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Honnen et al.

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[54] **FUEL DETERGENTS**

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[58] **Field of Search** ..... 44/66, 71, 72, 62, 44/63; 252/50; 260/404.5, 583 P, 561 R, 453 AR, 453 AL

[56] **References Cited**

UNITED STATES PATENTS

3,600,413	8/1971	Grimm	44/72
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[57] **ABSTRACT**

The reaction products of hydrocarbon polyamines having a long, substantially aliphatic, hydrocarbon chain bonded to a di- or higher polyamine with certain polyfunctional coupling agents find use as detergents in distillate fuel compositions. The hydrocarbon group is normally branched chain and derived from natural sources or polyolefins, substantially free of aromatic substitution and of about 420 to 10,000 molecular weight. The poly-functional coupling agents are certain polyhalides, polycarboxylic acids, and organic polyisocyanates.

16 Claims, No Drawings

FUEL DETERGENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

Deposits tend to build up in the carburetor throttle body and fuel-intake systems of modern internal combustion engines. The problem becomes critical in automobiles that frequently operate under idling conditions in heavy traffic, such as taxi fleets, delivery fleets, and the like. However, these deposits can be found in heavy amounts in virtually all services, including normal passenger car service. Common results of intake system deposits are carburetor malfunction, poor intake valve seating, heavy manifold deposits and restricted breathing. Detergents are included in distilate fuels to maintain carburetor cleanliness and to exert an extended detergent action over the entire intake system. It is extremely difficult to obtain a satisfactory detergent which is effective in the various areas and under the different conditions in which deposits occur in the internal combustion engine. These problems are made more difficult to solve by the low concentrations in which detergents are used in fuels.

2. Description of the Prior Art

Several recent patents have disclosed the usefulness of high molecular weight hydrocarbyl polyamines as effective detergent/dispersants in lubricating oil compositions and fuels, U.S. Pat. Nos. 3,438,757; 3,574,576; and 3,565,804.

SUMMARY OF THE INVENTION

The complex reaction products of certain high molecular weight branched chain, aliphatic N-hydrocarbyl alkylene polyamines with selected coupling agents which are polyfunctional low molecular weight carboxylic acids, acid halides, anhydrides, polyisocyanates, or hydrocarbon polyhalides can function as detergents in hydrocarbonaceous liquid fuels for internal combustion engines. The hydrocarbyl polyamine reactants have molecular weights in the range of about 450 to 10,000. The hydrocarbyl radical will normally be derived from mineral oils of relatively high molecular weight, or polyolefins, by halogenation of the hydrocarbon and displacement of a halogen with an appropriate polyamine, normally free of unsaturation. The coupling agents of value in the practice of this invention are normally telechelic, relatively low molecular weight, polyfunctional molecules such as certain organic polyhalides, polycarboxylic acids, and organic polyisocyanates which are reactive towards the polyamine. Depending on the coupling agent chosen, the product is a complex amide, imide, polyamide, higher order amine, N-hydrocarbylurea, polyurea, or other complex condensation product.

DETAILED DESCRIPTION OF THE INVENTION

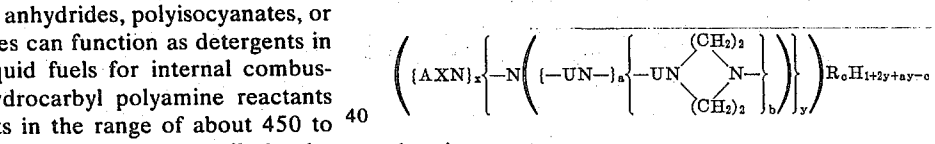
The compositions of this invention are the complex reaction products of certain high molecular weight branched chain, aliphatic N-hydrocarbyl alkylene polyamines with selected coupling agents which are polyfunctional low molecular weight carboxylic acids, acid halides, anhydrides, isocyanates or hydrocarbylhalides. Of course, the products of the coupling reactions are normally of higher average molecular weight than the hydrocarbyl polyamine reactants and normally consist of the condensation product of two hydrocarbyl polyamines through the coupling agent by reaction at a primary or secondary amino nitrogen of the polyamine. Considering the complexity of the polyamine reactants themselves, the several possible sites of reaction therein, and the possibility of coupling two, three or more polyamines, it is difficult to obtain a practical structural description of the product. Hence, the products are characterized by the following descriptions of the reactants and reaction conditions.

Hydrocarbyl-Substituted Polyamines

The hydrocarbyl-substituted polyamine reactants of this invention are high molecular weight branched chain aliphatic hydrocarbyl N-substituted alkylene polyamines. Hydrocarbyl, as used herein, denotes an organic radical composed solely of carbon and hydrogen, which may be aliphatic, alicyclic, or aromatic, or combinations thereof, e.g., aralkyl. Preferably, the hydrocarbyl groups will be relatively rree of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic. The hydrocarbyl polyamines will have average molecular weights in the range of about 450 to 10,000, more usually in the range of about 750 to about 6,000. When the hydrocarbyl groups are of lower molecular weight, the average number of hydrocarbyl substitutes in the polyamine can be greater than one. The hydrocarbyl will normally be aliphatic, having from zero to two sites of unsaturation, more usually zero to two sites of ethylenic unsaturation and preferably from zero to one site of ethylenic unsaturation.

The hydrocarbyl group will normally be derived from a polyolefin derived from olefins of from two to six carbon atoms (ethylene being copolymerized with an olefin of at least three carbon atoms), or from a high molecular weight petroleum-derived hydrocarbon.

For the most part, the polyamines used in this invention will be of the following general formula:



wherein:

U is alkylene of from two to six carbon atoms, more usually of from two to three carbon atoms, there being at least two carbon atoms between the nitrogen atoms;

a is an integer of from 0 to 10, usually of from 1 to 6, and more usually of from 1 to 4;

b is an integer of from 0 to 1 and preferably 0;

a+2*b* is an integer of from 1 to 10, more usually an integer of from 1 to 6 and preferably an integer of from 1 to 4;

c is an integer or fractional number (when averaged over the entire composition) in the range of from 1 to 5, preferably 1 to 3, and equal to or less than the number of nitrogen atoms in the molecule, usually on the average less than the total number of nitrogen atoms in the molecule;

R is an aliphatic or alicyclic branched hydrocarbyl radical derived from petroleum hydrocarbons or olefin monomers of from two to eight carbon atoms, preferably of from three to four carbon atoms, ethylene being copolymerized with a higher homolog (an olefin of at least three carbon atoms) and having from zero to two sites of aliphatic unsaturation, more usually from zero to two sites of ethylenic unsaturation and preferably from zero to one site of ethylenic unsaturation, having greater than 30 carbon atoms and not more than 300

carbon atoms, more usually 50 to 200 carbon atoms and preferably 60 to 200 carbon atoms;

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

X is hydrogen, hydrocarbyl of from one to 10 carbon atoms or hydroxyhydrocarbyl of from one to 10 carbon atoms and may be taken together with A and the hydrogen to which A and X are attached to form a ring of from five to six annular members having from zero to one oxygen annular members, one nitrogen annular member, and from four to five carbon annular members,

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.

The alkylene radical, indicated as U, will have from two to six carbon atoms, the nitrogens connected by U being separated by at least two carbon atoms. The alkylene group may be straight chain or branched chain, the remaining valences of the alkylene group being on different carbon atoms. Illustrative alkylene groups include ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, 1,2-propylene, 2-methyl-1,3-propylene, 1,4-(2,3-dimethylbutylene), etc.

The hydrocarbyl radical indicated by R may be aliphatic or alicyclic and, except for adventitious amounts of aromatic structure present in petroleum mineral oils, will be free of aromatic unsaturation. The hydrocarbon groups are derived from petroleum mineral oil or polyolefins, either homo-polymers or higher order polymers, of 1-olefins of from two to six carbon atoms, ethylene being polymerized with a higher homolog. The olefins may be mono- or poly-unsaturated, but the poly-unsaturated olefins require that the final product be reduced to remove substantially all of the residual unsaturation.

Illustrative sources for the high molecular weight hydrocarbons from petroleum mineral oils are naphthenic bright stocks. For the polyolefin, illustrative polymers include polypropylene, polyisobutylene, poly-1-butene, copolymer of ethylene and isobutylene, copolymer of propylene and isobutylene, poly-1-pentene, poly-4-methyl-1-pentene, poly-1-hexene, poly-3-methylbutene-1, etc.

The hydrocarbyl group will normally have at least one branch per six carbon atoms along the chain, preferably at least one branch per four carbon atoms along the chain, and particularly preferred that there be from 0.5 to one branch per carbon atom along the chain (at least one branch per two carbon atoms along the chain). These branched chain hydrocarbyl groups are readily prepared by the polymerization of olefins of from three to six carbon atoms and preferably from olefins of from three to six carbon atoms. The addition polymerizable olefins employed are normally 1-olefins. The branch will be from one to four carbon atoms, more usually of from one to two carbon atoms and preferably methyl.

The hydrocarbyl-substituted polyamine can be a polyethylene polyamine, or polypropylene polyamine, where, for example, the polyethylene polyamine is of the general formula:

$$\{-\overset{|}{N}(-CH_2CH_2\overset{|}{N}-)_{a^1}\}R^1_{c^1}H_{3+a^1-c^1}$$

wherein:

a^1 is in the range from 1 to 5;

c^1 is in the range from 1 to 4 and equal to or less than the number of nitrogen atoms; and

R^1 is a branched chain aliphatic hydrocarbyl group derived from olefins of from two to six carbon atoms and of average molecular weight in the range from about 420 to about 2,000, with the proviso that when the monomer is ethylene it is copolymerized with a higher homolog.

In order to include possible variations, the generic formula does not indicate to which nitrogen atom the R group and the H atoms are bonded. Rather, free valences are indicated by bars, and the total number of R groups and H atoms indicated next to the basic polyamine structure. The generic formula employed provides a simple means for including the possible variations that will occur when a polyamine is used having non-equivalent amine nitrogens. Numerous examples and illustrative compounds within the above formula are given in U.S. Pat. Nos. 3,438,757 and 3,574,576 which are incorporated herein by reference.

In preparing the hydrocarbyl-substituted polyamine reactants, rarely will a single compound be employed. With both the polymers and the petroleum-derived hydrocarbyl groups, the composition is a mixture of materials having various structures and molecular weights. Therefore, in referring to molecular weight, average molecular weights are intended. Furthermore, when speaking of a particular hydrocarbyl group, it is intended that the group include the mixture that is normally contained with materials which are commercially available; that is, polyisobutylene is known to have a range of molecular weights, and may also include very small amounts of very high molecular weight materials. Furthermore, depending on the method of preparation, the end group of the polymer may vary and may be terminated not only with an isobutene group, but with a 1- or 2- butene group.

Similarly, the alkylene polyamines which are commercially available are frequently mixtures of various alkylene polyamines having one or two species dominating. Thus, in commercially available tetraethylene pentamine, there will also be small amounts of pentaethylene hexamine and triethylene tetramine. In referring to tetraethylene pentamine, for example, it is intended not only to include the pure compound, but those mixtures which are obtained with commercially available alkylene polyamines. Finally, as indicated, in preparing the compounds of this invention, where the various nitrogen atoms of the alkylene polyamine are not equivalent, the product will be a mixture of the various possible isomers, and the coupling of the hydrocarbyl-substituted polyamines can produce a variety of possible final structures.

Coupling Agents

The coupling agents which function to yield detergents of the present invention upon reaction with the high molecular weight hydrocarbyl-substituted polyamines are normally telechelic (terminally reactive) polyfunctional molecules of relatively low molecular weight. They may be classified among several general groups of polyfunctionalities. These functionalities are chemical groupings distinguished by their ability to react with primary or secondary amino nitrogen atoms in a hydrocarbyl-substituted amine to yield products in which the coupling agent is bound to said amino nitrogen by a chemical bond.

Both structure and molecular weight are important considerations with respect to the performance of hydrocarbyl-substituted amines as gasoline additives. Molecular weights are increased by the reaction of hydrocarbyl-substituted polyamines with polyfunctional compounds. Reactions with the telechelic difunctional compounds of the present invention indicate that molecular weights are, in general, doubled, indicating dimerization. Since the molecular weight of the coupling compounds are small compared to that of the hydrocarbyl-substituted polyamines, the nitrogen contents are essentially unchanged.

Dimerization also alters the chemical nature of the amino nitrogen. The product of the reaction of polybutene ethylene diamine with 1,4-dichloro-2-butene is expected to have properties which differ from that of polybutene ethylene diamine, in that all the amino nitrogens are allylic instead of only one in the starting polybutene ethylene diamine. Similarly, the use of p-bis(chloromethyl)benzene as the coupling agent gives a product containing both benzylic and allylic amines. On the other hand, the use of acid halides, or acid anhydrides, converts the amines into amides with lower total bacisity as well as higher molecular weight.

1. Polycarboxylic acids, acid halides, anhydrides, or equivalents, which react with primary or secondary amino nitrogen to yield amides and polyamides, or react with primary amino nitrogen to form imides, are satisfactory coupling agents in the present invention. Examples of such polycarboxylic acids include oxalic, malonic, succinic, glutaric, adipic, pimelic, azelaic, sebacic and other α,ω-dibasic acids of relatively low molecular weight and the hydrocarbyl-substituted acids of the same name. Unsaturated polycarboxylic acids such as maleic, fumaric, itaconic are useful coupling agents, as are the substituted polycarboxylic acids such as tartronic, malic, tartaric, nitrile triacetic, and citric acids. Coupling agents include aromatic carboxylic acids and equivalents such as phthalic anhydride, terephthaloyl chloride, and preferably, pyromellitic dianhydride. In general, the polycarboxylic coupling agents will be characterized by molecular weights below about 300 and carbon numbers in the range from C_2 to about C_{20}.

2. Organic polyisocyanates, such as toluene diisocyanate (made from 2,1-amino toluene), react with primary or secondary amino nitrogen to yield hydrocarbyl-ureas or polyureas which are satisfactory fuel detergents. Examples of such organic polyisocyanates include phenylene diisocyanate, toluene diisocyanate, methylenediphenyldiisocyanate, alkylates methylenephenyldiisocyanate, hexamethylenediisocyanate, and polymeric isocyanates, such as polymethylenepolyphenylisocyanate. In general, the organic polyisocyanate coupling agents will be characterized by molecular weights below about 400 and carbon numbers in the range from about 8 to about 20.

3. Organic polyhalides which find use within the scope of this invention are low molecular weight telechelic dihalides, such as 1,4-dichloro-2-butene, or p-bis-(chloromethyl)benzene, generally C_4–C_{20}, in which the halogens are attached to different carbon atoms and preferably are separated by several carbon atoms. The organic dihalides react with primary or secondary amino nitrogen to yield higher order amines. They are preferred coupling agent of the invention because of their effectiveness in deposit control.

Method of Preparation

The coupling agents are illustrated by the known, comercially available, chemicals previously discussed. The method of preparation of the hydrocarbylpolyamines has been described and illustrated with numerous examples in U.S. Pat. Nos. 3,565,804, 3,574,576 and 3,438,757 which are herein incorporated by reference. The products of this invention are prepared by reacting a coupling agent with a hydrocarbyl polyamine by directly mixing the reactants, or solublizing in a mutual solvent such as benzene, xylene, or hexane. In general, the mole ratio of the reactants can range from 1:3 to 3:1. Normally, the reactions proceed by contacting the reagents, with stirring, at temperatures from about 25°C. to about 200°C. for from 1 to 48 hours. The organic product is usually washed, the aqueous phase removed, and the product is stripped of solvent. Infra-red spectra were taken routinely to check the product. Molecular weight measurements indicate the products correspond to the coupling of two hydrocarbyl polyamines. To illustrate, the products obtained in the following examples were largely "dimeric" as shown by molecular weight determinations.

EXAMPLE I: Polyisobutenyl ethylene diamine (500 g., 0.281 mole) wherein the polybutenyl is of average molecular weight 1,400, was heated to 115°C. and 1,4-dichloro-2-butene (21.9 g., 0.175 mole) was added in one step. The temperature was increased to 190°C. for 20 minutes, then lowered to 150°C. and held for 3.5 hours. The temperature was then increased to 210°C. over a 35-minute period. The mixture was cooled, diluted with 1 liter of mixed hexanes, 800 ml. of methanol and 500 ml. of dilute NaOH. The resulting mixture was heated to boiling and poured into a separatory funnel. The aqueous layer was removed and the organic layer was washed with 500 ml. of boiling water. The mixture was concentrated by distillation with final stripping carried out on the solvent stripper at 100°C for 1.5 hours to obtain 456 g. of dimerized material with the following analysis molecular weight, 2,530: percent nitrogen, 1.34.

EXAMPLE II: Polyisobutenyl tetraethylene pentamine (464 g., 0.33 mol) wherein the polybutenyl is of average molecular weight 950 was heated to 80°C, followed by the one-step addition of 20.4 g. (0.163 mol) of 1,4-dichloro-2-butene. The temperature was increased to 145°C and held for 1 hour and 20 minutes. Upon cooling, 600 ml. of mixed hexanes, 600 ml. of isopropyl alcohol, and 300 ml. of water containing 15 g. of NaOH was added. The aqueous layer was removed and 150 ml. more water added, followed by shaking. The aqueous layer was removed. Final washing was carried out with 300 ml. of water. The organic layer was concentrated by distillation, with final stripping to yield 465 g. of dimer: molecular weight 2,550: per cent nitrogen 4.33.

EXAMPLE III: Polyisobutenyl ethylene diamine of Example I (100 g., 0.056 mol) was heated to 120°C. p-bis(chloromethyl)benzene was added in one step and the temperature increased to 160°C and held for 3 hours 15 minutes. The mixture was diluted with hexane and isopropyl alcohol, washed with dilute NaOH and water, and stripped to yield 95 g. of dimer: molecular weight 2,700: percent nitrogen 1.48; IR 1,680 cm^{-1}.

EXAMPLE IV: Polyisobutenyl amine (206 g., 0.225 mol), wherein the polyisobutenyl amine is of average molecular weight 820, was heated to 110°C and 1,4-dichloro-2-butene (12.8 g., 0.133 mol) was added in one step. The mixture was heated for about 7 hours with the temperature rising to 133°C. The mixture was cooled, diluted with mixed hexanes, washed with dilute sodium hydroxide, then washed with water until washings were neutral. Solvent was removed from the mixture by stripping on the solvent stripper at 100°C for several hours to give 183.2 g. partially dimerized material having the following analysis: molecular weight, 1,290; percent nitrogen, 1.48.

EXAMPLE V: 25 ml. of pyridine and the polyisobutenyl ethylene diamine of Example I (100 g.) were dissolved in 50 ml. of benzene and heated to reflux. Pyromellitic dianhydride (6.1 g., 0.028 mol) and 40 ml. of hot pyridine were added drop-wise over a 10-minute period. A completely homogeneous solution resulted. Heating at reflux was continued for 1 hour 15 minutes, then solvent was removed by distillation until the temperature reached 180°C. The mixture was cooled to 150°C and held for 3 hours, then cooled to room temperature and 100 ml. of toluene and 25 ml. of n-butanol were added. The mixture was washed three times in 100 ml. portions of water containing 5 percent n-butanol, then concentrated by distillation with final stripping yielding 99 g. of product; molecular weight 3,550; per cent nitrogen 1.54; IR, 1,635 cm^{-1} (amide), and 1,725 cm^{-1} (imide); base number of product, 19 mg. KOH/g; base number of starting material, 53 mg. KOH/g; acid number of product, 6.1 mg. KOH/g.

EXAMPLE VI: Terephthaloyl chloride (5.7 g., 0.028 mol) and the polyisobutenyl ethylene diamine of Example I (100 g.) were dissolved in 100 ml. of benzene and heated to reflux for 20 minutes. Solvent was removed at distillation until the temperature reached 150°C. This temperature was held for 3.5 hours, followed by workup as in Example III giving 94 g. of material: molecular weight 3,380; percent nitrogen 1.53; IR 3,320 cm^{-1} (NH), 1,650 cm^{-1} (amide); base number of starting material 53 mg. KOH/g; base number of product 23 mg. KOH/g; acid number of product 1.8 mg. KOH/g.

EXAMPLE VII: Polyisobutenyl ethylene diamine of Example I (672 g.) was added to 150 ml. of toluene and 86.4 g. of diphenolic acid—dissolved in 300 ml. of tetrahydrofuran. The mixture was stirred at 151°C for 12 hours under nitrogen. The product was stripped to 325°F and weighed 753 g.

EXAMPLE VIII: 19.2 g. of trimellitic anhydride was mixed with the polyisobutenyl ethylene diamine of Example I (672 g.) in 125 ml. of tetrahydrofuran. The mixture was stirred for 12 hours at about 163°C under nitrogen. The product was stripped to 335°F and weighed 696 g.

EXAMPLE IX: Oleyl amine (52.6 g., 0.196 mol) in 150 ml. of xylene was heated to 100°C and 1,4-dichloro-2-butene (11.1 g., 0.098 mol) was added in one step. Heating was continued for 2½ hours at which time the temperature had increased to 141°C. The mixture was cooled, washed with dilute sodium hydroxide, then washed with water until the washings were neutral. The mixture was stripped on the solvent stripper to give 46.5 g. of material having the following analysis: molecular weight, 700; percent nitrogen, 4.48; percent chlorine, 1.64.

EXAMPLE X: Ethylene diamine tetra-acetic acid (29.2 g.) was mixed with the polyisobutenyl ethylene diamine of Example I (896 g.) and 100 ml. of toluene. The mixture was stirred at 325–335°F for 6 hours under a nitrogen atmosphere. About 6–7 cc. of H_2O was collected in a Stark trap and the product was stripped of toluene under reduced pressure.

EXAMPLE XI: N,N-bis-(2-hydroxyethyl)glycine (81.5 g.) was mixed with polyisobutenyl ethylene diamine of Example I (1,010 g.) in 150 cc. of toluene. The reaction mixture was stirred at 325–330°F. for 8 hours. The mixture was dissolved in hexane and filtered. The hexane was stripped off under reduced pressure.

EXAMPLE XII: Itaconic acid (26 g.) was mixed with polyisobutenyl ethylene diamine (808 g.) and 150 cc. of toluene. The mixture was stirred at 325–335°F for 12 hours under nitrogen atmosphere. The toluene was removed under reduced pressure.

EXAMPLE XIII: Polyepoxide (25 g.) was mixed with polyisobutenyl ethylene diamine of Example I (308 g.). The mixture was stirred at 280–290°F for 8 hours under a nitrogen atmosphere. The final product was stripped to 250°F.

EXAMPLE XIV: Epichlorohydrin (28 g.) was mixed with polyisobutenyl ethylene diamine of Example I (672 g.) and the mixture was stirred at 230–235°F for 15 hours. The mixture was stripped to 325°F under vacuum.

EXAMPLE XV: Polyisobutenyl ethylene diamine of Example I (900 g.) was mixed with 900 g. of a neutral oil and stirred at 200°F for 15 minutes. 43.5 g. of toluene 2,4-diisocyanate was then added and the mixture stirred at 295–320°F for 8 hours. The product was stripped, dissolved in hexane and filtered. The hexane was removed under reduced pressure.

EXAMPLE XVI: Fumaric acid (7.78 g.) was mixed with an approximately equimolar amount of the polyisobutenyl ethylene diamine of Example I (100 g.) in 600 ml. of xylene. N_2 was flushed during the reaction which occurred at xylene reflux temperature for 6 hours. 1.2 ml. of water was collected overhead. 500 ml. of methyl alcohol and 100 ml. of H_2O were added to the reaction product and the polymer layer separated from the aqueous layer. The hexane solubles were azeotroped with benzene to remove excess water and the solvents were stripped under vacuum. Molecular weight about 2,380; percent nitrogen 1.37.

EXAMPLE XVII: Maleic anhydride (5.4 g.) was mixed with 100 g. of the polyisobutenyl ethylene diamine of Example I in 600 ml. of xylene. The reaction mixture was flushed with N_2 and reaction occurred at the xylene reflux temperature for 6 hours. About 1 ml. of water was collected as a reaction product. The product was separated with ethanol-water several times, azeotroped with benzene and stripped under vacuum. Molecular weight about 2,997; percent 1.33.

EXAMPLE XVIII: d-tartaric acid (20 g.) was mixed with 100 g. of the polyisobutenyl ethylene diamine of Example I in 600 ml. of xylene. The system was flushed with nitrogen and reacted at xylene reflux temperature for 6 hours. About 5.9 ml. of water was collected as a reaction product. The polymer product was separated by adding about 500 ml. of ethanol (95 percent) and 100 ml. of water, boiling the mixture, and removing the non-aqueous layer. This was repeated. The polymer product was then azeotroped with benzene to remove the last traces of water and the product was stripped

under vacuum. Molecular weight about 2,980; percent nitrogen 1.34.

Compositions

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 in 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 may be formulated as a concentrate, using a suitable hydrocarbon solvent. Preferably, an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher boiling aromatics of aromatic thinners. Aliphatic alcohols of about three to eight carbon atoms, such as isopropanol, isobutanol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the detergent additive.

In the fuel, the concentration of the detergent will generally be at least 100 p.p.m. and usually not more than 4,000 p.p.m., more usually in the range of from about 200 to about 800 p.p.m. In concentrates, the detergent will generally be from 1 to 50 weight percent, more usually from about 5 to 30 weight percent, and will generally not exceed 80 percent by weight.

In gasoline fuels, other fuel additives may also be included such as anti-knock agents, e.g. tetramethyl lead, tetraethyl lead. Also included may be lead scavengers such as aryl halides, e.g. dichlorobenzene or alkyl halides, e.g. ethylene dibromide. A non-volatile 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. Similar hydrocarbon oils, such as polypropylene oils can also be used. These oils are believed to act as a carrier for the detergent and assist in removing and preventing deposits. They are employed in amounts of from about 0.05 to 0.5 percent by volume, based on the final gasoline composition.

Evaluation

To demonstrate the effectiveness of the compositions of this invention as detergents, a number of fuel compositions were tested in a single-cylinder engine having a compression ratio of 9:1, a bore of 3.25 inches, a stroke of 4.5 inches and the displacement of 37.22 cubic inches. To the fuel were added 1,000 p.p.m. of a carrier oil (naphthenic oil of 1,740 SUS at 100°F.) containing sufficient detergent to give a concentration of 250 p.p.m. detergent in the fuel. The duration of the test was 12 hours, at 1,800 rpm, a jacket temperature of 212°F, and engine manifold vacuum of 15-inch Hg, intake temperature of 95°F, air/fuel ratio of 14 and ignition spark timing 15° BTC. After the test, the engine was disassembled and the deposits on the intake valve were weighed after washing with hexane. The results were as follows.

TABLE II

Composition	Coupling Agent	Hexane Washed Valve Deposits in Mg
I	1,4-dichloro-2-butene	18
II	1,4-dichloro-2-butene	12
III	p-bis(chloromethyl)benzene	12
IV	1,4-dichloro-2-butene	11
V	pyromellitic dianhydride	30
VI	terephthaloyl chloride	15
IX	1,4-dichloro-2-butene	437
Reference	No additive	76

In Table II the roman numeral compositions refer to the examples previously given. The reference fuel contains 1,000 p.p.m. of carrier oil. The data graphically demonstrate the applicability of the compositions of this invention. Excellent detergent and dispersant results are obtained, which in most cases are superior to those obtained from well-known and widely used dispersant/detergent additives. It can be seen that the dimerized structures made from fairly low molecular weight amines, e.g. oleylamine, Example IX, have very poor intake valve performance, while the higher molecular weight polybutenyl amine products of Examples I, II and IV, with the same coupling agent, give a very small amount of deposit.

The additives of this invention are able to function in both lubricating oils and fuels. Moreover, they are readily available by simple synthetic methods and they provide detergency without producing ash.

As will be evident to those skilled in the art, various modifications of 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 of from the scope of the following claims.

We claim:

1. A composition which is the reaction product of a hydrocarbyl-substituted polyamine wherein the hydrocarbyl is of from 40 to 300 carbon atoms and is an aliphatic or alicyclic branched chain hydrocarbyl radical derived from petroleum hydrocarbons or polyolefins of monomers from two to six carbon atoms, with the proviso that when the monomer is ethylene it is copolymerized with a higher homolog; and a coupling agent selected from the group consisting of C_2–C_{20} polycarboxylic acids, C_8–C_{20} polyisocyanates having a molecular weight below 400 and C_2–C_{20} hydrocarbyl dihalides.

2. A composition according to claim 1, wherein the hydrocarbyl polyamine is of the general formula:

$$\left\{-\underset{|}{N}\left(-CH_2CH_2\underset{|}{N}-\right)_{a^1}\right\}R^1{}_{c^1}H_{3+a^1-c^1}$$

wherein:

a^1 is in the range of 1 to 5;

c^1 is in the range of 1 to 4 and equal to or less than the number of nitrogen atoms; and

R^1 is a branched chain aliphatic hydrocarbyl group derived from olefins of from three to four carbon atoms and of an average molecular weight in the range from about 560 to about 2,000.

3. A composition according to claim 2, wherein the hydrocarbyl polyamine is a polyisobutenyl ethylene diamine having from one to two polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.

4. A composition according to claim 2, wherein the hydrocarbyl polyamine is a polyisobutenyl diethylenetriamine having from one to two polyisobutenyl groups

of from about 560 to about 2,000 average molecular weight.

5. A composition according to claim **2,** wherein the hydrocarbyl polyamine is a polyisobutenyl triethylenetetramine having from one to three polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.

6. A composition according to claim **2,** wherein the hydrocarbyl polyamine is a polyisobutenyl tetraethylenepentamine having from 1 to 3 isobutenyl groups of from about 560 to about 2,000 average molecular weight.

7. A fuel composition having a major amount of a hydrocarbonaceous liquid fuel and in an amount to provide detergency, the reaction product of a hydrocarbyl amine wherein the hydrocarbyl is of from 40 to 300 carbon atoms and is an aliphatic or alicyclic branched chain hydrocarbyl radical derived from petroleum hydrocarbons or polyolefins of monomers from two to six carbon atoms, with the proviso that when the monomer is ethylene, it is copolymerized with a higher homolog; and a coupling agent selected from the group consisting of C_2–C_{20} polycarboxylic acids, C_8–C_{20} polyisocyanates having a molecular weight below 400 and C_2–C_{20} hydrocarbyl dihalides.

8. A composition according to claim **7,** wherein the hydrocarbyl polyamine is of the general formula:

$$[-N(-CH_2CH_2N-)_{a^1}]R^1_{c^1}H_{3+a^1-c^1}$$

wherein:

a^1 is in the range of 1 to 5;

c^1 is in the range of 1 to 4 and equal to or less than the number of nitrogen atoms; and

R^1 is a branched chain aliphatic hydrocarbyl group derived from olefins of from three to four carbon atoms and of an average molecular weight in the range from about 560 to about 2,000.

9. A composition according to claim **8,** wherein the hydrocarbyl polyamine is a polyisobutenyl ethylene diamine having from one to two polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.

10. A composition according to claim **8,** wherein the hydrocarbyl polyamine is a polyisobutenyl diethylenetriamine having from one to two polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.

11. A composition according to claim **8,** wherein the hydrocarbyl polamine is a polyisobutenyl triethylenetetramine having from one to three polyisobutenyl triethylenetetramine having from one to three polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.

12. A composition according to claim **8,** wherein the hydrocarbyl polyamine is a polyisobutenyl tetraethylenepentamine having from one to three polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.

13. A composition according to claim **7,** wherein the coupling agent is dichlorobutene.

14. A composition according to claim **7,** wherein the coupling agent is terephthaloyl chloride.

15. A composition according to claim **7,** wherein the coupling agent is p-bis(chloromethyl)benzene.

16. A composition according to claim **7,** wherein the coupling agent is toluene diisocyanate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,785,789 Dated January 15, 1974

Inventor(s) LEWIS R. HONNEN and MARVIN D. COON

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

Column 11, line 28, the formula should read:

$$--\{-N(-CH_2CH_2N-)_{a^1}\}R^1{}_{c^1}H_{3+a^1-c^1}--$$

Column 12, lines 16 - 20, should read:

--having from one to three polyisobutenyl groups of from about 560 to about 2,000 average molecular weight.--

Signed and sealed this 5th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents