

1

2

3,438,757 HYDROCARBYL AMINES FOR FUEL DETERGENTS

Lewis R. Honnen and Robert Gordon Anderson, Novato, Calif., assignors to Chevron Research Company, San Francisco, Calif., a corporation of Delaware
No Drawing. Continuation-in-part of applications Ser. No. 408,686, Nov. 3, 1964, Ser. No. 481,916, Aug. 23, 1965, Ser. No. 488,775, Sept. 20, 1965, and Ser. No. 538,571, Mar. 30, 1966. This application June 21, 1967, Ser. No. 647,611

Int. Cl. C10I 1/22

U.S. Cl. 44—58

12 Claims

ABSTRACT OF THE DISCLOSURE

Hydrocarbyl amines and polyamines substantially free of aromatic unsaturation of from about 450 to 10,000 molecular weight find use as detergents in fuels, particularly in combination with a small amount of an oil. The amine portion is primarily amino or alkylene polyamine.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. Nos. 538,571, filed Mar. 30, 1966, now abandoned; 488,775, filed Sept. 20, 1965; 481,916, filed Aug. 23, 1965, now abandoned; and 408,686, filed Nov. 3, 1964.

BACKGROUND OF THE INVENTION

Field of the invention

Deposits resulting from polymeric materials in fuels remain a continuing problem in the smooth operation of internal combustion engines. The narrow tolerances and constricted openings, particularly in the carburetor, ports and valves of the engine, permit of numerous opportunities for deposits to seriously reduce operating efficiency. Therefore, detergents are included in fuels not only to maintain the carburetor clean, but extended detergent action is also desirable. That is, the detergent should also operate to clean the ports and valves through which the fuel-air mixture moves, so as to permit unrestricted flow into the piston chambers. It is extremely difficult to obtain a satisfactory detergent which is effective in the various areas and under the different conditions at which deposits occur in the engine. The problems are made more severe by the low concentrations which must be used in the fuel.

Description of the prior art

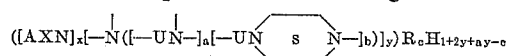
Numerous patents have issued disclosing relatively low molecular weight amine derivatives as fuel detergents. See, for example, U.S. Patents 3,231,348 and 3,050,043. Higher molecular weight succinimide derivatives are reported as fuel detergents in 3,219,666.

SUMMARY OF THE INVENTION

High molecular weight branched chain aliphatic hydrocarbon N-substituted amines and alkylene polyamines are provided as detergents and dispersants, particularly for extended detergent action, in hydrocarbonaceous liquid fuels for internal combustion engines. The detergents used in the fuel have molecular weights in the range of about 425 to 10,000 more usually in the range of about 450 to 5,000.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions which find use in this invention will for the most part have the following formula:



The above symbols are defined as follows:

- A—hydrogen, hydrocarbyl of from 1 to 10 carbon atoms, and hydroxyhydrocarbyl of from 1 to 10 carbon atoms
- X—hydrogen, hydrocarbyl of from 1 to 10 carbon atoms, hydroxyhydrocarbyl of from 1 to 10 carbon atoms, and may be taken together with A to form a ring of from 5 to 6 annular members and up to 12 carbon atoms
- U—alkylene of from 2 to 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms
- R—an aliphatic hydrocarbon radical of from about 400 to 5,000 average molecular weight
- a—an integer of from 0 to 10
- b—an integer of from 0 to 1
- a+2b—an integer of from 1 to 10
- c—an integer of from 1 to 5 and is as an average in the range of 1 to 4, and equal to or less than the number of nitrogen atoms in the molecule
- x—an integer of from 0 to 1
- y—an integer of from 0 to 1
- x+y—equal to 1

The hydrocarbon radical indicated by R is relatively free of aliphatic unsaturation; that is, it will usually have not more than 2 sites of olefinic unsaturation and generally not more than 1 site of olefinic unsaturation and no acetylenic unsaturation.

The aliphatic hydrocarbon radical will ordinarily be prepared by polymerizing olefins of from 2 to 6 carbon atoms (ethylene being copolymerized with another olefin so as to provide a branched chain). The branched chain hydrocarbon radical will generally have at least 1 branch per 6 carbon atoms along the chain, preferably at least 1 branch per 4 carbon atoms along the chain and particularly preferred that there be at least 1 branch per 2 carbon atoms along the chain. That is, the preferred branched chain hydrocarbon radicals are polypropylene and polyisobutylene. The branches will be of from 1 to 2 carbon atoms usually, preferably 1 carbon atom, i.e., methyl.

In most instances, the compositions of this invention are not a pure single product, but rather a mixture of compounds having an average molecular weight. Usually, the range of molecular weights will be relatively narrow and peaked near the indicated molecular weight. Similarly, for the more complicated polyamines, the compositions will be a mixture of amines having as the major product the compound indicated as the average composition and having minor amounts of analogous compounds relatively close in compositions to the dominant compound.

Monoamines

The compositions which will be considered first are those where y is 0.

The monoamine compositions will have the following formula:



The above symbols are defined as follows:

- R¹—a branched chain aliphatic hydrocarbon radical, usually of from about 425 to about 3,000 average molecular weight, preferably up to 1,500 molecular weight, and particularly preferred of polypropylene or polyisobutylene

A¹—hydrogen, hydrocarbyl or hydroxyhydrocarbyl of from 1 to 10 carbon atoms, preferably aliphatic, and usually hydrogen; alkyl or hydroxyalkyl of from 1 to 6 carbon atoms, more usually of from 1 to 3 carbon atoms

X¹—the same or different from A¹ and hydrogen, hydrocarbyl or hydroxyhydrocarbyl of from 1 to 10 carbon atoms, preferably aliphatic, and usually hydrogen, alkyl or hydroxyalkyl of from 1 to 6 carbon atoms, more usually of from 1 to 3 carbon atoms

A¹ and X¹—when taken together with the nitrogen to which they are attached form a ring having 5 to 6 annular members, which may have from 0 to 1 oxygen atom as an annular member to form, for example, morpholine.

Illustrative compositions include polypropenyl amine, polyisobutenyl amine, N-polyisobutenyl dimethylamine, N-polyisobutenyl methylethylamine, N-polypropenyl diethylamine, N-polypropenyl di(2-hydroxyethyl) amine, N-polyisobutenyl N-methyl aniline, N-polyisobutenyl morpholine, N-polyisobutenyl piperidine, N-poly(1-butene) propylamine, N-polypropenyl N-(2-hydroxyethyl) amine, etc.

The preferred monoamine compositions which find use in fuels have the following formula:



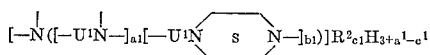
The above symbols are defined as follows:

R¹—a branched chain aliphatic hydrocarbon radical, substantially free of olefinic unsaturation, of from about 420 to 1,250 average molecular weight

A^{1'}—either hydrogen or lower alkyl, preferably of from 1 to 3 carbon atoms

Polyamines

The polyamine compositions which find use in this invention are for the most part described by the following formula:



The above symbols are defined as follows:

U¹—alkylene of from 2 to 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms and preferably of from 2 to 3 carbon atoms

R²—an aliphatic hydrocarbon radical, usually a branched chain aliphatic hydrocarbon radical of from about 400 to 5,000 average molecular weight, preferably of from 400 to 3,000 average molecular weight

a¹—an integer of from 0 to 5

b¹—an integer of from 0 to 1

a¹+2b¹—an integer in the range of from 1 to 5

c¹—an integer of from 1 to 4, for the average composition being in the range of about 1 to 3, on the average there being fewer R² groups than nitrogen atoms

The alkylene radical indicated as U¹ will have from 2 to 6 carbon atoms and more usually, from 2 to 3 carbon atoms, the nitrogen atoms connected by U¹ being separated by at least 2 carbon atoms. The alkylene group may be straight chain or branched and is preferably polymethylene of from 2 to 3 carbon atoms.

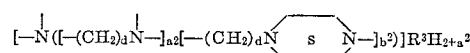
Illustrative alkylene groups are ethylene, 1,2-propylene, 2,2-dimethyl propylene-1,3, trimethylene, hexamethylene, 2-methyl-1,3-propylene, etc.

The alkylene polyamines which are substituted with the hydrocarbon radical may be derived from such alkylene amines as ethylene diamine, diethylene triamine, tetraethylene pentamine, nonaethylene decamine, 2-aminoethyl piperazine, 1,3-propylene diamine, 1,2-propylene diamine, tetramethylene diamine, etc.

As already indicated, in many instances a single compound will not be used as a reactant in the preparation of the compositions of this invention. That is, mixtures will be used in which one or two compounds will predominate

and the average composition or molecular weight is indicated. For example, tetraethylene pentamine prepared by the polymerization of aziridine or reaction of dichloroethylene and ammonia will have both lower and higher members, e.g., triethylene tetramine and pentaethylene hexamine, but the composition will be mainly tetraethylene pentamine and the empirical formula of the total composition will closely approximate that of tetraethylene pentamine. Similarly, the molecular weight reported for the branched chain aliphatic hydrocarbon group is an average for a mixture which is sharply peaked when graphing the number average molecular weight distribution. Also, when the nitrogens of the alkylene polyamines are not equivalent, substitution on different nitrogens will afford different compounds.

As is evident from the above formulae, the alkylene polyamines may have only one hydrocarbon substituent or may be polysubstituted with hydrocarbon radicals. The mono-substituted alkylene polyamine compositions will have the following formula:



The above symbols are defined as follows:

a²—an integer of from 0 to 5, preferably of from 0 to 4

b²—an integer of from 0 to 1, preferably 0 when a² is greater than 0

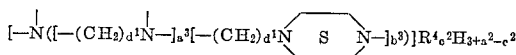
a²+2b²—an integer of from 1 to 5

d—an integer of from 2 to 3

R³—a branched chain aliphatic hydrocarbon radical derived from polymerizing olefins of from 2 to 6 carbon atoms, preferably of from 3 to 4 carbon atoms, and particularly preferred of propylene and isobutylene and having an average molecular weight in the range of 500 to 3,000, preferably 400 to 2,500

Illustrative compounds within the above formula are as follows: N-polyisobutenyl ethylene diamine, N-polypropenyl ethylene diamine, N-poly(1-butenyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine (alternating copolymers of ethylene and isobutylene may be achieved by the cationic polymerization of 4-methylpentene-1), N-polypropenyl 2-aminoethylpiperazine, N-polyisobutenyl 2-aminoethylpiperazine, N-polypropenyl diethylene triamine, N-polyisobutenyl diethylene triamine, N-poly(1-pentenyl) diethylene triamine, N-polypropenyl trimethylene diamine, N-polyisobutenyl trimethylene diamine, N-polypropenyl di(trimethylene) triamine, N-polyisobutenyl di(trimethylene) triamine, N-polyisobutenyl 1,2-propylene diamine, N-polyisobutenyl di(1,2-propylene) triamine, N-polypropenyl triethylene tetramine, N-polyisobutenyl triethylene tetramine, N-(alternating copolymer of ethylene and isobutylene) triethylene tetramine, N-polypropenyl tetraethylene pentamine, N-polyisobutenyl tetraethylene pentamine, N-polyisobutenyl pentaethylene hexamine, etc.

The polyhydrocarbon radical substituted alkylene polyamine compositions have the following formula:



The above symbols are defined as follows:

a³—an integer of from 0 to 5, preferably an integer of from 1 to 4

b³—an integer of from 0 to 1, preferably 0 when a³ is greater than 0

a³+2b³—an integer of from 1 to 5

c²—an integer in the range of 1 to 3, on the average there being fewer R³ groups than nitrogen atoms

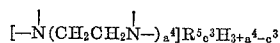
d¹—an integer of from 2 to 3

R⁴—a branched chain aliphatic hydrocarbon radical either free of or having aliphatic unsaturation, e.g., olefinic and of from 400 to 3,000 average molecular weight, preferably of from 400 to about 2,500 average molecular weight

(As indicated by the above formula, the number of hydrocarbon substituents need not be a whole number when averaged over the total composition; generally, a mixture will be obtained containing mono-, di- and tri- or higher substituted molecules averaging out to a fractional or whole number.)

Illustrative compounds coming within the above formula are as follows: N,N'-di(polypropenyl) diethylene triamine, N,N'-di(polyisobutenyl) diethylene triamine, N,N'-di(polyisobutenyl) triethylene tetramine, N,N'-di(polypropenyl) tetraethylene pentamine, N,N'-di(polyisobutenyl) tetraethylene pentamine, N,N'-tri(polyisobutenyl) tetraethylene pentamine, N,N'-di(polyisobutenyl) 2-aminoethylpiperazine, N,N'-di(poly-1-butenyl) triethylene tetramine, N,N'-di(polyisobutenyl) di(trimethylene) triamine, etc.

The preferred compositions are those having the straight chain alkylene polyamines, particularly ethylene diamine and polyethylene polyamines. These compositions have the following formula:

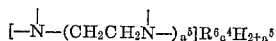


The above symbols are defined as follows:

a^4 —an integer of from 1 to 5, preferably of from 1 to 4
 c^3 —an integer in the range of 1 to 3, on the average over the entire composition being in the range of from 1 to 2, per molecule there being fewer R^4 groups than nitrogen atoms

R^5 —a branched chain aliphatic hydrocarbon radical of from 400 to 3,000 average molecular weight, preferably of from 400 to 2,500 average molecular weight, and, particularly preferred, either polypropenyl or polyisobutenyl

Particularly preferred fuel detergent compositions have the following formula:



The above symbols are defined as follows:

a^5 —an integer of from 1 to 3

c^4 —an integer of from 1 to 3, averaging over the entire composition in the range of 1 to 2

R^6 —a branched chain aliphatic hydrocarbon radical of from about 420 to 1,500 average molecular weight, preferably polypropylene or polyisobutylene

Synthesis

The compositions of this invention are readily prepared by combining an aliphatic or alicyclic halide with the desired amine in the proper mole proportions. The halide is prepared from the hydrocarbon by halogenation: ionically or free radically.

As already indicated, the hydrocarbon groups may be prepared by ionic or free radical polymerization of olefins of from 2 to 6 carbon atoms (ethylene must be copolymerized with another olefin) to an olefin of the desired molecular weight. The olefins which find use are ethylene, propylene, isobutylene, 1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, etc., preferably propylene and isobutylene.

As previously indicated, there should be at least 1 branch per 6 carbon atoms along the chain and preferably at least 1 branch per 4 carbon atoms along the chain. The preferred olefins, propylene and isobutylene, have from 0.5 to 1 branch per atom along the hydrocarbon chain.

The halogen may be introduced into the hydrocarbon molecule by various means known in the art. Most readily, either chlorine or bromine (halogen of atomic number 17-35) may be introduced by the free radical catalyzed halogenation of the hydrocarbon, or ionic addition to olefinic unsaturation. Various free radical catalysts may be used, such as peroxides, azo compounds, bromine, iodine, as well as light. Ionic catalysts are exemplified

by ferric chloride. Methods of halogenation are well known in the art and do not require extensive exemplification or illustration here.

The amount of halogen introduced will depend on the particular hydrocarbon used, the desired amount of amine to be introduced into the molecule, the particular alkylene amine used, and the halogen used. The amount of halogen introduced will generally be in the range from about 1 to 5 halogen atoms per molecule, depending on the reactivity of the resulting halide. On a weight percent basis, the amount of halide will generally range from about 1 to 25, more usually from about 1 to 10.

The halohydrocarbon and amine may be brought together neat or in the presence of an inert solvent, particularly a hydrocarbon solvent. The inert hydrocarbon solvent may be aliphatic or aromatic. Also, aliphatic alcohols may be used by themselves or in combination with another solvent, when capable of dissolving the reactants.

The reaction may be carried out at room temperature (20° C.), but elevated temperatures are preferred. Usually, the temperature will be in the range of from about 100° to 225° C. Depending on the temperature of the reaction, the particular halogen used, the mole ratios and the particular amine, as well as the reactant concentrations, the time may vary from 1 to 24 hours, more usually from about 3 to 20 hours. Times greatly in excess of 24 hours do not particularly enhance the yield and may lead to undesirable degradation. It is therefore preferred to limit the reaction time to fewer than 24 hours.

The mole ratio of halohydrocarbon to amine will generally be in the range from about 0.2 to 20 moles of amine per mole of halohydrocarbon, more usually 0.5 to 10 moles of amine per mole of halohydrocarbon. The mole ratio will depend upon the amount of halogen present in the halohydrocarbon, the particular halogen and the desired ratio of hydrocarbon to amine. If complete suppression of polysubstitution of the alkylene polyamines is desired, then large mole excesses of the amine will be used.

Small amounts of residual halogen in the final composition are not deleterious. Generally, the residual halogen as bound halogen will be in the range of 0 to 10 weight percent of the composition. Small amounts of halogen may be present as the hydrohalide salt of the hydrocarbon substituted alkylene polyamines.

Generally, the hydrocarbons used will have aliphatic unsaturation. In particular instances, the amines may react in a way resulting in the elimination of hydrogen halide, introducing further aliphatic unsaturation into the hydrocarbon radical. Therefore, the hydrocarbon radicals usually will be olefinically unsaturated. However, the olefinic unsaturation does not significantly affect the utility of the product, and when available, saturated aliphatic halide may be used.

After the reaction has been carried out for a sufficient length of time, the reaction mixture may be extracted with a hydrocarbon medium to free the product from any low molecular weight amine salt which has formed. The product may then be isolated by evaporation of the solvent. Further separation from unreacted hydrocarbon or purification may be carried out as desired, e.g., chromatography.

Depending on the particular application of the composition of this invention, the reaction may be carried out in the medium in which it will ultimately find use and be formed at concentrations which provide a concentrate of the detergent composition. Thus, the final mixture may be in a form to be used directly upon dilution in fuels.

The detergent will generally be employed in a hydrocarbon base liquid fuel. The detergent additive may be formulated as a concentrate, using a suitable hydrocarbon alcohol solvent boiling in the range of about 150° to 400° F. Preferably, an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher boiling

aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the detergent additive. In the concentrate, the amount of the additive will be ordinarily at least 10 percent by weight and generally not exceed 70 percent by weight.

The amount of the detergent used in the fuel will generally be from about 100 to 1,000 p.p.m.

In gasoline fuels, other fuel additives may also be included such as antiknock agents, e.g., tetramethyl lead or tetraethyl lead. Also included may be lead scavengers such as aryl halides, e.g., dichlorobenzene or alkyl halides, e.g., ethylene dibromide.

A nonvolatile lubricating mineral oil, e.g., petroleum spray oil, particularly a refined naphthenic lubricating oil having a viscosity at 100° F. of 1,000 to 2,000 SUS, is a suitable additive for the gasoline compositions used with the detergents of this invention and its use is preferred. These oils are believed to act as a carrier for the detergent and assist in removing and preventing deposits. They are employed in amounts from about 0.05 to 0.5 percent by volume, based on the final gasoline composition.

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

Example A

Into a reaction flask was introduced 950 g. of polyisobutylene (approximate molecular weight=950) dissolved in 1,000 ml. of carbon tetrachloride. The mixture was stirred and chlorine was introduced at a rate of 235-250 ml. per minute, the temperature being maintained at 0° C. After the reaction mixture had taken up 51 g. of chlorine, the introduction of chlorine was terminated, the carbon tetrachloride removed in vacuo and the chlorinated polyisobutylene isolated and analyzed. Analysis: wt. percent chlorine, 7.0.

Example B

Into a reaction flask was introduced 225 g. of N-bromosuccinimide, 750 g. of polyisobutylene (approximately 930 average molecular weight) and 750 ml. of carbon tetrachloride, the flask swept with nitrogen and the solution heated to 70° C. while maintaining a positive nitrogen pressure on the flask. To the solution was then added dropwise 0.5 g. of benzoyl peroxide in 50 ml. of carbon tetrachloride. At the end of the addition, the solution was cooled and the succinimide filtered off. The carbon tetrachloride was removed in vacuo. Analysis: wt. percent bromine, 8.86, 8.80.

Example 1

Into a reaction flask was charged 1,156 g. of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 7.8 weight percent chlorine), 75 ml. of xylene and 330 ml. of ethylene diamine, followed by the addition of 330 ml. of n-butanol. The mixture was then raised to a temperature of 100° C. over one hour and the temperature was then raised to about 160° C. and maintained there for about 4½ hours. About 330 ml. of distillate was obtained while raising the temperature from 130° to 160° C. The reaction mixture was transferred to a separatory funnel with the aid of one liter of benzene, and the mixture washed repeatedly first with a dilute aqueous solution of isopropyl alcohol, then with a dilute aqueous solution of a combination of isopropyl alcohol and butanol and finally with water. The volatile materials were then removed from a sample of the washed product by sparging with nitrogen to constant weight on a steam plate. Analysis: titrimetric equivalent wt., 806, equal to 1.74% N; wt. percent chlorine, 0.62.

One thousand four hundred thirty-four g. or about half of the volatile solvents was removed from the main portion of the washed product. This solution containing about 25% volatile solvent (titrimetric equivalent weight=1,051)

was combined with 240 g. of a mixture of other materials prepared similarly to provide a final product having a titrimetric equivalent weight of 985, the product being polyisobutenyl ethylene diamine.

Example 2

Into a reaction flask was introduced 1,000 g. of chloropolyisobutene (polyisobutene of approximately 420 molecular weight chlorinated to approximately 8 weight percent chlorine), 270 ml. of ethylene diamine and 270 ml. of n-butanol. The mixture was heated gradually to 170° C. during 1½ hours; distillate was collected mainly between 130° C. and 160° C. The mixture was then heated for about 3 hours at 170° C. At the end of this time, 1,000 ml. of toluene and 250 ml. of methyl isobutyl carbinol were added and the mixture washed with dilute aqueous isopropyl alcohol followed by repeated washings with water. Some of the volatile solvents were then removed on a steam bath using a nitrogen stream. The combined products from two similar runs were then filtered, yielding 3,911 g. Analysis: titrimetric equivalent wt., 840, equal to 1.67 wt. percent N. Complete removal of volatile solvents from a small sample indicated the product contains about 40% solvents, i.e., toluene and methyl isobutyl carbinol.

Example 3

Following the procedure of Example 2, 1,000 g. of chloropolypropylene (polypropylene of about 800 molecular weight chlorinated to about 6 weight percent chlorine) was reacted with 270 g. of ethylene diamine. The product as finished contained about 15% volatile solvents. Analysis: titrimetric equivalent wt., 1,080, equal to 1.3 wt. percent N.

Example 4

Into a reaction flask was introduced 1,500 g. of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 5.6 weight percent chlorine), 285 g. of alkylene polyamine having an average composition of tetraethylene pentamine and 1,200 ml. of benzene, the mixture heated to reflux, followed by stripping off the benzene and heating the mixture at about 170° C. for about 4 hours. The mixture was then allowed to cool, diluted with equal volumes of mixed hexanes and absolute ethanol, heated to reflux and ½ volume of 10 weight percent aqueous sodium carbonate added. The phases were separated, and the organic phase washed with water, followed by removing the volatile materials in vacuo. Analysis: wt. percent N, 4.15, 4.15; molecular weight (ThermoNam), 1,539.

Example 5

Following the procedure of Example 2, 950 g. of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 4.48 weight percent chlorine) was combined with 270 ml. of ethylene diamine in 270 ml. of n-butanol. The product as finished contained about 20 percent volatile solvents. Analysis: titrimetric equivalent wt., 976, equal to 1.44 wt. percent N.

Example 6

Into a high pressure bomb was introduced 1,200 g. of polyisobutenyl chloride (approximately 500 molecular weight, wt. percent chlorine, ~8) and 400 g. of liquid ammonia, the bomb sealed and heated at 150° C. with rocking for about 15 hours. After cooling, the pressure was vented and the reaction mixture taken up in mixed hexanes, water and alcohol. The organic phase was then washed with 500 ml. of 5 percent sodium hydroxide, followed by repeated washings with water. The solvents were then distilled off and the residue, which weighed 767 g., filtered through Celite.

Titration of the product showed an equivalent weight of 1,090, indicating that the material was 40 percent active (contained 40 percent by weight of polyisobutenyl amine).

In order to demonstrate the effectiveness of the compositions of this invention as detergents and dispersants in fuels, both extended detergent action performance and harm tests were carried out. In the extended detergent action performance test, the ability of the detergent to act to prevent deposits throughout the intake system is determined, while in the harm test, the formation of deposits by the detergent is investigated.

In carrying out the performance test, a 1953 Chevrolet 6-cylinder engine is used, starting with clean cylinder head and intake system. The run is carried out for 200 hours under cyclic conditions, at the end of which time the head and intake system are disassembled and all intake areas from the carburetor to and including the intake valves are inspected. The conditions under which the run is carried out are as follows: Jacket temperature: 185° F.; oil temperature: 185° F.; cycle: idle at 600 r.p.m. 31% of the time, acceleration 16% of the time, cruise at 1,500 r.p.m. or 2,500 r.p.m. 26% of the time, and deceleration 27% of the time. In evaluating the engine, port and valve deposits are rated on a scale of 0 (clean) to 10 (very heavy deposits) and valve deposit weights determined. The remainder of the intake system is rated on a linear scale of 0 (clean) to 16 (deposit 1/16" thick). Also, any stuck intake valves are observed and reported.

The harm test is carried out on a 1960 Chevrolet 6-cylinder engine. Starting with a clean cylinder head, intake system, pistons and new rings, the test is carried out for 200 hours under cyclic conditions. At the end of this time, the engine is disassembled and the parts are inspected. The conditions under which the run is carried out are as follows: Jacket temperature: 200° F.; oil temperature: 125° F.; cycle: idle at 600 r.p.m. 40% of the time, low speed acceleration 20% of the time, high speed acceleration 13% of the time, and cruise at 1,400 r.p.m. 27% of the time. The rating is as follows: port and valve deposits are rated on a scale of 0 (clean) to 10 (very heavy deposits). The percent of oil ring plugging is measured. The piston varnish is rated on a scale of 0 to 10, with 10 as clean. Finally, any stuck intake valves and piston rings are reported.

The following table indicates the results of both the performance and the harm test described above using 250 p.p.m. of the detergent additive.

TABLE.—EXTENDED DETERGENT ACTION TESTS

Additive example	Wt. percent oil ¹	Performance test					Harm test					
		Valve rating	Valve deposit, wt. gms.	Port rating	Intake system	Stuck valves	Valve rating	Port rating	Oil ring plugging	Piston varnish	Stuck valves	Stuck rings
1.....	0.5	2.3	-----	0.7	1	6	1.0	1.0	0	9.6	4	0
2.....	0.5	3.7	3.8	0.2	0	0	1.9	0	0	7.7	0	0
3.....	0.2	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
4.....	0.2	2.0	0.6	0.1	0	0	2.2	0	0	8.1	1	0
5.....	0.2	1.6	1.0	0	0	0	1.3	0.2	0	8.1	1	0
6.....	-----	2.0	-----	0.4	2	1	-----	-----	-----	-----	-----	-----
Base fuel.....	2.2	1.5	1.1	4	4	1	-----	-----	-----	-----	-----	-----
Do.....	0.5	2.0	1.1	0.7	3	0	² 1.9	2.5	0	8.7	2	0

¹ A solvent refined neutral oil, 21.9° API gravity, viscosity at 100° F., 1,685 SUS, viscosity at 210° F., 87 SUS.

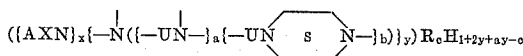
² Average of two base fuel runs.

The data graphically demonstrate the excellent effectiveness of the compositions of this invention. The compositions are excellent detergents, without having serious detrimental side effects. The detergent compositions are readily available by simple synthetic methods, do not produce ash in the engine and either do not or only to an insignificant degree create deposits from their own decomposition products. Moreover, the detergents are effective in cleaning the ports, valves and intake system, so as to provide extended detergent action. Also, good water tolerance can be achieved.

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 fuel composition having a major amount of a hydrocarbonaceous liquid fuel and in an amount to provide detergency and dispersancy, a composition having a molecular weight in the range of 425 to 10,000 of the formula:



wherein

A is hydrogen, hydrocarbyl of from 1 to 10 carbon atoms or hydroxyhydrocarbyl of from 1 to 10 carbon atoms,

X is hydrogen, hydrocarbyl of from 1 to 10 carbon atoms or hydroxyhydrocarbyl of from 1 to 10 carbon atoms and may be taken together with A and the nitrogen to which A and X are attached to form a ring of from 5 to 6 annular members having from 0 to 1 oxygen annular member, 1 nitrogen annular member and from 4 to 5 carbon annular members,

U is alkylene of from 2 to 6 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms, R is an aliphatic hydrocarbon radical or from about 400 to 5,000 average molecular weight,

a is an integer of from 0 to 10,

b is an integer of from 0 to 1,

a+2b is an integer of from 1 to 10,

c is an integer of from 1 to 5 and equal to or less than the number of nitrogen atoms in the molecule,

x is an integer of from 0 to 1,

y is an integer of from 0 to 1, and

x+y is equal to 1.

2. A fuel composition according to claim 1, wherein x is 0,

R is a branched chain aliphatic hydrocarbon radical of from 400 to 3,000 molecular weight,

U is alkylene of from 2 to 3 carbon atoms,

a is an integer of from 0 to 5,

a+2b is an integer in the range of 1 to 5, and

c is an integer of from 1 to 4 and equal to or less than the number of nitrogen atoms in the molecule.

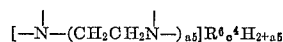
3. A fuel composition according to claim 2, wherein U is polymethylene of from 2 to 3 carbon atoms, and c is 1.

4. A fuel composition according to claim 2, wherein U is polymethylene of from 2 to 3 carbon atoms, and c is greater than 1 and equal to or less than 3.

5. A fuel composition according to claim 1, having from 0.05 to 0.5% by volume of a mineral lubricating oil.

6. A fuel composition according to claim 2, having from 0.05 to 0.5% by volume of a mineral lubricating oil.

7. A fuel composition according to claim 2, wherein said composition to provide detergency and dispersancy is of the formula:



wherein a⁵ is an integer of from 1 to 3; c⁴ is an integer of from 1 to 3, averaging over the entire composition in the range of 1 to 2, and R⁶ is a branched chain aliphatic

11

hydrocarbon radical of from about 420 to 1,500 average molecular weight.

8. A fuel composition according to claim 7, wherein R^6 is polyisobutylene.

9. A fuel composition according to claim 7, having from 0.05 to 0.5 percent by volume of a mineral lubricating oil.

10. A fuel composition having a major amount of a hydrocarbonaceous liquid fuel and in an amount to provide detergency and dispersancy, a composition of the formula:



wherein

R^1 is a branched chain aliphatic hydrocarbon radical of from about 425 to about 3,000 molecular weight,

A^1 is hydrogen, hydrocarbyl or hydroxyhydrocarbyl of from 1 to 10 carbon atoms, and

X^1 is hydrogen, hydrocarbyl or hydroxyhydrocarbyl of from 1 to 10 carbon atoms and may be taken together with A^1 and the nitrogen to which A^1 and X^1 are

12

attached to form a ring of from 5 to 6 annular members, having from 0 to 1 oxygen annular member, 1 nitrogen annular member and from 4 to 5 carbon annular members.

11. A fuel composition according to claim 10, wherein A^1 and X^1 are hydrogen or alkyl of from 1 to 6 carbon atoms.

12. A fuel composition according to claim 10, having from 0.05 to 0.5% by volume of a mineral lubricating oil.

References Cited

UNITED STATES PATENTS

3,050,043	8/1962	Barusch	44—72 XR
3,231,348	1/1966	Lindstrom et al.	44—72
3,275,554	9/1966	Wagenaar	252—50

PATRICK P. GARVIN, *Primary Examiner*.

U.S. Cl. X.R.

44—63, 72; 260—247, 247.5, 268, 583, 584