

1

3,701,640 COMPOSITION

Charles A. Lease, Chicago, Seymour H. Patinkin, Skokie, and Frank J. Chloupek, South Holland, Ill., assignors to Atlantic Richfield Company, New York, N.Y.
No Drawing. Continuation of application Ser. No. 44,612, June 8, 1970, now abandoned. This application Nov. 5, 1971, Ser. No. 196,241
Int. Cl. C101 1/22

U.S. Cl. 44-66

20 Claims

ABSTRACT OF THE DISCLOSURE

A hydrocarbon gasoline composition containing, as an additive, a minor amount, sufficient to improve the detergency of said gasoline, of the reaction product of:

- (A) a monocarboxylic acid or derivative thereof;
- (B) a polyamine having at least three nitrogen atoms, at least two primary and at least one secondary;
- (C) an alkyl-substituted phenol; and
- (D) formaldehyde;

A preferred reaction product contains 4,7,10-tris(2-hydroxy-5-alkyl) benzyltetraethylenepentamine-1,13 palmitic acid diamide.

This application is a continuation of Ser. No. 44,612, filed June 8, 1970, now abandoned.

The present invention is directed to novel hydrocarbon gasoline compositions having improved detergency. More specifically, the present invention concerns the use as gasoline additives of reaction products of a monocarboxylic acid or derivatives thereof, an alkyl-substituted phenol, a polyamine having at least three nitrogen atoms, at least two primary and at least one secondary, and formaldehyde and the modified derivatives thereof wherein the phenolic hydrogen is replaced by other groups.

Recently, increased engine deposits due largely to various emission control devices required on automobiles have been encountered in several critical engine areas. For instance, deposit build-ups occur in the PCV device and carburetor. These deposits upset normal PCV flow, idling speed and the air-fuel ratio; additionally, these deposits, aggravate further engine deposits such as sludge and varnish in the crankcase, piston, and rocker arm areas. This invention, however, provides gasoline detergent additives which reduce engine deposits even while operating with modern emission control devices.

In accordance with the present invention, it has been found that the reaction products of a monocarboxylic acid or a derivative thereof, an alkyl-substituted phenol, a polyamine having at least three nitrogen atom, at least two primary and at least one secondary, and formaldehyde, and the modified derivatives thereof wherein the phenolic hydrogen is replaced by other groups, provide compositions having excellent detergency when added to hydrocarbon gasolines in small amounts. An advantageous modification of the phenolic hydroxyl group of these reaction products is accomplished by the partial or complete neutralization thereof with basic materials, for instance ammonium and metal components such as their hydroxides, carbonates and bicarbonates. Metals of Groups I-B, II-A, II-B, IV-A, V-A and VIII, e.g. calcium, nickel, zinc, barium, iron, copper, cobalt, tin, lead and bismuth, are particularly useful. Specific, exemplary

2

compounds which can be used to accomplish the neutralization of the phenolic hydroxyl group are ammonium hydroxide, calcium hydroxide, nickel hydroxide, zinc carbonate, iron carbonate, copper carbonate and cobalt bicarbonate. Another modification of the phenolic hydroxyl group is accomplished by the esterification or etherification thereof. The phenolic hydroxyl group may be esterified or etherified either prior or subsequent, preferably prior, to the formation of the reaction products described herein. Suitable acids and alcohols useful in this modification often contain up to about 8 carbon atoms, e.g. acetic, propionic or butyric acids and methanol or ethanol. The esterification and etherification are accomplished by methods well known in the art.

The sequence in which the reactants can be combined to afford the gasoline detergent additives of the present invention may be varied depending upon the products which are being prepared. Regardless of the sequence of reaction and reaction conditions, however, about 0.05 to 2 moles, preferably about 0.2 to 1 mole, of reactive carboxylic acid group (including an anhydride group as two such carboxyl groups) is generally reacted per average basic, reactive primary nitrogen atom present in one mole of the amine; and at least about 0.2 mole, preferably up to about 2 moles, of each of the alkylated phenol and formaldehyde per average basic reactive, secondary nitrogen atom present in a mole of amine reactant, is reacted. Advantageously, each of the alkylated phenol and formaldehyde is reacted in an amount of about 0.2 to 1 mole per average basic reactive, secondary nitrogen atom per mole of the amine.

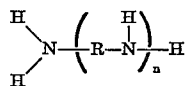
The four reactants which are employed to form the reaction products of the invention will be described under separate headings.

THE MONOCARBOXYLIC ACID REACTANT

The carboxylic acid useful in the present invention is a monocarboxylic acid of from 2 to about 24 carbon atoms including the corresponding acid anhydrides, esters or acid halides, e.g. acid chlorides, of the carboxylic acids. The acid can be straight chain or branched, saturated or unsaturated, aliphatic (including cycloaliphatic), aromatic or heterocyclic. The preferred carboxylic acids are the aliphatic monocarboxylic acids of 4 to about 24 carbon atoms. Particularly suitable monocarboxylic acids and anhydrides are the saturated and unsaturated fatty acids, preferably of about 10 to 24 carbon atoms, such as lauric acid, stearic acid, palmitic acid, oleic acid, arachidic acid, myristic acid, linoleic acid and the like acids or mixtures thereof.

POLYAMINE REACTANT

The amine component of the reaction products of the invention is a polyamine having at least three nitrogen atoms, at least two primary and at least one secondary. Suitable polyamines of the invention include polyalkylene polyamines represented by the formula:



wherein n is a number of at least 2, commonly 2 to 10; R is an alkylene radical of 2 to about 25 carbon atoms,

5

of a blend of hydrocarbon mineral oil fractions boiling primarily in the aforementioned range and will contain varying proportions of paraffins, olefins, naphthenes and aromatics derived by distillation, cracking and other refining and chemical conversion processes practiced upon crude oil fractions. Straight run gasolines, gasolines derived from cracking gas oil, gasolines or reformat from reforming straight run naphtha over a platinum-alumina catalyst in the presence of hydrogen, etc., are components frequently used in making up a gasoline composition. A typical premium gasoline, besides containing a small amount of a tetra-lower-alkyl lead compound as an anti-knock agent may also contain small amounts of other non-hydrocarbon constituents used to impart various properties to the gasoline in its use in internal combustion engines, e.g., halohydrocarbon scavengers, oxidation, inhibitors, etc. Such gasolines frequently have a Research Method octane number of about 90 and 105, and a Motor Method octane number of about 80 to 98.

The reaction products described herein are incorporated in the gasoline in minor amounts sufficient to provide a composition exhibiting improved detergent properties. The actual amount of the additive employed may vary depending upon the particular gasoline employed, its lead content, etc. Often about 10 to 500 or more pounds of the detergent, preferably about 15 to 100 or 400 pounds per 1,000 barrels of gasoline, are employed.

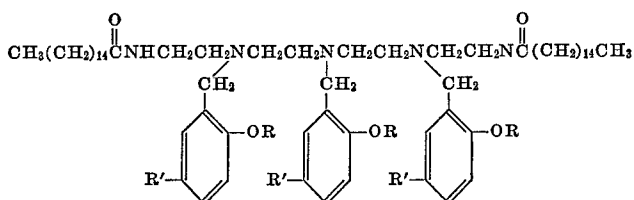
The following examples further illustrate the present invention.

EXAMPLE I

Preparation of the reaction product of palmitic acid, octylphenol, formaldehyde and tetraethylene pentamine

Product "A" of the present invention can be prepared in the following manner:

Palmitic acid (768 g.), tetraethylenepentamine (284 g.) and 99 g. of mineral lubricating oil having a viscosity of 1505 SUS at 100° F. are introduced into a 5-liter, four-necked, round-bottom flask fitted with a mechanical stirrer, water separator, reflux condenser, thermometer, and nitrogen gas inlet. The mixture is heated and stirred for about 4 hours under a nitrogen blanket at about 100° C. The temperature is increased to about 150° C. over a two-and-one-half-hour period and 50 g. of water is collected (pH=11). The mixture is then allowed to cool overnight. Octylphenol (927 g.) and 750 g. of the same mineral oil are added to the reaction mixture and the mixture is heated to 90° C. Formaldehyde solution (38%, 366 g.) is added dropwise with stirring over about one-and-one-half hours. Stirring is maintained throughout the addition and the temperature is held at 90–95° C. for an additional two-and-one-half hours. The temperature is then slowly increased to 150° C. and 292 g. of water are collected (pH=5), leaving the product designated "A" having a major component of the following formula:



wherein R is hydrogen and R' is 1,1,3,3-tetramethylbutyl.

Examples II through V describe product "A" modified with various neutralization agents.

EXAMPLE II

Ammonium neutralized "A"

Product "A" is heated with stirring to 80° C. and 125 g. of 28% ammonium hydroxide solution is added over 75

6

about one-and-one-half hours. The mixture is stirred at 80–85° C. for 5 hours and then slowly heated to 150° C. Water (95 g., pH=11) is collected, 240 g. of mineral lubricating oil having a viscosity of 150 SUS at 100° F. added, and the mixture is then allowed to cool overnight. The mixture is diluted with 3 liters of benzene and filtered. The benzene is flash distilled off, giving 3828 g. of product.

EXAMPLE III

Zinc neutralized "A"

Product "A" is heated with stirring to 80° C. and 50 g. of water is added. Zinc carbonate (124 g.) is then added portionwise over about one-and-one-half hours. The reaction mixture is stirred an additional 3 hours at 80° C., and then slowly heated to 150° C. After cooling overnight, 3 liters of benzene are added and the mixture filtered. The benzene is then flash distilled off, giving 3816 g. of product.

EXAMPLE IV

Calcium neutralized "A"

Product "A" is heated with stirring to 80° C. and 50 g. of water is added. Calcium hydroxide (75 g.) is then added portionwise over about one-and-one-half hours. The reaction mixture is stirred an additional 5 hours at 80° C. and then slowly heated to 150° C. After cooling overnight, 3 liters of benzene are added and the mixture filtered. The benzene is then flash distilled off, giving about 3800 g. of product.

EXAMPLE V

Nickel neutralized "A"

Product "A" is heated with stirring to 80° C. and 50 g. of water is added. Nickel hydroxide (66 g.) is then added portionwise over about one-and-one-half hours. The reaction mixture is stirred an additional 5 hours at 80° C. and then slowly heated to 150° C. After cooling overnight, 3 liters of benzene are added and the mixture filtered. The benzene is flash distilled off, giving 3800 g. of product.

In addition to the salts described above, other useful salts of the reaction product of Example I which can be prepared are those of copper and other metals.

EXAMPLE VI

The additives of present invention were evaluated in a 96-hour cycling test using a 1966 Chevrolet V-8 engine. To aggravate engine dirtiness, a slipstream of exhaust gases was routed to the intake air cleaner. This flow and the PCV flow were adjusted to the same level at the start of each test, but then not further adjusted during the test.

The engine was completely overhauled (cleaned) between tests and a new PCV device installed. The PCV was checked for deposit plugging at 24-hour intervals in a bench test apparatus. Cleanliness ratings and photographs of selected engine parts were made at the end of the test.

The following Table I shows results comparing cleanliness ratings of the base gasoline XP-8*, with the same

* A commercial type laboratory leaded gasoline.

fuel plus 35 pounds of Calcium Neutralized Product "A"/
1000 bbl. gasoline.

TABLE I

Test No.	Fuel	Detergent additive	PCV flow rate, ft. ³ /min. at—					
			5" vac.		12" vac.		20" vac.	
			0 hr.	96 hrs.	0 hr.	96 hrs.	0 hr.	96 hrs.
1	XP-8*	None	5.00	4.48	2.65	2.02	2.08	1.09
2	XP-8*	35 #/M bbl. Prod. "A" calcium neutralized.	5.46	5.24	2.67	2.72	2.18	2.18
3	XP-8*	35 #/M bbl. Prod. "A" calcium neutralized.	4.73	4.74	2.86	2.82	2.11	2.09
4	XP-8*	None	4.80	4.40	2.62	2.28	2.00	1.41

*A commercial type laboratory leaded gasoline.

The differences in 0 hour determinations reflect normal manufacturing tolerances in the new PCV devices used in the individual tests. Comparisons of data in the table show little change in flow (little deposit plugging) during the tests when the additive was used. For example, at 20" vacuum, 2.09 ft.³/min. flowed through the valve at the end of Test 3 compared to 2.11 at the start. In contrast, there were observed substantial changes in flow (indicating deposit plugging) on the tests without the additive. Again, at 20" vacuum, the flow dropped from 2.08 to 1.09 in Test 1 and from 2.00 to 1.41 in Test 4.

EXAMPLE VII

A visual rating system provides another method of evaluating effectiveness of detergents. This rating system, shown in Table II, was carried out at the conclusion of the test, after the engine was disassembled. A rating of 10 indicates a perfectly clean part or surface, and lower numbers indicate respective degrees of dirtiness.

TABLE II

			Cleanliness ratings						
			Rocker arm covers						
			Right		Left		Pan		Piston skirt
Test No.	Fuel	Detergent additive	Varnish	Sludge	Varnish	Sludge	Varnish	Sludge	varnish
1	XP-8*	None	10	9.5	10	9.5	10	9.7	9.9
2	XP-8*	+35# /M bbl. calcium neutralized Prod. "A"	10	10	10	10	10	9.9	9.9
3	XP-8*	do	10	10	10	10	10	10	9.9
4	XP-8*	+None	10	9.3	9.8	9.1	10	9.7	-----

*Commercial-type laboratory leaded gasoline.

EXAMPLE III

In addition to the rating tests of the previous examples, comparative photographs were taken of engine parts following the use of fuel containing calcium neutralized Product "A" as compared to fuel without calcium neutralized Product "A." In the test, using the calcium modified Product "A," the rocker-arm covers and pan were decidedly cleaner than in the test without calcium-modified Product "A."

I claim:

1. A gasoline composition comprising a hydrocarbon gasoline and a minor amount, sufficient to improve the detergent properties of said gasoline, of an additive which is the reaction product of:

- (A) monocarboxylic acid of 2 to about 24 carbon atoms;
- (B) polyamine having at least three nitrogen atoms, at least two primary and at least one secondary;
- (C) a component selected from the group consisting of an alkylated phenol having at least one alkyl group of about 4 to 20 carbon atoms and at least one reactive

ortho or para position, an alkyl ester of said alkylated phenol, and alkyl ether of said alkylated phenol and mixtures thereof, said ester and ether linkages containing up to about 8 carbon atoms; and

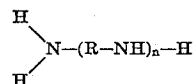
(D) formaldehyde;

wherein about 0.05 to 2 moles of reactive carboxylic acid group is reacted per average, reactive primary nitrogen atom per mole of component B, and components C and D are each reacted in an amount of about 0.2 to 2 moles per average basic, reactive secondary nitrogen atom per mole of component B.

2. The composition of claim 1 wherein said component C is an alkylated phenol having at least one alkyl group of about 4 to about 20 carbon atoms and at least one reactive ortho or para position.

3. The composition of claim 2 wherein component A is a fatty acid of about 10 to 24 carbon atoms.

4. The composition of claim 2 wherein component B is a polyalkylene polyamine of the formula:



wherein n is from 2 to about 10 and R is alkylene of 2 to about 8 carbon atoms.

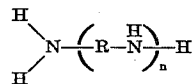
5. The composition of claim 2 wherein about 0.2 to 1 mole of reactive carboxylic acid group is reacted per average, reactive primary nitrogen atom per mole of component B.

6. The composition of claim 2 wherein the phenolic hydroxyl group of the reaction product is modified to form ammonium or metal salts thereof.

7. The composition of claim 2 wherein about 10 to 500 pounds of reaction product are present per one thousand barrels of gasoline.

8. The composition of claim 2 wherein the phenolic hydroxyl group of said reaction product is modified to form an alkyl ester or alkyl ether thereof, said alkyl ester and alkyl ether containing up to about 8 carbon atoms.

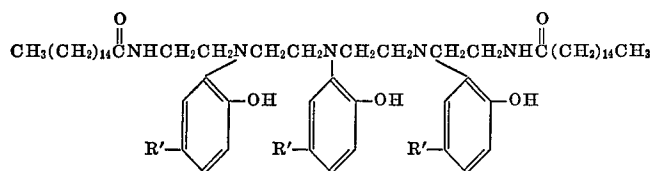
9. The composition of claim 1 wherein component A is a fatty acid which contains from about 10 to 24 carbon atoms; component B has a formula as follows:



wherein n is from 2 to about 10 and R is an alkylene radical containing from 2 to about 25 carbon atoms; component C is selected from the group consisting of para alkyl substituted phenol, an alkyl ester of said para alkyl phenol, an alkyl ether of said para alkyl phenol and mixtures thereof; from about 0.2 to 1 mole of reactive carboxylic acid group is reacted per average, reactive primary nitrogen atom per mole of component B; and components C and D are each reacted in an amount of about 0.2 to 1

9

mole per average basic, reactive secondary nitrogen atom per mole of component B.



10

18. The composition of claim 2 wherein a major component of said reaction product has the following formula:

10. The composition of claim 9 wherein R contains from 2 to about 10 carbon atoms and component C is said para alkyl substituted phenol.

11. The composition of claim 10 wherein the gasoline detergent additive is a metal or ammonium salt of the phenolic hydroxyl group of the reaction product.

12. The composition of claim 10 wherein said phenolic hydroxyl group of said reaction product is modified to form an alkyl ester or alkyl ether thereof, said alkyl ester and alkyl ether containing up to about 8 carbon atoms.

13. The composition of claim 11 wherein the metal is calcium.

14. The composition of claim 11 wherein the metal is nickel.

15. The composition of claim 11 wherein the metal is zinc.

16. The composition of claim 10 wherein the reaction product contains a major portion of a 4,7,10-tri(2-hydroxy-5-alkyl)benzyltetraethylenepentamine-1,13 palmitic acid diamide.

17. The composition of claim 10 wherein about 10 to 500 pounds of reaction product are present per one thousand barrels of gasoline.

wherein R' is 1,1,3,3 tetramethylbutyl, said reaction product being present in an amount from about 10 to 500 pounds per one thousand barrel of said composition.

19. The composition of claim 18 wherein phenolic hydroxyl group of the reaction product is modified to form an ammonium, calcium, nickel or zinc salt thereof.

20. The composition of claim 18 wherein said phenolic hydroxyl group of said reaction product is modified to form an alkyl ester or alkyl ether thereof, said alkyl ester and alkyl ether containing up to about 8 carbon atoms.

References Cited

UNITED STATES PATENTS

3,498,766	3/1970	Gee et al.	44—68
3,280,097	10/1966	Cizek	260—404.5
3,279,901	10/1966	Robbins et al.	44—66

DANIEL E. WYMAN, Primary Examiner

Y. H. SMITH, Assistant Examiner

U.S. Cl. X.R.

44—68, 71; 260— 404.5

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

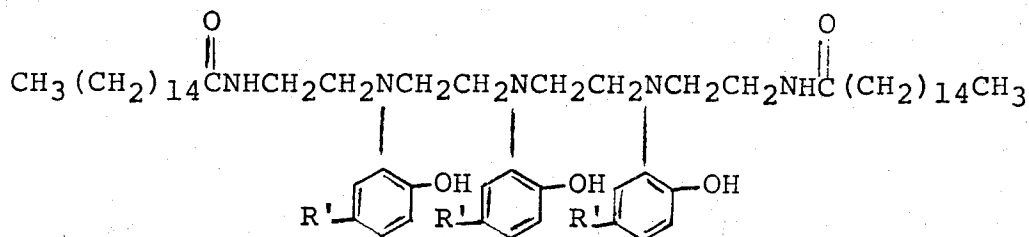
Patent No. 3,701,640

Dated October 31, 1972

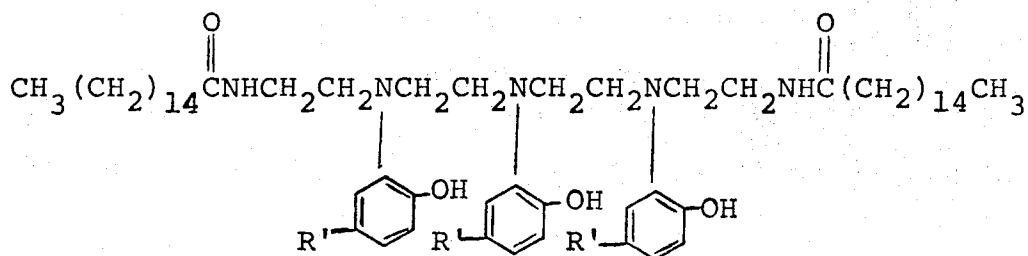
Inventor(s) Charles A. Lease, Seymour H. Patinkin and Frank J. Chloupek

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

Column 9, lines 4 to 11, delete the following structure:



Column 10, lines 4 to 11, insert the following structure:



Column 9, line 30, after the number 10-, delete "tri" and insert in place thereof ---tris---

Signed and sealed this 6th day of March 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents