average at least 4 relatively long aliphatic hydrocarbon groups pendant from the copolymer and usually not more than an average of 12 long chain hydrocarbon groups. The total number of carbon atoms comprising the relatively long hydrocarbon chains pendant from the copolymer will be in the range of about 100 to about 800.

At least about 50 and usually at least about 70 percent of the maleic anhydride groups present in the polymer will be reacted to form carboxamide or maleimide with the substituted alkylene amine. As high as 90 percent or even 100 percent of the maleic anhydride groups may be reacted with the substituted alkylene amine to form carboxamide or imide derivatives.

Preparation of product

The reaction product is prepared by combining at elevated temperatures the maleic anhydride-olefin copolymer with the substituted alkylene polyamine, usually neat or in the presence of a small amount of an inert hydrocarbonaceous diluent. Usually, from about 0.5 to 1.1 mole ratio of substituted alkylene amine to moles of maleic anhydride present will be used, more usually from about 0.75 to about 1.05. Excesses of the alkylene polyamine beyond those specified may be used, but are generally wasteful of material.

For the most part, the reaction is carried out neat. Frequently, in order to obtain a relatively homogeneous reaction mixture, one or both of the reactants may be dissolved in an inert aromatic hydrocarbon, e.g., benzene, the reactants poured together and the volatile solvent removed. Occasionally, from about 5 to 35 weight percent of the reaction mixture may be an inert hydrocarbonaceous diluent such as neutral oil, pale oil, etc.

The reaction temperature will be at least 75° C. and generally not exceed 185° C. usually being in the range of about 85° C. to 160° C. Depending on the temperature, the time may vary from about ½ hour to 9 hours, more usually being in the range of about 45 minutes to 3 hours.

An inert atmosphere may be used over the reaction mixture, e.g., nitrogen, helium, etc. The pressure for the system will generally be atmospheric or below, with the water being removed from the reaction mixture as formed.

When the reaction has been terminated, the reaction mixture is allowed to cool and may be purified in a variety of ways. Usefully, the reaction mixture may be purified by solvent extraction. The reaction mixture is taken up in an aliphatic hydrocarbon solvent, e.g., pentane, hexane, etc., and then a polar solvent added, e.g., acetone. The solution-dissolution of the product may be repeated as many times as considered necessary and the final insoluble phase used.

Alternatively, the product may be purified by dialysis, or other convenient means.

Reactants

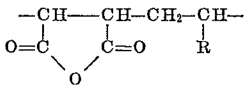
Turning now to a consideration of the reactants. The first reactant to be considered will be the olefin-maleic anhydride copolymer. The copolymers will have on the average from about 6 to 18 recurring units and individually may have as few as 4 and as many as 20 recurring units. Preferably, on the average, there will be from about 6 to 14 recurring units.

The olefins will be from about 6 to 22 carbon atoms, having on the average from about 8 to 18 carbon atoms, more usually from about 8 to 16 carbon atoms.

Individual olefins or mixtures may be used, the mixtures having the desired average number of carbon atoms. Mixtures of olefins are preferred, having at least 3 olefins present, each in an amount of at least 15 mole percent, and not more than 50 mole percent, more usually not more than 30 mole percent of one olefin.

The olefins used are 1-olefins, that is olefins having mono-terminal unsaturation. The olefins are straight chain, i.e., h-(1-alkenes) although small amounts (less than 15 mole percent of branched chain olefins may be present.

The polymers will for the most part have recurring units of the following formula:



wherein R is a straight chain alkyl group of from 4 to 20 carbon atoms, more usually of from 8 to 18 carbon atoms and will be substantially free of aliphatic unsaturation. That is, in some instances, less than about 10 percent of the alkyl groups may be alkenyl groups (having olefinic unsaturation). As already indicated, the number of recurring units in the polymer will be in the range of from 4 to 20.

The copolymers are readily prepared by copolymerizing an aliphatic 1-olefin (some diolefins may be present) with maleic anhydride by means of free radical catalysis. The copolymerization of maleic anhydride with aliphatic 1-olefins is well known in the art. See for example U.S. Patent No. 3,051,562.

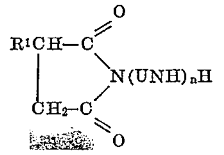
Illustrative 1-olefins are hexene, octene, decene, dodecene, tetradecene, pentadecene, hexadecene, octadecene, eicosene, etc.

The free radical catalyst may be any organic compound which at a temperature in the range of 50° to 100° C. decomposes to form free radicals which may then initiate the polymeric chain, although temperatures outside this range may be used advantageously under some conditions. Usually, peroxidic free radical catalysts will be used.

In carrying out the polymerization, inert halohydrocarbons or hydrocarbons may be used, wherein the solvent is from about 20 to 80 weight percent of the reaction mixture. The ratio of olefin to maleic anhydride will generally be about 0.9–1.2:1.2–0.9 and the ratio of olefin to catalyst will generally be about 1:0.005–0.1 mole ratio.

Turning now to a consideration of the substituted alkylene polyamines, the succinimide substituted alkylene polyamines will be considered first.

For the most part the alkyl or alkenyl succinimides will have the following formula:



wherein R^1 is an alkyl or alkenyl group, of from about 25 to 100 carbon atoms. Usually, the alkyl or alkenyl group will be branched, having at least one branch per 6 carbon atoms along the chain and preferably at least one branch per 2 carbon atoms along the chain, e.g., propylene or isobutylene. U is alkylene of from 2 to 6 carbon atoms, usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms. *n* is an integer of from 1 to 5, more usually an integer of from 1 to 3.

Preparation of the succinimides as well as carboxamides of aklylene polyamines is exhaustively discussed and exemplified in the U.S. Patent No. 3,219,666, issued Nov. 23, 1965. The succinimide is prepared by heating at a temperature in the range of about 80° to 200° C., preferably in the presence of a hydrocarbonaceous solvent, and in the presence of an excess of the alkylene amine. Usually, a mole ratio of at least 2 moles of amine per mole of succinic anhydride is used and as high as 25 moles of alkylene polyamine per mole of succinic anhydride may be used or even higher.

As indicated, the temperature is at least about 80° C. and will generally not exceed 200° C., more usually in the range of about 100° C. to 150° C. Solvents can include hydrocarbonaceous oils, benzene, toluene, and when using an aromatic hydrocarbon, either by itself or in combination with other solvents, the water of reaction may be removed by azeotroping the hydrocarbon solvent.

At the completion of the reaction, any volatile solvent present and excess alkylene polyamine may be removed and the residue used directly with the copolymer. The volatile solvent and amine, when possible, may be removed by vacuum distillation. The amine may also be removed by solvent extraction or partition.

The hydrocarbyl substituted alkylene polyamines will generally have aliphatic branched chain hydrocarbon groups having at least one branch per 6 carbon atoms along the chain and more usually one branch per 2 carbon atoms along the chain, e.g., propenyl and isobutenyl, with the hydrocarbon group being of from about 25 to 100 carbon atoms. Usually, there will be from about 1 to 2 hydrocarbon substituents per alkylene polyamine, preferably averaging about 1 to 1.2. A description of the preparation of the aliphatic hydrocarbon substituted alkylene polyamines may be found in U.S. Patent No. 3,275,554.

The reaction is conveniently carried out by combining a halogenated polyolefin, wherein the halogen is preferably allylic, with the desired alkylene polyamine; the reaction mixture may be either neat or contain an inert solvent, particularly a hydrocarbon solvent. The inert solvent may be aliphatic or aromatic. The reaction temperature may be room temperature (20° C.), but elevated temperatures are preferred. Usually, the temperature will be in the range of about 100° to 225° C. and depending on the temperature used and the reactants, the time may vary from 1 to 24 hours, more usually from about 3 to 20 hours.

For the most part, the substituted alkylene polyamines of this invention having the nitrogen directly bonded to an aliphatic carbon will have the following formula:

$$[NH(UN)_p]H_{p-q+2}R_q^2$$

where U is alkylene of from 2 to 6 carbon atoms, more usually of from 2 to 3 carbon atoms and having 2 carbon atoms between the nitrogen atoms, R^2 is a branched chain alkyl or alkenyl group of from 25 to 100 carbon atoms (see the definition of R^1), p is an integer of from 1 to 5, usually of from 1 to 3, and q is an integer of from 1 to 2.

Also included in the scope of this invention are acylated alkylene polyamines wherein monocarboxylic acids are used. These may be prepared in a manner similar to that described for the succinimides. For the most part, these compositions will have the following formula:

$$[NH(UN)_{p^1}]H_{p^1-q^1+2}(R^3CO—)_{q^1}$$

wherein U is as defined previously, R^3 is a branched alkyl or alkenyl group of from 25 to 100 carbon atoms (see the definition of R^1), p^1 is an integer of from 1 to 5 and q^1 is an integer of from 1 to 2. Depending on the conditions of the reaction, some imidazoline may be formed, but under hydration conditions, the imidazoline will revert to the carboxamide.

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

EXAMPLE A.—PREPARATION OF POLYISOBUTENYL ETHYLENE DIAMINE

Into a reaction flask was introduced 8 kg. of 70 weight percent solution in benzene of chloropolyisobutylene (approx. 6 weight percent chlorine, approximately 1350 molecular weight) and 1600 g. of a composition consisting predominantly of ethylene diamine and the mixture heated to 170° C. for 18 hours, first driving off the benzene. At the end of this time, the mixture was allowed to cool and filtered, followed by extraction. The reaction mixture was taken up in an equal volume of hexane, and 95% ethanol added in an amount of about ⅔ volume of the hexane solution. The mixture was then heated to boiling and water added in an amount of about ⅓ volume of the total solution. After allowing the mixture to cool, the phases were separated, the hexane phase isolated and the volatile materials removed in vacuo.

Analysis.—Percent N, 1.52, 1.52.

EXAMPLE B.—PREPARATION OF POLYISOBUTENYL SUCCINIMIDE OF DIETHYLENE TRIAMINE

Into a reaction flask was introduced 500 grams of a composition having the average composition of diethylene triamine and over a period of ½ hours, a 40 weight percent solution in neutral oil of polyisobutenyl succinic anhydride (polyisobutenyl) of approximately 640 average molecular weight) was added while maintaining the mixture of about 80° C. At the end of this time, the temperature was raised to 150° C. and maintained for one hour. The mixture was then allowed to cool, diluted with an equal volume of hexane, followed by ⅔ volume based on the hexane solution of 95% ethanol. A ⅓ volume of water was added based on the total solution and the phases allowed to separate, the hexane phase being isolated. Volatile materials were then removed in vacuo.

Analysis.—Percent N, 1.44, 1.45.

EXAMPLE C.—PREPARATION OF CRACKED WAX OLEFIN MALEIC-ANHYDRIDE COPOLYMER

Into a reaction flask was introduced 243 grams (1.0 mole) of C_{15-20} cracked wax 1-olefins [1], 98 grams (1.0 mole) of maleic anhydride and 341 grams of benzene. The mixture was stirred at a temperature of 140° F. and 9.7 grams (0.04 mole) of benzoyl peroxide in a minimum of benzene added. The solution was then heated at 185° F. for 12 hours. The reaction product was precipitated with methanol and redissolved in benzene. The benzene was distilled off and the product isolated. The yield was 290 grams (85%).

EXAMPLE I

Into a reaction flask was introduced 44.5 grams of a copolymer of cracked wax olefin and maleic anhydride prepared as described in Example C, 200 grams of benzene, and 257 grams of the product of Example A dissolved in 45 grams of benzene. The benzene was distilled off and the mixture maintained at 150° C. for 2 hours. After allowing the residue to cool, it was dissolved in 2.5 liters of pentane and 2 liters of acetone added. The material which precipitated was isolated, redissolved in pentane and reprecipitated using acetone. The final product was isolated and dried.

Analysis.—Percent N, 1.80, 1.85.

EXAMPLE II

Into a reaction flask was introduced 89 grams of the product prepared as described in Example C, 400 milliliters of benzene and 514 grams of the product of Example A dissolved in 90 milliliters of benzene. The reaction mixture was heated at 150° C. for 2 hours and then allowed to cool. The product was then dissolved in 5 liters of pentane and 4 liters of acetone added. The material which precipitated was isolated, redissolved in pentane and reprecipitated with acetone. The final product was isolated and dried.

Analysis.—Percent N, 1.78, 1.81.

EXAMPLE III

Into a reaction flask was introduced 760 grams of the product prepared in Example B, 400 milliliters of benzene and 89 grams of a product prepared as described in Example C. The benzene was distilled off and the residue heated at 150° C. for 2 hours. The reaction mixture was then taken up in volumes of mixed hexanes, followed by the addition of 5 volumes of acetone. The bottom layer was isolated and an additional 5 volumes of acetone added. The hexane layer was isolated again, the hexane removed by distillation and the residue isolated.

Analysis.—Percent, N, 4.32, 4.30.

EXAMPLE IV

Into a reaction flask was introduced 42.1 grams of a cracked wax olefin maleic anhydride copolymer prepared as described in Example C and then dissolved in 380 milliliters of benzene. To this mixture was then added 109.9 grams of polyisobutenyl succinimide prepared as described in Example B (polyisobutenyl of average molecular weight of approximately 1,000; percent N, 2.86, 2.88). The benzene was stripped and the residue heated at 150° C. for 2 hours. At the end of this time the mixture was allowed to cool and isolated.

Analysis.—Percent N, 2.64, 2.65.

As has already been indicated, the compositions of this invention find use as detergents in lubricating oil. They are found to be effective over a wide variety of conditions: not only under the hot conditions of the diesel engine, but the much more variable temperature conditions of the automobile engine.

The compositions of this invention may be formulated with various lubricating fluids (hereinafter referred to as oils) which are either derived from natural or synthetic sources. 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 of synthetic oils are: hydrocarbon oils such as polymers of various olefins, generally of from 2 to 8 carbon atoms, and alkylated aromatic hydrocarbons; and nonhydrocarbon oils, such as polyalkylene

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[1] C_{15-20}:

No. of carbon atoms:	Mole percent
14	1
15	12
16	19
17	18
18	18
19	17
20	14
21	1
1-olefin	94
Straight chain	86

oxides, aromatic ethers, carboxylate esters, phosphate esters, and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

The above oils may be used individually or together whenever miscible or made so by the use of mutual solvents.

When the detergents of this invention are compounded with lubricating oils for use in an engine, the detergents will be present in at least about 0.1 weight percent and usually not more than 20 weight percent, more usually in the range of about 1 to 10 weight percent. The compounds can be prepared as concentrates due to their excellent compatibilty with oils. As concentrates, the compounds of this invention will generally range from about 10 to 70 weight percent, more usually from about 20 to 50 weight percent of the total composition.

A preferred aspect in using the compounds of this invention in lubricating oils is to include in the oil from about 1 to 50 mm./kg. of a dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are from about 4 to 36 carbon atoms. Usually, the hydrocarbyl groups will be alkyl or alkaryl groups. The remaining valence of the phosphorodithioate will usually be satisfied by zinc, but poyalkyleneoxy or a third hydrocarbyl group may also be used. (Hydrocarbyl is an organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic, or aromatic.)

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

In order to demonstate the excellent effectiveness of the compounds of this invention as detergents and dispersants in lubricating oils, a number of the compounds were tested in a 1–G Caterpillar test (MIL-L-45199 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 about 12 to 15 carbon atoms) was included. The following table indicates the particular derivative used, the amount used, the time for which the run was carried out and the results.

TABLE I

Detergent Ex.	Wt. percent	Hours	Rating	
			Groove deposits	Land deposits
II	1.44	60	51–5–0–0	140–20–20
		120	80–8–0–0	230–30–30
III	1.3	60	36–3–0–0	145–5–0
		120	73–9–0–0	400–155–15

To demonstrate the effectiveness of the compositions of this invention in an automobile internal combustion engine, a modified FL–2 test procedure, as described in June 21, 1948 report of the Coordinating Research Council, was employed. A standard procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2,500 r.p.m. and 45 brake horsepower for a period of 40 hours (closely simulating the relatively "cold" engine conditions which are normally experienced in city driving). At the end of each test, the engine is dismantled and the amount of sludge (rating of 0 to 50, no sludge being 50) and varnish (rated in the same way) is determined. Also determined is ring clogging reported as percent ring clogging.

The above test was modified by increasing the time and periodically raising the oil sump temperature from 165° F. to 205° F. and the water jacket temperature from 95° F. to 170° F.

Using a Mid-Continent SAE 30 base stock, each candidate detergent was empoyed at approximately the same concentration; also included in the oil was 12 mm./kg. of zinc O,O-di(alkyl) dithiophosphate (alkyl of from 4 to 6 carbon atoms). The following table indicates the results obtained. For comparison, without the additive, the engine is incapable of running after about 12 hours.

TABLE II

Detergent Ex.	Wt. percent [1]	Hours	Rating		
			Total varnish	Total sludge	Percent ring clogging
I	2.0	100	41.1	50	0
		175	34.3	49.7	3
II	0.75	100	30.1	40.3	51
IV	0.75	92	33.2	37.8	38

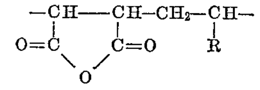
[1] Weight percent based on active material as determined by solvent extraction.

It is evident from the above results that the compositions of this invention are excellent detergents and dispersants in lubricating oils under the varying conditions of different types of internal combustion engines. The compositions of this invention are stable for very long periods of time under the extremely hot conditions of the disel engine. By contrast, they are able to maintain sludge dispersed in oil under the relatively "cold" conditions of the internal combustion engine. The detergents of this invention greatly enhance lubricant protection over the presently available detergents which provide excellent detergency. The useful life of the lubricating oil is thus greatly extended.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

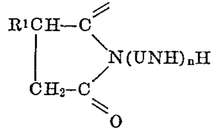
We claim:

1. A composition useful as a detergent in a lubricating oil prepared by contacting a copolymer consisting essentially of from 4 to 20 recurring units of the formula:



wherein R is a straight chain alkyl group of from 4 to 20 carbon atoms; with a substituted alkylene polyamine selected from the group consisting of a composition of the formula:

(I)



wherein R^1 is a branched chain alkyl or alkenyl group of from about 25 to 100 carbon atoms, U is alkylene of from 2 to 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, and n is an integer of from 1 to 5; a composition of the formula:

(II) $[NH(UN)_p]H_{p-q+2}R_q^2$

wherein U is as defined previously, R^2 is a branched chain alkyl or alkenyl group of from 25 to 100 carbon atoms, p is an integer of from 1 to 5 and q is an integer of from 1 to 2; and a composition of the formula:

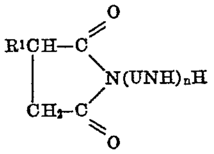
(III) $[NH(UN)_{p^1}]H_{p^1-q^1+2}(R^3CO—)_{q^1}$

wherein U is as defined previously, R^3 is a branched chain alkyl or alkenyl group of from 25 to 100 carbon atoms, p^1 is an integer of from 1 to 5 and q^1 is an integer of from 1 to 2; at a temperature in the range of 75° to 185° C. for a period of time in the range of 30 minutes to 9 hours and at a mole ratio of substituted alkylene amine to maleic anhydride in the range of 0.5–1.1:1.

2. A composition according to claim **1**, wherein the contacting is carried out in a liquid hydrocarbon medium.

3. A composition according to claim **2**, wherein the temperature is in the range of 85° to 160° C. and the mole ratio of alkylene amine to maleic anhydride is in the range of 0.75–1.05:1.

4. A composition according to claim **1**, wherein said substituted alkylene polyamine is of the formula:



wherein the symbols are as defined previously.

5. A composition according to claim **4**, wherein *n* is an integer of from 1 to 3 and U is alkylene of from 2 to 3 carbon atoms.

6. A composition according to claim **4**, wherein *n* is an integer of from 1 to 3, U is alkylene of from 2 to 3 carbon atoms and R^1 is polyisobutenyl.

7. A composition according to claim **1**, wherein said substituted alkylene polyamine is of the formula:

$$[NH(UN)_p]H_{p-q+2}R_q^2$$

wherein *p* is an integer of from 1 to 3, U is alkylene of from 2 to 3 carbon atoms and R^2 is polyisobutenyl.

8. An oil of lubricating viscosity having in an amount sufficient to provide detergency, a composition according to claim **1**.

9. An oil according to claim **8**, having from 1 to 50 mm./kg. of a dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are of from about 4 to 36 carbon atoms.

10. An oil of lubricating viscosity having in from 10 to 70 weight percent of the total composition of a composition according to claim **1**.

References Cited

UNITED STATES PATENTS

2,892,786	6/1959	Stewart et al.	
3,048,544	8/1962	Stewart et al.	
3,219,666	11/1965	Norman et al.	
3,275,554	9/1966	Wagenaar ----------	252—50

PATRICK P. GARVIN, Primary Examiner

U.S. Cl. X.R.

252—46.7, 51.5; 260—78.5, 326.3

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,455,827 Dated July 15, 1969

Inventor(s) ENVER MEHMEDBASICH and LEWIS R. HONNEN

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

Col. 1, line 7, after "94947" insert --assignors to Chevron Research Company, San Francisco, Calif., a corporation of Delaware.--

The assignment was recorded in the Patent Office on August 4, 1969, on Reel 2519, Frame 227.

SIGNED AND
SEALED
MAY 26 1970

(SEAL)
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Attesting Officer

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Commissioner of Patents