

- [54] **HYDROCARBYL AMINES FOR LUBRICATING OIL DETERGENTS**
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[56] **References Cited**

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[57] **ABSTRACT**

Hydrocarbon substituted amines and alkylene polyamines, substantially free of aromatic unsaturation, having molecular weights in the range of about 450 to 10,000 find use as detergents in lubricating oils.

13 Claims, No Drawings

Z¹ and B¹ — when taken together with the nitrogens 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.

Preferred monoamine detergents and dispersants for lubricating oils have the following formula:



The above symbols are defined as follows:

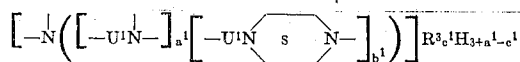
R² — a branched chain aliphatic hydrocarbon radical of from about 50 to 200 carbon atoms

A² — hydrogen or lower alkyl

The preferred hydrocarbon radicals are polyisobutylene and polypropylene.

Polyamines

Turning now to a consideration of the compositions when *x* is 0, these compositions, for the most part, will be described by the following formula:



The above symbols are defined as follows:

U¹ — alkylene of from two to six carbon atoms, there being at least two carbon atoms between the nitrogen atoms and preferably of from two to three carbon atoms

R³ — a hydrocarbon radical substantially free of aromatic unsaturation (less than 5 number % of the carbon atoms are incorporated in aromatic systems) and usually a branched chain aliphatic hydrocarbon radical of from about 400 to 5,000 molecular weight, preferably of from 400 to 3,000 molecular weight

a¹ — an integer of from 0 to 10, preferably 0 to 6

b¹ — an integer of from 0 to 1

a¹ + 2b¹ — an integer of from 1 to 10, preferably 1 to 6

c¹ — an integer of from 1 to 4, and on the average over the entire composition a number in the range of about 1 to 3, there being fewer R² groups than nitrogen atoms averaging over the entire composition

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

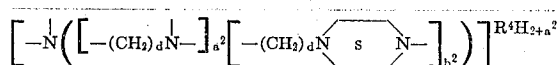
Illustrative alkylene groups are ethylene, 1,2-propylene, 2,2-dimethyl propylene-1,3, trimethylene, hexamethylene, 2-methyl-1,3-propylene, etc.

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 1 or 2 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 1 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

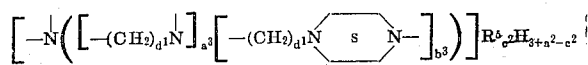
d — an integer of from 2 to 3

R⁴ — a branched chain aliphatic hydrocarbon radical derived from polymerizing olefins of from three to six carbon atoms, preferably of from three to four 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-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 poly(hydrocarbon radical)substituted alkylene polyamine compositions have the following formula:



The above symbols are defined as follows:

a^3 — an integer of from 0 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 — an integer in the range of 1 to 3, averaging over the composition fewer R^5 groups than nitrogen atoms

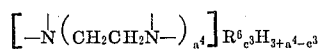
d^1 — an integer of from 2 to 3

R^5 — a branched chain aliphatic hydrocarbon radical 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.)

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',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 of from 1 to 3, preferably of from 1 to 2, per molecule there being fewer R^6 groups than nitrogen atoms

R^6 — a branched chain aliphatic hydrocarbon radical of from 400 to 3,000 molecular weight, preferably of from 400 to 2,500 molecular weight, and, particularly preferred, either polypropenyl or polyisobutenyl

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 co-

polymerized 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 six carbon atoms along the chain and preferably at least 1 branch per four carbon atoms 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 per cent basis, the amount of halide will generally range from about 1 to 25, more usually from about 1 to 10.

The haloalkane 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 haloalkane to amine will generally be in the range from about 0.2 to 20 moles of amine per mole of haloalkane, more usually 0.5 to 10 moles of amine per mole of haloalkane. The mole ratio will depend upon the amount of halogen present in the haloalkane, 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 per cent 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.

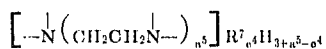
After the reaction has been carried out for a sufficient length of time, the reaction mixture may be extracted with a hydrocarbon medium to free the product from any low molecular weight amine salt which has formed. The product may then be isolated by evaporation of the solvent. Further separation from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

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.

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 how the lubricating oil is to be employed.

Preferred polyamine detergents and dispersants for lubricating oils for automobile and diesel engines have the following formula:



The above symbols are defined as follows:

a^5 — an integer of from 2 to 4

c^4 — an integer in the range of from 1 to 2

R^7 — 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 having as high as 80 weight per cent of the detergent in lubricating oil. Generally, concentrates will vary from about 10 to 80 weight per cent. 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 per cent, more usually from 0.25 to 10 weight per cent. The lubricating oil compositions may therefore vary in the amount of detergent from 0.1 to 80 weight per cent.

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. Nonhydrocarbon 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.

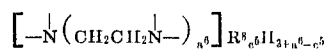
The above base oils may be used individually or in combination, whenever miscible or made so by the use of mutual solvents.

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 0,0-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 per cent 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 are considered a lubricating oil additive, the detergent operates in a mixed lubricating oil-fuel environment.

Preferred polyamine 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 of from 1 to 2, preferably about 1

R^8 — 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.

For 2-cycle engine oils, 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 1 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.

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

Preparations of Halogenated Hydrocarbons

Example A

Into a reaction flask was introduced 950 g. of polyisobutylene (approximate average 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. % 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. % bromine, 8.86, 8.80.

Example C

Into a reaction flask was charged 5,000 g. of polyisobutylene (approximately 950 average molecular weight) and 2 kg. of benzene. With stirring, chlorine gas was introduced at a rate of about 235 ml. per minute and the reaction allowed to proceed for about 20 hours. Any dissolved hydrogen chloride was removed by heating the solution at reflux for about 1 to 2 hours. Analysis: wt. % chlorine, 4.21.

Example D

Into a reaction flask was charged 910 g. of polyisobutylene (approximately 950 average molecular weight) and 625 ml. of carbon tetrachloride and the solution

purged with nitrogen. Chlorine was introduced at a "5" flow rate (Fisher and Porter No. 9144 flow meter) for 2 hours and 35 minutes while maintaining the temperature at about 8° to 10°C. The reaction mixture was then purged with nitrogen and the carbon tetrachloride stripped in vacuo, the pot temperature reaching 120°C. and the final pressure being 5 mm. Hg. Analysis: wt. % chlorine, 4.48.

Preparation of Substituted Amines

Example 1

Into a reaction flask was introduced 873 g. of bromopolyisobutylene (polyisobutylene of approximately 930 average molecular weight brominated to 4.93 weight per cent 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. % nitrogen, 1.1; wt. % 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 per cent) 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. % nitrogen, 0.53; wt. % basic nitrogen, 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 per cent 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 per cent 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. % nitrogen, 2.26, 2.21; wt. % basic nitrogen, 1.09; wt. % 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 per cent 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 per cent 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. % nitrogen, 4.66, 4.76; wt. % 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 per cent 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. % nitrogen, 1.82, 1.83; wt. % basic nitrogen, 1.65, 1.63.

Example 6

Into a reaction flask was introduced 3,000 g. of a 70 weight per cent solution in benzene of chloropolyisobutylene (polyisobutylene of approximately 1,300 molecular weight chlorinated to 4.3 weight per cent 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 per cent 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. % nitrogen, 1.44; wt. % basic nitrogen, 0.89; wt. % 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 per cent solution in benzene of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to ~10 weight per cent) and 155 g. of diethylene triamine were combined. Analysis: wt. % nitrogen, 1.59, 1.60; wt. % basic 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 per cent) 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 per cent 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 per cent aqueous sodium carbonate, followed by washing with water, and the volatile materials then removed in vacuo. Analysis: wt. % nitrogen, 3.03, 3.06; wt. % 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 per cent), 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. % nitrogen, 4.10, 4.05; wt. % basic nitrogen, 3.07; wt. % 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 per cent chlorine) was combined with 350 g. of alkylene polyamine having an average composition of tetraethylene pentamine in one liter of benzene. Analysis: wt. % 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 per cent chlorine) was combined with 286 g. of an alkylene polyamine having an average composition of nonaethylene decamine (DowAmine 400 provided by the Dow Chemical Co.) in 1.4 liters of benzene. Analysis: wt. % nitrogen, 4.14, 4.20.

Example 12

Following the procedure of the previous examples, 600 g. of chloropolyisobutylene (polyisobutylene of approximately 2,700 average molecular weight chlorinated to about 2 weight per cent chlorine) was combined with 40 g. of alkylene polyamine having an average composition of tetraethylene pentamine and 540 ml. of benzene. Analysis: wt. % 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 per cent 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 solu-

tion 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 percent nitrogen; wt. % 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 percent 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 per cent 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. % 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 per cent chlorine) was reacted with 270 g. of ethylene diamine. The product as finished contained about 15 percent volatile solvents. Analysis: titrimetric equivalent wt., 1,080, equal to 1.3 wt. % 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 per cent chlorine) was combined with 285 g. of alkylene polyamine having an average composition of tetraethylene pentamine in 1,200 ml. of benzene. Analysis: wt. % nitrogen, 4.15, 4.15; molecular wt. (ThermoNAM), 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 per cent chlorine) was combined with 270 ml. of ethylene diamine in 270 ml. of n-butanol. The product as finished contained about 20 per cent volatile solvents. Analysis: titrimetric equivalent wt., 976, equal to 1.44 wt. % nitrogen.

Example 18

Into a high pressure vessel was introduced 1,185 g. of polyisobutenyl chloride (approximately 1,000 molecular weight, wt. % chlorine = 5.9), 150 g. of ammonia, 500 ml. of benzene and 100 ml. of methanol, the vessel sealed and rocked at 150°C. for 13 hours. At the end

of this time, the vessel was permitted to cool, the gaseous material vented and the reaction product recovered. The product was extracted with mixed hexanes and alcohol, water being added to aid in the separation of the phases. The volatile materials were then removed in vacuo at elevated temperatures. Analysis: wt. % nitrogen, 1.13, 1.14; molecular wt. (ThermoNAM), 1,426.

Example 19

Into a high pressure bomb was introduced 1,200 g. of polyisobutenyl chloride (approximately 500 molecular weight, wt. % 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 per cent 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 per cent active (contained 40 per cent by weight of polyisobutenyl amine).

Example 20

Following the procedure of Example 2, 1,100 g. of polypropenyl chloride (approximately 850 molecular weight, wt. % chlorine = 5.94) was contacted with 400 g. of liquid ammonia. The product weighed 1,050 g. Titration indicated an equivalent weight of 1,860, indicating 48.4 per cent active.

Example 21

A. Into a high pressure bomb was charged 1,000 g. of polyisobutenyl chloride (approximately 1,000 molecular weight, wt. % chlorine = 6), 500 ml. of benzene, 100 g. of methanol and 100 g. of monomethylamine and cooled to 0°C. The bomb was sealed and heated to 150°C. and allowed to rock at this temperature for about 24 hours. After allowing the reaction mixture to cool, the mixture was diluted with hexane, filtered and then further diluted with about one-half volume of 95 per cent ethanol. The mixture was then heated to reflux and approximately one-third volume of water added and the aqueous phase separated. After pumping all volatiles from the hydrocarbon phase, the product was isolated. Analysis: wt. % nitrogen, 1.01, 1.09; molecular wt. (ThermoNAM), 1,149.

B. Repeating the same reaction under the same conditions with the same amounts of materials, a product was obtained which analyzed: wt. % nitrogen, 1.33, 1.30; wt. % basic nitrogen, 1.24, 1.27.

Example 22

Into a reaction flask was charged 1,500 ml. of a 75 wt. per cent solution of polyisobutenyl chloride (approximately 1,000 molecular weight, wt. % chlorine = 5.9) in benzene, 300 g. of ethanolamine and the mixture heated at reflux for ~1.5 hours. The benzene was then distilled off and the residue heated at 170°C. for 4 more hours. The reaction mixture was then diluted with an equal volume of hexane and a one-third volume of 95 per cent ethanol and the mixture heated to reflux. To this mixture was then added approximately one-third volume of water, the phases allowed to separate and the organic phase isolated. The volatile materials were then distilled from the organic phase in vacuo. Analysis: wt. % nitrogen, 1.01, 1.02; wt. % basic nitrogen, 0.98, 0.98.

Example 23

Into a high pressure bomb was charged 500 g. of polypropenyl chloride (approximately 800 molecular weight, wt. % chlorine = 5.9), 300 ml. of benzene and 100 g. of liquid ammonia, the mixture cooled to 0°C. and the bomb sealed. The bomb was then heated to 150°C. and allowed to rock overnight at that temperature. After allowing the mixture to cool, the mixture was diluted with 1 liter of mixed hexane, the ammonium chloride filtered off and then 800 ml. of alcohol added. After heating the mixture to reflux, water was added to provide phase separation. The hydrocarbon phase was separated, and freed of volatile materials in vacuo. Analysis: wt. % nitrogen, 0.96, 0.94; wt. % basic nitrogen, 0.65, 0.66.

Example 24

Into a high pressure bomb was introduced 550 g. of a 75 per cent solution of polyisobutenyl chloride (approximately 950 molecular weight, wt. % chlorine = 5.9) in benzene, 200 g. of dimethylamine, the bomb sealed and the mixture heated at 150°C. overnight (approximately 18 hours). After allowing the mixture to cool, it was diluted with mixed hexanes and filtered. To the filtrate was added approximately two-thirds volume of 95 per cent ethanol, the resulting mixture heated to reflux and approximately one-third of volume water then added. After separating the organic phase from the aqueous phase, the volatile materials were removed in vacuo. The product was then analyzed. Analysis: wt. % nitrogen, 1.40, 1.42; wt. % basic nitrogen, 1.35, 1.34.

Example 25

Into a pressure vessel was introduced 900 g. of chlo-

ropolyisobutylene (approximately 2,700 molecular weight, wt. % chlorine = 5.9), 150 g. of ammonia and 400 g. of benzene, the vessel sealed and heated at 150°C. with rocking overnight. The vessel was then allowed to cool, the gas vented, the product mixed with 1 liter of mixed hexanes and the ammonium chloride which precipitated was filtered off. The mixture was then further diluted with about 800 ml. of 95 per cent alcohol. After heating the entire mixture at reflux, water was added and the phases cooled and separated. The hydrocarbon phase was isolated and the volatile materials removed in vacuo. Analysis: wt. % nitrogen, 0.41, 0.42; wt. % basic nitrogen, 0.25, 0.21; molecular wt. (ThermoNAM), 3,510.

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 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 this invention in lubricating oils.

The first test was the L-1 Supp. 1 (MIL-L-2104B, Supp. 1 Specifications). The oil was formulated containing 0.03 weight per cent nitrogen and 8 mM./kg. of 0,0-dialkyl phosphorodithioate (alkyl of from four to six 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

Example	Grooves ^a	Lands ^b
1	4-0.5-0-0	75-0-75
2	4-1-2-1	435-100-25
Base Oil	38-18-10-10*	800-800-800*

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

^aMeasured on a rating of 0 to 100, 100 being completely filled

^bMeasured on a rating of 0 to 800, 800 being completely black

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 0,0-di(alkylphenyl) phosphorodithioate (the alkyl is polypropylene of an average of 14 carbon atoms). The test was carried out for 60 hours. The following results were obtained.

TABLE II

Example	Wt. % of Candidate Detergent	Phosphorodithioate mM/kg	Grooves ^a	Lands ^a	U.H ^b
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	58-3-0-0	155-10-5	6.4
11	3.7	13	69-9.2-2.4-0.9	745-420-185	
18	6.7	18	25-10-1-1	320-50-40	
Base Oil		12	93-15-5-3	500-800-370	

^aUsed the same rating as in Table I

^bRated 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 per cent of nitrogen; also in-

the finished oil contained 0.126 weight per cent 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. % in oil of Candidate Detergent	P ¹ V	Ring Sticking		G.D. No. ² Top 2nd	Land Dep. ³		Exh. ⁴ Ports	Piston ⁵ Und.	Total Rating
			Top	2nd		Top	2nd			
MCCULLOCH										
5	7	9.2	360	F	— 6	500	250	5	8.3	37.0
6	9	7.5	360	F	— 8	700	640	7	7.8	30.8
18	11.1	9.4	F	F	2 1	750	600	7	8.7	38.7
19	11	7.7	360	F	— 11	750	550	7	7.2	30.5
21A	12	9.7	180	F	— 1	450	240	6	9.3	41.5
22	12.5	7.3	360	F	— 5	680	310	7	9.1	34.3
24	8.9	7.9	360	F	— 5	740	680	12	7.8	30.4
25	30	8.1	360	F	— 3	650	420	5	6.4	32.1
Base Oil	—	6.4	360	F	— 5	580	610	10	6.0	28.7
YAMAHA										
5	7	8.6	360	F	— 10	640	620	12	6.2	30.2
18	11.1	9.0	360	F	— 4	720	480	15	4.7	29.5
21B	9.2	9.2	360	F	— 4	750	560	22	5.4	29.0
Base Oil	—	6.0	360	160	— —	700	750	15	1.4	19.6

¹PV - piston varnish

²G.D.No. - groove deposit number

³Land Dep. - land deposit number

⁴Exh. Ports - exhaust ports

⁵Piston Und. - piston underhead

cluded in the oil was 10 mM./kg. of zinc 0,0-di(alkyl) dithiophosphate (alkyl of from four to six carbon atoms) and 2 mM./kg. of zinc 0,0-di(alkylphenyl) dithiophosphate (alkyl is polypropylene of from 12 to 15 carbon atoms). The following table indicates the results obtained.

TABLE III

Example	Wt % of Candidate Detergent	Piston Varnish	Total Varnish	Total Sludging	Clogging		Time Hr.
					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 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. 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 lubricating oils under severe field conditions—the hot diesel engine, the variable temperature stop-and-go automobile engine, and the 2-cycle engine. 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 composition of the formula:



wherein R^1 is a branched chain hydrocarbon radical substantially free of unsaturation of from about 425 to about 3,000 molecular weight,

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

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

2. A composition according to claim 1, wherein A^1 and Z^1 are hydrogen or alkyl of from one to six carbon atoms.

3. A lubricating oil composition having in an amount sufficient to provide detergency and dispersancy, a composition according to claim 1.

4. A lubricating oil composition according to claim 3, having from 1 to 50 mM./kg. of a zinc phosphorodithioate.

5. A composition according to claim 1 wherein R is a branched chain aliphatic hydrocarbon radical derived from polymerizing olefins of from three to six carbon atoms.

6. A composition according to claim 1 wherein R is polyisobutylene.

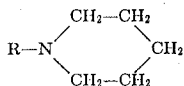
7. A composition according to claim 1 wherein R is polypropylene or polyisobutylene.

8. A compound of the formula



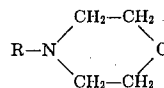
where R is a branched chain hydrocarbon radical having a molecular weight of from about 425 to about 3,000 and R_1 and R_2 are selected from the group consisting of hydrocarbon radicals having from one to about 10 carbon atoms and hydrogen.

9. A compound of the formula



where R is a branched chain hydrocarbon radical having a molecular weight of from about 425 to about 3,000.

10. A compound of the formula



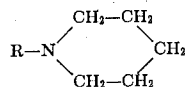
where R is a branched chain hydrocarbon radical having a molecular weight of from about 425 to about 3,000.

11. A lubricant composition comprising a major amount of a lubricating oil and a minor amount of a compound of the formula



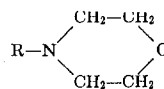
where R is a hydrocarbon radical having a molecular weight from about 425 to about 3000 and R_1 and R_2 are selected from the group consisting of hydrocarbon and hydroxyhydrocarbon radicals having from one to about 10 carbon atoms and hydrogen.

12. A lubricant composition comprising a major amount of a lubricating oil and a minor amount of a compound of the formula



where R is a hydrocarbon radical having a molecular weight of from about 425 to about 3,000.

13. A lubricant composition comprising a major amount of a lubricating oil and a minor amount of a compound of the formula



where R is a hydrocarbon radical having a molecular weight of from about 425 to about 3,000.

* * * * *