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DISTILLATE FUEL COMPOSITIONS HAVING A HYDROCARBON SUBSTITUTED ALKYLENE POLYAMINE

Lewis R. Honnen and Robert Gordon Anderson, Novato, Calif., assignors to Chevron Research Company, San Francisco, Calif.

No Drawing. Continuation-in-part of abandoned application Ser. No. 408,686, Nov. 3, 1964. This application Sept. 20, 1965, Ser. No. 488,775

The portion of the term of the patent subsequent to Apr. 15, 1986, has been disclaimed

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9 Claims

ABSTRACT OF THE DISCLOSURE

Fuel compositions having polypropylene or polyisobutylene substituted polyamines as detergents or dispersants.

This application is a continuation-in-part of application Ser. No. 408,686, filed Nov. 3, 1964, now abandoned.

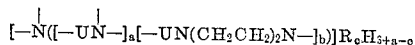
This invention concerns novel high molecular weight hydrocarbon polyamines and their use as detergents in fuels and lubricating oils. More particularly, this invention concerns novel high molecular weight branched chain aliphatic hydrocarbon substituted polyamines, their use as detergents in fuels and lubricating oils and the fuel and lubricating oil compositions containing the novel polyamines.

The formation of deposits and sludge remains a continuing problem in the smooth operation of internal combustion engines. The presence of constricted openings and narrow tolerances in the areas of moving parts provides numerous opportunities for deposits to seriously reduce the operating efficiency of the engine. With fuels, the nozzles, ports and valves, by or through which the fuel is introduced into the piston chamber, must all be maintained relatively free of deposits in order to maintain optimum engine efficiency. With lubricating oil, the lubricated parts, such as the pistons and piston rings, must also be maintained relatively free of deposits. In order to keep these various areas and parts relatively clean and open or free to move, detergents are frequently used in fuels and lubricating oils.

It is not sufficient, however, that a detergent be able to maintain deposits suspended in solution, but the detergent itself must not significantly enhance the formation of sludge and deposits. Under the harsh conditions present in the engine, compounds which have good deterative capability are found to be unacceptable because of the greatly enhanced formation of deposits resulting from their decomposition.

Pursuant to this invention, high molecular weight branched chain aliphatic hydrocarbon N-substituted alkylene polyamines are provided which are superior detergents and dispersants in both lubricating oils and hydrocarbonaceous fuels for internal combustion engines, being effective under wide variations in operating conditions. The compositions of this invention have molecular weights in the range of about 450 to 10,000, more usually in the range of 450 to 5,000 and preferably in the range of 450 to 3,500.

For the most part, the compositions of this invention are described by the following formula:



The above symbols are defined as follows:

U—alkylene of from 2 to 6 carbon atoms

a—an integer of from 0 to 10

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b—an integer of from 0 to 1

a+2b—an integer of from 1 to 10

c—an integer or fractional number of from 1 to 5, but per molecule less than the number of nitrogen atoms in the molecule

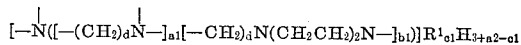
R—hydrocarbon radical relatively free of aromatic unsaturation of from about 400 to 5,000 molecular weight.

The alkylene radical, indicated as U, will have from 2 to 6 carbon atoms, the nitrogens connected by U being separated by at least 2 carbon atoms. (By alkylene is intended the normal meaning that the valences be on different carbon atoms.) The alkylene group may be straight chain or branched. Various alkylene groups include ethylene, 1,2-propylene, trimethylene, pentamethylene, hexamethylene, 2-methyl 1,3-propylene, etc.

The hydrocarbon radical indicated by R may have a variety of structures and may be aliphatic or alicyclic, and is generally free of aromatic unsaturation. Conveniently, the hydrocarbon radical may be a polymer of olefins of from 2 to 6 carbon atoms (if ethylene is used, the ethylene will be copolymerized with an olefin of at least 3 carbon atoms) or may be derived from naturally occurring products of relatively high molecular weight, e.g., naphthenic bright stock.

The alkylene polyamines may be derived from various amino compounds such as ethylene diamine, diethylene triamine, tetraethylene pentamine, octaethylene nonamine, nonaethylene decamine, 2-aminoethyl piperazine, 1,3-propylene diamine, 1,2-propylene diamine, tetramethylene diamine, etc.

The preferred compositions of this invention will generally be of the following formula:



The above symbols are defined as follows:

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 or fractional number in the range of 1 to 3, generally per molecule there being fewer R¹ groups than nitrogen atoms

d¹—an integer in the range of 2 to 3

R¹—a branched chain aliphatic radical of from about 400 to 3,000 molecular weight.

As indicated, R¹ is an aliphatic branched chain hydrocarbon radical. R¹ may be aliphatically saturated or have aliphatic unsaturation, e.g., olefinic. Generally, R¹ will have from 0 to 1 sites of aliphatic unsaturation. By branched it is intended that on the average there be at least one branch per 6 carbon atoms along the chain, preferably at least 1 branch per 4 atoms along the chain and particularly preferred that there be from 0.5 to 1 branch per carbon atom along the chain (at least one branch per two carbon atoms along the chain).

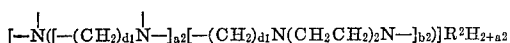
The branched chain aliphatic hydrocarbon radical is readily prepared by polymerizing olefins of from 2 to 6 carbon atoms (copolymerizing an olefin of from 3 to 6 carbon atoms with ethylene) and preferably polymerizing olefins of from 3 to 6 carbon atoms, particularly isobutylene.

In most instances a single compound will not be used as a reactant in the preparation of the compounds 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 or dichloroethylene and ammonia will have both lower and higher members, e.g., triethylene tetramine and pentaethylene hexamine, but the composition will be mainly tetraethylene pent-

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amine 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:

a^2 —an integer of from 0 to 5, preferably of from 0 to 4
 b^2 —an integer of from 0 to 1, preferably 0 when a^2 is greater than 0

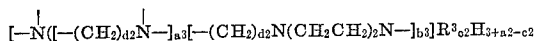
$a^2 + 2b^2$ —an integer of from 1 to 5

d^1 —an integer of from 2 to 3

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

Illustrative compounds within the above formula are as follows: N-polyisobutenyl ethylene diamine, N-propenyl ethylene diamine, N-poly(1-butenyl) ethylene diamine, N-(alternating copolymers 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:

a^3 —an integer of from 1 to 5, preferably an integer of from 1 to 4

b^3 —an integer of from 0 to 1, preferably 0 when a^3 is greater than 0

$a^3 + 2b^3$ —an integer of from 1 to 5

c^2 —a fractional or whole number in the range of 1 to 3, generally per molecule there are fewer R^3 groups than nitrogen atoms

d^2 —an integer of from 2 to 3

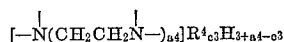
either free of or having aliphatic unsaturation e.g., olefinic and of from 400 to 3,000 molecular weight, preferably of from 400 to about 2,500 molecular weight.

(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.)

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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-N'-di(polyisobutenyl) triethylene tetramine, N,N'-di(polypropenyl) tetraethylene pentamine, N,N'-di(polyisobutenyl) tetraethylene pentamine, N,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 or fractional number of from 1 to 3, preferably of from 1 to 2, generally per molecule there being fewer R^4 groups than nitrogen atoms

R^4 —a branched chain aliphatic hydrocarbon radical of from 40 to 3,000 molecular weight, preferably of from 400 to 2,500 molecular weight, and, particularly preferred, either polypropenyl or polyisobutenyl.

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 one branch per 6 carbon atoms along the chain and preferably at least one branch per 4 carbons along the chain. The preferred olefins, propylene and isobutylene, have from 0.5 to 1 branch per atom along the hydrocarbon chain.

Alternatively, various naturally occurring materials may be used which have the desired molecular weight and aliphatic or alicyclic character.

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 haloalkane and alkylene polyamine or polyalkylene polyamine 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 alkylene amine will generally be in the range from about 0.2 to 10 moles of alkylene amine per mole of halohydrocarbon, more usually 0.5 to 5 moles of alkylene 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.

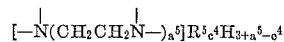
Generally, the hydrocarbons used will have aliphatic unsaturation. In particular instances, the amines may react in a way resulting in the elimination of hydrogen halide, introducing further aliphatic unsaturation into the hydrocarbon radical. Therefore, the hydrocarbon radicals usually will be olefinically 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 reaction mixture may be in a form to be used directly upon dilution in lubricating oils or fuels.

As has already been indicated, the compositions encompassed by this invention have a broad spectrum of uses as detergents and dispersants. Not only do they find use as detergents and dispersants in lubricating oils under the "hot" conditions of the diesel engine and the relatively cooler conditions of the automobile internal combustion engine, where wide fluctuations in temperature occur, but the detergents of this invention may also be used in 2-cycle spark ignition engines—where the lubricating oil containing the detergent is introduced into the fuel—and directly in fuels, such as diesel and gasoline fuels. Because of the broad changes in conditions under which the compositions of this invention will operate, there will be to some degree, preferred subgenera for the various uses. Moreover, depending on the particular use, different additives will be used in conjunction with the detergents and the dispersants of this invention. Finally, obviously the media in which the detergents and the dispersants will be employed will vary depending on whether a lubricating oil or a fuel is used and how the lubricating oil is to be employed.

The lubricating oil composition will be considered first. Preferred detergents and dispersants for lubricating oils have the following formula:



The above symbols are defined as follows:

a^5 —an integer of from 2 to 4

c^4 —a number in the range of from 1 to 2, including whole and fractional numbers

R^{b} —a branched chain aliphatic hydrocarbon radical of from about 750 to 3,000 molecular weight, more preferred of from about 750 to 1,500 molecular weight.

Illustrative preferred compounds are: polyisobutenyl triethylene tetramine, di(polyisobutenyl) tetraethylene pentamine, polypropenyl diethylene triamine, polyisobutenyl triethylene tetramine, etc.

The preferred hydrocarbon radicals are polyisobutylene and polypropylene.

The detergents may be prepared as concentrates as high as 80 weight percent of the detergent in lubricating oil. Generally, concentrates will vary from about 10 to 80 weight percent. However, when the oil is to be used in the engine, the amount of the detergent generally will vary from about 0.1 to 15 weight percent, more usually from 0.25 to 10 weight percent. The lubricating oil compositions may therefore vary in the amount of detergent from 0.1 to 80 weight percent.

The compositions of this invention can be used with various base oils which find use as lubricating oils. Naturally occurring base oils include naphthenic base, paraffin base, asphaltic base and mixed base lubricating oils. Synthetic hydrocarbon oils include alkylene polymers, such as polymers of propylene, butylene, 1-octene, and mixtures thereof and alkylated aromatic hydrocarbons. Non-hydrocarbon lubricating oils include: alkylene oxide type polymers; carboxylic acid esters such as octyl adipate, nonyl azelate, decyl sebacate, butyl alkenylsuccinate, etc.; also, inorganic esters such as phosphates and silicates.

The above base oils may be used individually or in combination, whenever miscible or made so by the use of mutual solvents.

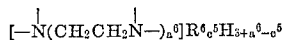
Preferably, the detergents of this invention are used in lubricating oils with an oxidation inhibitor and extreme pressure agent. The preferred inhibitors are metal dithiophosphates, particularly zinc O,O-di(hydrocarbyl) phosphorodithioate, where the hydrocarbyl groups are generally from 4 to 36 carbon atoms. (Hydrocarbyl is an organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl or alkaryl, and may be aliphatically saturated or unsaturated, e.g., ethylenic unsaturation.) Preferably, the hydrocarbyl groups are alkyl or alkaryl groups. Also, S-alkyl and S-polyalkyleneoxy esters of the phosphorodithioate may be used. Usually, about 6 to 50 mM./kg. of the phosphorodithioate is used in the oil.

Other additives may also be included in the lubricating oil. These additives include pour point depressants, viscosity index improvers, antiwear agents, rust inhibitors, corrosion inhibitors, other detergents and dispersants, etc. Generally, the total amount of additives exclusive of the detergent will be in the range of from about 0.1 to 5 weight percent of the lubricating oil composition.

A special situation in which the lubricating oil is employed is the 2-cycle spark ignition engine. With the 2-cycle engine, the oil is incorporated with the fuel and burned directly in the piston chamber. The oil/gasoline mixture first enters the crankcase where the mixture of lubricant and unvaporized fuel contacts and lubricates the various moving parts including the bearings, pistons, piston rings and cylinders. Any lubricant that does not deposit on the surfaces in the lower part of the engine passes into the combustion chamber where it is burned

along with the fuel. An effective detergent solubilizes any deposit precursors and the deposit precursors are carried into the combustion chamber and burned. While the dispersant and detergent is considered a lubricating oil additive, the detergent operates in a mixed lubricating oil-fuel environment.

Preferred compositions for use in the 2-cycle engine have the following formula:



The above symbols are defined as follows:

a^6 —an integer of from 1 to 4

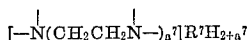
c^5 —an integer or fractional number of from 1 to 2, preferably 1

R^6 —a branched chain aliphatic hydrocarbon radical having a molecular weight of from about 750 to 1,500, preferably a polymer of propylene or isobutylene.

Illustrative compounds which come within the above formula are polyisobutenyl ethylene diamine, polypropenyl ethylene diamine, as well as the previously indicated compounds which are included in the above formula.

Generally, hydrocarbonaceous lubricating oils will be used, particularly petroleum derived, such as the mixed base, paraffinic and naphthenic base oils. Moreover, in place of phosphorodithioate inhibitors, other oxidative inhibitors such as bis(phenols), etc. may be used. When phosphorodithioate additives are used, concentrations in the oil may be as low as one mM./kg. Finally, a halide scavenger for the lead will also be added, usually to enhance the halide already present in the gasoline. Alkylene halide scavengers such as ethylene dibromide may be used with the detergent compositions of this invention, but aryl halides, e.g., dichlorobenzene, are preferred. Other additives, already described for the lubricating oils, may also be included.

Finally, the use of the detergents and dispersants of this invention in fuels will be considered. The preferred compositions which find use in fuels have the following formula:



The above symbols are defined as follows:

a^7 —an integer of from 1 to 3

R^7 —a branched chain aliphatic hydrocarbon radical of from about 450 to 1,500 molecular weight, preferably polypropylene or polyisobutylene.

Sufficient illustrations of the compounds within the above formula have already been indicated.

The detergent will generally be employed in a hydrocarbon base 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 light mineral lubricating oil, such as petroleum spray oil is also 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 introduced 873 g. of bromopolyisobutylene (polyisobutylene of approximately 930 average molecular weight brominated to 4.93 weight percent bromine) and 87 g. of tetraethylene pentamine (a mixture of compounds having the average composition of tetraethylene pentamine). The reaction was stirred for one-half hour and then heated to 185° C. for about 18 hours. At the end of this time, the mixture was allowed to cool, diluted with 3 volumes of n-hexane, and the hydrobromide salt permitted to settle. The supernatant liquid was then decanted and the remaining salt extracted with ethanol and water. After evaporation of the volatile material, the final product analyzed as follows: wt. percent nitrogen=1.1; wt. percent bromine=0.2.

EXAMPLE 2

Into a reaction flask was introduced 800 g. of a chlorinated paraffinic base oil (average molecular weight approximately 570 chlorinated to approximately 6.4 weight percent) and 80 g. of tetraethylene pentamine and the mixture heated at 185° C. for 6 hours. At the end of this time, the reaction mixture was cooled and diluted with 3 volumes of n-hexane and 1 volume of ethanol followed by dilute sodium carbonate and water washes. The mixture was then heated to reflux and then dilute sodium carbonate was added until the cloud point was reached, the phases separated, the organic phase diluted with one volume of ethanol, and then the mixture extracted with water. The volatile products were then pumped from the organic phase. Analysis: wt. percent N=0.53; wt. percent basic N=0.36.

EXAMPLE 3

Into a reaction flask was introduced 1,780 g. of brominated polyisobutylene (polyisobutylene of approximately 930 average molecular weight brominated to 8.6 weight percent bromine) and 350 g. of a mixture of polyethylene amines having an average composition of tetraethylene pentamine and allowed to stand overnight at ambient temperatures. The mixture was then heated at 150° C. for several hours (approximately 5 to 6), cooled and diluted with several volumes of n-pentane and allowed to stand. The solution was then concentrated to about one-half its original volume, about 1 liter of ethanol and about 1 liter of 10 percent aqueous sodium carbonate

added. The phases were separated and the sodium carbonate extraction repeated, followed by washing the hexane phase with water. Volatile materials were removed in vacuo by heating the organic phase to 100° C., leaving a residue of 1,369 g. Analysis: wt. percent nitrogen=2.26, 2.21; wt. percent basic nitrogen=1.09; wt. percent bromine=1.08, 0.99; molecular wt. =2,318 (determined by ThermoNAM, a differential vapor pressure technique).

EXAMPLE 4

Into a reaction flask was introduced 433 g. of chlorinated polyisobutylene (polyisobutylene of approximately 950 average molecular weight chlorinated to 9.3 weight percent chlorine) and 240 g. of alkylene polyamine having an average composition of tetraethylene pentamine and 640 ml. of benzene added. The mixture was heated to reflux and the benzene distilled off. The residue was then heated at 150° C. for 4 hours. After cooling the reaction mixture and diluting with mixed hexanes, 200 ml. of ethanol was added and the organic phase extracted with 10 weight percent aqueous sodium carbonate, the phases separated and the extraction of the organic phase repeated, the phases separated again and finally the organic phase washed with water. The volatile materials were then removed in vacuo. Analysis: wt. percent nitrogen=4.66, 4.76; wt. percent chlorine=3.16; molecular wt. (ThermoNAM)=1,318.

EXAMPLE 5

Into a pressure vessel was introduced 1,500 ml. of a solution of 5 parts of chlorinated polyisobutylene (approximately 1,300 molecular weight) and 2 parts of benzene (the solution analyzing to 3.66 weight percent chlorine) and 300 g. of ethylene diamine (the vessel sealed and heated at 150° C. with rocking overnight). The vessel was then allowed to cool, vented and to the reaction mixture was added an equal volume of n-hexane and a one-third volume of ethanol, the resulting mixture being heated to reflux. Approximately one-third volume of water was then added, the phases separated and the hydrocarbon phase isolated. The volatile materials were removed in vacuo and the residue analyzed. Analysis: wt. percent nitrogen=1.82, 1.83; wt. percent nitrogen=1.65, 1.63.

EXAMPLE 6

Into a reaction flask was introduced 3,000 g. of a 70 weight percent solution in benzene of chloropolyisobutylene (polyisobutylene of approximately 1,300 molecular weight chlorinated to 4.3 weight percent chlorine) and 210 g. of alkylene polyamine having an average composition of triethylene tetramine and the mixture heated to reflux, the benzene stripped off and the mixture further heated at 170° C. for 4 hours. At the end of this time, the mixture was allowed to cool, and then diluted with equal volumes of mixed hexanes and absolute ethanol, heated to reflux and then one-third volume of 10 weight percent aqueous sodium carbonate added. The phases were separated, and the organic phase washed with water and then the volatile materials removed in vacuo. Analysis: wt. percent nitrogen=1.44; wt. percent basic nitrogen=0.89; wt. percent chlorine=1.45; molecular weight (ThermoNAM)=2,419, 2,371.

EXAMPLE 7

Following the procedure described in Example 6, 1,500 g. of a 70 weight percent solution in benzene of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to ~10 weight percent) and 155 g. of diethylene triamine were combined. Analysis: wt. percent nitrogen=1.59, 1.60; wt. percent nitrogen=0.96, 0.97.

EXAMPLE 8

Into a reaction flask was introduced 800 g. of benzene, 846 g. of chlorinated polyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 5.6

weight percent) and 300 g. of alkylene polyamine having an average composition of triethylene tetramine and the mixture heated to reflux and benzene gradually stripped off. The temperature was then increased to 175° C. and maintained for 3.5 hours. After allowing the mixture to cool, equal volumes of both mixed hexanes and 95 percent ethanol were added and the resulting solution separated into 2 equal portions. One of the portions was allowed to sit in a separatory funnel and the alcoholic phase permitted to separate. The hydrocarbon portion was separated from the alcoholic portion, washed with 10 weight percent aqueous sodium carbonate, followed by washing with water, and the volatile materials then removed in vacuo. Analysis: wt. percent nitrogen=3.03, 3.06; wt. percent basic nitrogen=2.26, 2.28.

EXAMPLE 9

Into a reaction flask was introduced 600 g. of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 5.6 weight percent), 550 ml. of benzene and 220 g. of alkylene polyamine of the average composition of triethylene tetramine and the mixture allowed to stand at ambient temperatures for 2 days. The benzene was then distilled off, and the temperature of the mixture raised to 150° C. and maintained for 4 hours. The usual extraction procedure using mixed hexanes and ethanol, followed by sodium carbonate and water washes was carried out and the volatile materials then removed in vacuo. Analysis: wt. percent nitrogen=4.10, 4.05; wt. percent basic nitrogen=3.07; wt. percent chlorine=0.57; molecular wt.

(ThermoNAM)=1,510

EXAMPLE 10

Following the procedures of the previous examples, 1,500 g. of chloropolyisobutylene (polyisobutylene of approximately 2,700 molecular weight chlorinated to 6.11 weight percent chlorine) was combined with 350 g. of alkylene polyamine having an average composition of tetraethylene pentamine in one liter of benzene. Analysis: wt. percent nitrogen=1.53, 1.53.

EXAMPLE 11

Following the procedures of the previous examples, 1,423 g. of chloropolyisobutylene (polyisobutylene of approximately 950 average molecular weight chlorinated to approximately 5 weight percent chlorine) was combined with 286 g. of an alkylene polyamine having an average composition of nonaethylene decamine (Dow-Amine 400 provided by the Dow Chemical Co.) in 1.4 liters of benzene. Analysis: wt. percent nitrogen=4.14, 4.20.

EXAMPLE 12

Following the procedures of the previous examples, 600 g. of chloropolyisobutylene (polyisobutylene of approximately 2,700 average molecular weight chlorinated to about 2 weight percent chlorine) was combined with 40 g. of alkylene polyamine having an average composition of tetraethylene pentamine and 540 ml. of benzene. Analysis: wt. percent nitrogen=0.99; molecular weight (ThermoNAM)=approximately 4,400.

EXAMPLE 13

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 14

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° 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 nitrogen. Complete removal of volatile solvents from a small sample indicated the product contains about 40% solvents, i.e., toluene and methyl isobutyl carbinol.

EXAMPLE 15

Following the procedure of Example 14, 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 nitrogen.

EXAMPLE 16

Following the procedure of Example 6, 1,500 g. of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 5.6 weight percent chlorine) was combined with 285 g. of alkylene polyamine having an average composition of tetraethylene pentamine in 1,200 ml. of benzene. Analysis: wt. percent nitrogen=4.15, 4.15; molecular wt. (Thermo-NAM)=1,539.

EXAMPLE 17

Following the procedure of Example 14, 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 nitrogen.

In order to demonstrate the wide applicability of the compounds within the scope of this invention, various compounds were tested under a wide variety of conditions simulating a variety of situations in which lubricating oils and fuels are used. Three different engine tests were carried out of varying severity and varying demands on detergents to demonstrate the excellent effectiveness of the compositions of the invention in lubricating oils.

The first test was the L-1 Supp. 1 (MIL-L-2104B, Supp. 1 Specifications). The oil was formulated contain-

ing 0.03 weight percent nitrogen and 8 mM./kg. of O,O-dialkyl phosphorodithioate (alkyl of from 4 to 6 carbon atoms) in a Mid-Continent SAE 30 base oil. The test was carried out for 120 hours, the following table indicating the results.

TABLE I

	Grooves ¹	Lands ²
Example 1....	4-0.5-0-0	75-0-75
Example 2....	4-1-2-1	435-100-25
Base oil.....	3 ³ 38-18-10-10	3 ³ 800-800-800

¹ Measured on a rating of 0 to 100, 100 being completely filled.

² Measured on a rating of 0 to 800, 800 being completely black.

³ Tested under the less severe L-1 conditions (MIL-L-2104A).

To further demonstrate the effectiveness as detergents and dispersants of the compositions of this invention, a number of compositions were tested under Caterpillar 1-G conditions (MIL-L-45199). To a Mid-Continent SAE 30 base oil was added the detergent and zinc O,O-di(alkylphenyl) phosphorodithioate (the alkyl polypropylene of an average of 14 carbon atoms). The test was carried out for 60 hours. The following results were obtained.

TABLE II

	Wt. percent of candidate detergent	Phosphorodithioate, mM./Kg.	Grooves ¹	Lands ¹	U.H. ²
Example:					
3.....	6.76	18	24-2.3-0-0.2	135-15-40	-----
4.....	4.1	12	58-5-0.6-0.3	510-35-40	-----
5.....	4.04	12	15-2-0-0	191-7-10	7.0
6.....	5.25	12	12-3-0-0	85-0-0	7.5
7.....	4.62	12	43-4-1-1	70-0-0	7.5
8.....	2.90	8	21-5-0-0	170-50-65	7.5
9.....	3.5	12	12-2.5-0.2-0.2	125-46-25	-----
10.....	4.80	8	53-3-0-0	155-10-5	6.4
11.....	3.7	13	69-9.2-2.4-0.9	745-420-185	-----
Base oil.....	-----	12	93-15-5-3	500-800-370	-----

¹ Used the same rating as in Table I.

² Rated 0 to 10, 10 being completely clean.

As a further test of the usefulness of the compositions of this invention in lubricating oils, a modified FL-2 test procedure, as described in June 21, 1948 report of the Coordinating Research Council, was employed. This test simulates automobile engine performance. A standard procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2,500 r.p.m. and 45 brake horsepower for 40 hours (closely simulating the relatively "cold" engine conditions which are normally experienced in city driving). At the end of each test, the engine is dismantled and the amount of total sludge (rating of 0 to 50, no sludge being 50) and clogging of the rings and oil screen (rating of 0 to 100, no clogging being 0) is determined. Also, the piston varnish is rated (rating of 0 to 10, no varnish being 10) and the total varnish is evaluated (rating of 0 to 50, no varnish being 50). The above test was modified by increasing the time and periodically raising the oil sump temperature from 165° F. to 205° F. and the water jacket temperature from 95° to 170° F.

Using a Mid-Continent SAE 30 base stock, each candidate detergent was employed at concentrations to provide a constant weight percent of nitrogen; also included in the oil was 10 mM./kg. of zinc O,O-di(alkyl) dithiophosphate (alkyl of from 4 to 6 carbon atoms) and 2 mM./kg. of zinc O,O-di(alkylphenyl) dithiophosphate (alkyl is polypropylene of from 12 to 15 carbon atoms). The following table indicates the results obtained.

TABLE III

Example:	Wt. percent of candidate detergent	Piston varnish	Total varnish	Total sludging	Clogging		Time, hrs.
					Ring	Screen	
4.....	0.98	3.5	16	35	27	20	80
6.....	3.50	4.3	23	48	2	4	100
7.....	2.64	4.5	14	37	25	3	100
8.....	1.44	4.1	23	41	18	10	100
12.....	4.35	4.3	17	49	0	1	100
Base oil*							

*Engine stopped in approximately 12 hours.

The results demonstrate that the branched chain hydrocarbon substituted polyamines provide excellent versatility in providing detergency and dispersancy under broad variations in conditions and varying engine requirements.

Turning now to a consideration of the use of the detergents and dispersants of this invention in oils to be used in 2-cycle spark ignition engines. Two different engines were used: a Yamaha engine which is used on motorcycles, and a McCulloch engine which is used for chain saws.

In the McCulloch engine test, the engine is a Model 1-81 approximately 85 cc. displacement. The test is carried out for 10 hours, the engine being run at 7,000 r.p.m., at a temperature of 435° F. and with a wide open throttle. Using regular gasoline, a fuel-oil mixture in the ratio of 20:1 is prepared, the oil composition being a blend of detergent in SAE 40 grade base oil, such that the finished oil contained 0.126 weight percent nitrogen.

The Yamaha engine test uses a 75 cc. Model YG-1 motorcycle engine. The same conditions as described for the McCulloch engine are also used for the Yamaha engine.

The following table indicates the results obtained with a variety of detergents in the McCulloch engine and in the Yamaha engine tests.

TABLE IV.

Example	Wt. percent in oil of candidate detergent	PV ¹	Ring Sticking		G.D.No. ²		Land Dep. ³		Exh. ⁴ Ports	Piston ⁵ Und.	Total rating
			Top	2nd	Top	2nd	Top	2nd			
McCulloch:											
Example 5..	7	9.2	360	F	6	500	250	5	8.3	37.0	
Example 6..	9	7.5	360	F	8	700	640	7	7.8	30.8	
Base Oil.....		6.4	360	F	5	580	610	10	6.0	28.7	
Yamaha:											
Example 5..	7	8.6	360	F	10	640	620	12	6.2	30.2	
Base oil.....		6.0	360	160		700	750	15	1.4	19.6	

¹ PV-piston varnish.

² G.D. No.-groove deposit number.

³ Land dep.-land deposit number.

⁴ Exh. ports.-exhaust ports.

⁵ Piston und.-piston underhead.

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: 195° 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 V.—EXTENDED DETERGENT ACTION TESTS

Additive	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
Example:												
13.....		2.3		0.7	1	6	1.0	1.0	0	9.6	4	0
13.....	0.5						1.9	0	0	7.7	0	0
14.....	0.5	3.7	3.8	0.2	0	0						
15.....	0.2						2.2	0	0	8.1	1	0
16.....	0.2	2.0	0.6	0.1	0	0	1.3	0.2	0	8.1	1	0
17.....	0.2	1.6	1.0	0	0	0						
Base fuel.....		2.2	1.5	1.1	4	0	1.9	2.5	0	8.7	2	0
Base fuel.....	0.5	2.0	1.1	0.7	3	0						

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

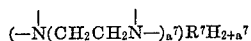
² Average of two base fuel runs.

The data graphically demonstrate the wide range of applicability of the compositions of this invention. The excellent detergent and dispersant results are obtained under a wide variety of conditions in a wide variety of engines closely simulating extreme operating field conditions. Despite the relative simplicity of the molecules, as compared to the wide variety of detergents that have preceded them, the compositions of this invention are able to function in both lubricating oils and fuels effectively. Moreover, the compounds are readily available by simple synthetic methods, provide detergency without producing ash and either do not or only to an insignificant degree create deposits from their own decomposition products.

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 gasoline composition having in an amount sufficient to provide detergency and dispersancy of from 100 to 1000 p.p.m. a composition of the formula:



wherein a^7 is an integer of from 1 to 3 and R^7 is either polypropylene or polyisobutylene of from about 450 to 1,500 molecular weight.

2. A gasoline composition having from 100 to 1000 p.p.m. of a polyisobutenyl ethylene diamine wherein said polyisobutenyl is of from 450 to 1,500 molecular weight.

3. A fuel concentrate having from 10 to 70 weight percent of a polyisobutenyl ethylene diamine wherein said polyisobutenyl is of from about 450 to 1,500 molecular weight and the remainder is an aromatic hydrocarbon solvent, an alcohol, or mixtures thereof, boiling in the range of about 150° to 400° F.

4. A gasoline composition having from 100 to 1000 p.p.m. of a polyisobutenyl diethylene triamine wherein said polyisobutenyl is of from 450 to 1,500 molecular weight.

5. A fuel concentrate having from 10 to 70 weight percent of a polyisobutenyl diethylene triamine wherein said polyisobutenyl is of from about 450 to 1,500 molecular weight and the remainder is an aromatic hydrocarbon solvent, an alcohol, or mixtures thereof, boiling in the range of about 150° to 400° F.

6. A gasoline composition having from 100 to 1000 p.p.m. of a polyisobutenyl triethylene tetramine wherein said polyisobutenyl is of from 450 to 1,500 molecular weight.

7. A fuel concentrate having from 10 to 70 weight percent of a polyisobutenyl triethylene tetramine wherein said polyisobutenyl is of from about 450 to 1,500 molecular weight and the remainder is an aromatic hydrocarbon solvent, an alcohol, or mixtures thereof, boiling in the range of about 150° to 400° F.

8. A gasoline composition having from 100 to 1000 p.p.m. of a polyisobutenyl tetraethylene pentamine wherein said polyisobutenyl is of from 450 to 1,500 molecular weight.

9. A fuel concentrate having from 10 to 70 weight percent of a polyisobutenyl tetraethylene pentamine wherein said polyisobutenyl is of from about 450 to 1,500 molecular weight and the remainder is an aromatic hydrocarbon solvent, an alcohol, or mixtures thereof, boiling in the range of about 150° to 400° F.

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252-32.7E, 50; 260-583