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3,366,569

**LUBRICATING COMPOSITIONS CONTAINING THE REACTION PRODUCT OF A SUBSTITUTED SUCCINIC ACID-PRODUCING COMPOUND, AN AMINO COMPOUND, AND AN ALKENYL CYANIDE**

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This application is a continuation-in-part of earlier application Ser. No. 126,809 filed July 21, 1961, now U.S. 3,219,666 and is a continuation of co-pending application Ser. No. 402,617, now abandoned, which is a division of co-pending application Ser. No. 348,760 filed Mar. 2, 1964, now U.S. 3,278,550.

This invention relates to substituted polyamines and to processes for preparing the same. The substituted polyamines of this invention are useful as anti-wear agents, anti-rust agents, insecticides, plasticizers, detergents, etc. They are especially useful as additives in lubricating compositions, fuels, hydrocarbon oils, and power-transmitting fluids.

Deterioration of lubricating oils, especially mineral oils, has been a great concern in the formulation of lubricating compositions for internal combustion engines, transmissions, gears, etc. Deterioration of the oil results in the formation of products which are corrosive to the metal surfaces with which the oil comes into contact. It also results in the formation of products which agglomerate to form sludge- and varnish-like deposits. The deposits cause sticking of the moving metal parts and obstruct their free movement. They are a principal cause of malfunctioning and premature breakdown of the equipment which the oil lubricates.

It is known that water is a common contaminant in the crankcase lubricant of an engine. It may result from the decomposition of the lubricating oil or come from the combustion chamber as a blow-by product of the burning of the fuel. The presence of water in the lubricant seems to promote the deposition of a mayonnaise-like sludge. This type of sludge is more objectionable because it is tenacious to metal surfaces and is not removed by the oil filter. If the engine is operated under conditions such that the crankcase lubricant temperature is continuously high, the water will be eliminated about as fast as it accumulates and only a very small amount of the mayonnaise-like sludge is formed. On the other hand, if the crankcase lubricant temperature is intermittently high and low or consistently low, the water will accumulate and a substantial quantity of the mayonnaise-like sludge will be deposited in the engine.

High operating temperatures are characteristic of an engine that is consistently run at relatively high speed and continuously for a lengthy period. However, where an automobile is primarily used for trips of short distance such as is characteristic of urban, home-to-work use, a significant portion of the operation occurs before the engine has reached its optimum, high temperature. An ideal environment thus obtains for the accumulation of water in the lubricant. In this type of operation, the problem of mayonnaise sludge has been especially troublesome. Its solution has been approached by the use in the lubricant of detergents such as metal phenates and sulfonates which have been known to be effective in reducing deposits in engines operated primarily at high temperatures. Unfortunately, such known detergents have not been particularly effective in solving the problems associated with low temperature operation, particularly those problems which

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are associated with crankcase lubricants in engines which are operated at low or alternating high and low temperatures.

It is accordingly a principal object of this invention to provide novel compositions of matter.

It is also an object of this invention to provide compositions which are adapted for use as additives in hydrocarbon oils.

It is also an object of this invention to provide compositions which are effective as detergents in lubricating compositions.

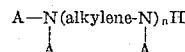
It is another object of this invention to provide novel compositions which are effective dispersants in lubricant compositions intended for use in engines operated at low or alternating high and low temperatures.

It is another object of this invention to provide improved lubricating compositions.

It is another object of this invention to provide improved fuel compositions.

These and other objects are attained in accordance with this invention by providing a process for preparing a nitrogen-containing composition comprising the reaction of a hydrocarbon-substituted succinic acid-producing compound having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent with at least about 0.5 equivalent of an alkylene amine and at least about 0.1 equivalent of an alkenyl cyanide.

The alkylene amines from which the products of this invention are derived include principally those conforming for the most part to the formula



wherein  $n$  is an integer preferably less than about 10,  $A$  is a hydrogen radical or a substantially hydrocarbon preferably having up to about 30 carbon atoms, and the alkylene radical is preferably a lower alkylene radical having less than about 8 carbon atoms. The alkylene amines include principally methylene amines, ethylene amines, butylene amines, propylene amines, pentylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines, and also the cyclic and the higher homologues of such amines such as piperazines and amino-alkyl-substituted piperazines. They are exemplified specifically by: ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene)triamine, 2-heptyl - 3 - (2 - aminopropyl)imidazoline, 4 - methyl-imidazoline, 1,3 - bis(2 - aminoethyl)imidazoline, pyrimidine, 1 - (2 - aminopropyl)piperazine, 1,4 - bis(2 - aminoethyl)piperazine, and 2 - methyl - 1 - (2 - aminobutyl)-piperazine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful.

The ethylene amines are especially useful. They are described in some detail under the heading "Ethylene Amines" in "Encyclopedia of Chemical Technology" Kirk and Othmer, volume 5, pages 898-905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia. The reaction results in the production of somewhat complex mixtures of alkylene amines, including cyclic condensation products such as piperazines. These mixtures find use in the process of this invention. On the other hand, quite satisfactory products may be obtained also by the use of pure alkylene amines. An especially useful alkylene amine for reasons of economy as well as effectiveness of the products derived therefrom is a mixture of ethylene amines prepared by the reaction of ethyl-

ene chloride and ammonia and having a composition which corresponds to that of tetraethylene pentamine.

Hydroxyalkyl-substituted alkylene amines, i.e., alkylene amines having one or more hydroxyalkyl substituents on the nitrogen atoms, likewise are contemplated for use herein. The hydroxyalkyl-substituted alkylene amines are preferably those in which the alkyl group is a lower alkyl group, i.e., having less than about 6 carbon atoms. Examples of such amines include N-(2-hydroxyethyl) ethylene diamine, N,N' - bis(2 - hydroxyethyl)ethylene diamine, 1 - (2 - hydroxyethyl)piperazine, mono-hydroxypropyl-substituted diethylene triamine, 1,4 - bis(2 - hydroxypropyl)piperazine, di - hydroxypropyl - substituted tetraethylene pentamine, N - (3 - hydroxypropyl)tetramethylene diamine, and 2 - heptadecyl - 1 - (2 - hydroxyethyl)-imidazoline.

Higher homologues such as are obtained by condensation of the above illustrated alkylene amines or hydroxy alkyl-substituted alkylene amines through amino radicals or through hydroxy radicals are likewise useful. It will be appreciated that condensation through amino radicals results in a higher amine accompanied with removal of ammonia and that condensation through the hydroxy radicals results in products containing ether linkages accompanied with removal of water.

The substantially hydrocarbon-substituted succinic acid-producing compounds used in the above process include the succinic acids, anhydrides, halides, and esters. An important aspect of this invention is the size of the substantially hydrocarbon substituent on the succinic acid-producing compound. Thus, only the substituted succinic acid-producing compounds having at least about 50 aliphatic carbon atoms in the substantially hydrocarbon substituent are contemplated as being within the scope of this invention. This lower limit is based not only upon a consideration of the oil-solubility of the substituted polyamines but also upon the effectiveness of such compounds in application contemplated by this invention.

The substantially hydrocarbon substituent of the succinic compound may contain polar groups provided, however, that the polar groups are not present in proportions sufficiently large to alter significantly the hydrocarbon character of the substituent. The polar groups are exemplified by the chloro, bromo, keto, ether, aldehyde, nitro, etc. The upper limit with respect to the portion of such polar groups in the substituent is approximately 10% based on the weight of the hydrocarbon portion of the substituent.

The sources of the substantially hydrocarbon substituent include principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono-olefins having from 2 to 30 carbon atoms. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. They are illustrated by 2-butene, 3-pentene, and 4-octene.

Also useful are the interpolymers of the olefins such as those illustrated above with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins. Such interpolymers include, for example, those prepared by polymerizing isobutene with styrene; isobutene with butadiene; propene with isoprene; ethylene with piperylene; isobutene with chloroprene; isobutene with p-methyl styrene; 1-hexene with 1,3-hexadiene; 1-octene with 1-hexene; 1-heptene with 1-pentene; 3-methyl-1-butene with 1-octene; 3,3-dimethyl-1-pentene with 1-hexene; isobutene with styrene and piperylene, etc.

The relative proportions of the mono-olefins to the other monomers in the interpolymers influence the stability and oil-solubility of the final products derived from such interpolymers. Thus, for reasons of oil-solubility and

stability the interpolymers contemplated for use in this invention should be substantially aliphatic and substantially saturated, i.e., they should contain at least about 80%, preferably at least about 95%, on a weight basis of units derived from the aliphatic monoolefins and no more than about 5% of olefinic linkages based on the total number of carbon-to-carbon covalent linkages. In most instances, the percentage of olefinic linkages should be less than about 2% of the total number of carbon-to-carbon covalent linkages.

Specific examples of such interpolymers include the copolymer of 95% (by weight) of isobutene with 5% of styrene; the terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; the terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene; the terpolymer of 80% of isobutene with 20% of 1-pentene and 20% of 1-octene; the copolymer of 80% of 1-hexene and 20% of 1-heptene; terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propene; and the copolymer of 80% of ethylene and 20% of propene.

Another source of the substantially hydrocarbon radical comprises saturated aliphatic hydrocarbons such as highly refined high molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of high molecular weight olefin polymers illustrated above or high molecular weight olefinic substances.

The use of olefin polymers having molecular weight of about 750-5000 is preferred. Higher molecular weight olefin polymers having molecular weights from about 10,000 to about 100,000 or higher have been found to impart also viscosity index improving properties to the final products of this invention. The use of such higher molecular weight olefin polymers often is desirable.

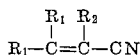
The succinic acid-producing compounds useful in the above process are preferably substantially hydrocarbon-substituted succinic acids and anhydrides. These succinic compounds are readily available from the reaction of maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as the olefin polymer described hereinabove. The reaction involves merely heating the two reactants at a temperature about 100°-200° C. The product from such a reaction is an alkenyl succinic anhydride. The alkenyl group may be hydrogenated to an alkyl group. The anhydride may be hydrolyzed by treatment with water or steam to the corresponding acid. Either the anhydride or the acid may be converted to the corresponding acid halide or ester by reaction with, e.g., phosphorus halide, phenols, or alcohols.

In lieu of the olefins or chlorinated hydrocarbons, other hydrocarbons containing an activating polar substituent, i.e., a substituent which is capable of activating the hydrocarbon molecule in respect to reaction with maleic acid or anhydride, may be used in the above-illustrated reaction for preparing the succinic compounds. Such polar substituents may be illustrated by sulfide, disulfide, nitro, mercaptan, bromine, ketone, or aldehyde radicals. Examples of such polar-substituted hydrocarbons include polypropene sulfide, di-polyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc. Another method useful for preparing the succinic acids and anhydrides involves the reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature usually within the range from about 100° C. to about 200° C.

The acid halides of the succinic acids can be prepared by the reaction of the acids or their anhydrides with a halogenation agent such as phosphorus tri-bromide, phosphorus pentachloride or thionyl chloride. The esters of such acids can be prepared simply by the reaction of the acids or their anhydrides with an alcohol or a phenolic compound such as methanol, ethanol, octadecanol, cyclohexanol, phenol, naphthol, octylphenol, etc. The

esterification is usually promoted by the use of an alkaline catalyst such as sodium hydroxide or sodium alkoxide or an acidic catalyst such as sulfuric acid. The nature of the alcoholic or phenolic portion of the ester radical appears to have little influence on the utility of such ester as reactant in the process described hereinabove.

The alkenyl cyanides useful in the process of this invention are preferably the vinyl cyanides conforming to the structural formula



wherein  $R_1$  and  $R_2$  are hydrogen or hydrocarbon radicals. Especially useful are the vinyl cyanides in which the two  $R_1$  radicals are each hydrogen or an alkyl group having up to about 12 carbon atoms and the  $R_2$  radical is hydrogen or a lower alkyl group having up to about 6 carbon atoms. Examples of such vinyl cyanides include vinyl cyanide (i.e., acrylonitrile), 1-methylvinyl cyanide, 1-butylvinyl cyanide, 1-hexylvinyl cyanide, 1-cyclohexylvinyl cyanide, 1-tertiary-butylvinyl cyanide, and 1-isopropylvinyl cyanide. Other vinyl cyanides useful herein include 2-methyl vinyl cyanide (i.e., crotonic nitrile), 2-dodecylvinyl cyanide, 2,2'-didodecylvinyl cyanide, 2-cyclopentylvinyl cyanide, 2-octyl-2-methylvinyl cyanide, 2-decyl-2-hexylvinyl cyanide, and 2-tertiary-pentylvinyl cyanide.

Alkenyl cyanides in which the cyanide group is separated from the olefinic group by one or more methylene radicals likewise are useful in the process of this invention. They are exemplified by 3-hexenyl cyanide, 2-octenyl cyanide, etc. Also useful are the aryl-substituted alkenyl cyanides such as 1-phenylvinyl cyanide, 2-phenylvinyl cyanide, 1-tolylvinyl cyanide, or 2-phenethylvinyl cyanide.

The process of this invention may be carried out by mixing the succinic reactant, the alkylene amine and the alkenyl cyanide and heating the mixture at the desired reaction temperature. Alternatively, the succinic reactant may be reacted first with the alkylene amine and then with the alkenyl cyanide. The preferred mode of carrying out the process involves first reacting the alkylene amine with the alkenyl cyanide to form an intermediate and then reacting the intermediate with the succinic reactant. The temperature at which the process of this invention may be carried out usually ranges from about 80° C. to 250° C. or higher. A lower temperature may be used in some instances such as where a relatively reactive succinic acid or anhydride is used. The upper temperature limit is the decomposition point of the reaction mixture.

The process is preferably carried out in the presence of a diluent or solvent such as benzene, naphtha, toluene, chlorobenzene, or dioxane. Mineral oil is especially useful as a solvent.

The relative amounts of the reactants to be used in the process are such that for each equivalent of the succinic reactant, there should be at least about 0.5 equivalent of the alkylene amine and at least about 0.1 equivalent of the alkenyl cyanide. Preferably, from 1 to 5 equivalents of the alkylene amine and from 0.5 to 4 equivalents of the alkenyl cyanide are used for each equivalent of the succinic reactant. More of the alkylene amine or the alkenyl cyanide may be used. The upper limit of the amounts of these reactants depends to a large extent upon the number of amino groups in the molecular structure of the alkylene amine. Ordinarily, no more than two moles of each of the alkylene amine and the alkenyl cyanide are used per equivalent of the succinic reactant. It will be noted that the equivalent weight of the succinic reactant is based on the number of the carboxylic acid-producing radicals in a molecule, the equivalent weight of the alkylene amine is based on the number of amino groups in a molecule, and the equivalent weight of the alkenyl cyanide is based on the number of the olefin linkages in a molecule. Thus, a hydrocarbon-substituted succinic acid or anhydride hav-

ing one succinic group in its molecular structure has two equivalents per mole; an alkylene pentamine has five equivalents per mole, and a vinyl cyanide has one equivalent per mole.

The chemical constitution of the nitrogen-containing products of the process of this invention is not fully understood. It is known, however, that the nitrogen atom of the amino groups from the alkylene amine is attached directly to the succinic radical to form an acylated amine having linkages representative of an amide, imide, amidine, or salt. The product usually has a mixture of such linkages. It is also known that the reaction of the alkenyl cyanide ordinarily involves the olefinic group present in its molecular structure. Such reaction is believed to consist of the addition of an amino group of the alkylene amine or the acylated amine to the olefinic group of the alkenyl cyanide. The cyanide group of the alkenyl cyanide appears not to be directly involved in the reaction, although in some instances it may be combined with an amino group of the alkylene amine or the acylated amine. In any event, the product of the process, irrespective of the relative proportions of the linkages present in its molecular structure, is useful for the purposes of this invention.

It will be noted that the formation of an acylated amine having predominantly an amide or a salt linkage between the carboxylic radical of the succinic reactant and the amino group of the alkylene amine involves one equivalent of each of the two reactants and the formation of an acylated amine having predominantly imide linkages involves two equivalents of the succinic reactant and one equivalent of the alkylene amine. On the other hand, the formation of an acylated amine such as an imidazoline having predominantly amidine linkages involves one equivalent of the succinic reactant and two equivalents of the alkylene amines. Thus, the chemical constitution of the product of the process of this invention depends to some extent on the relative proportions of the reactants used in the process. Also, a relatively low reaction temperature such as below 100° C. tends to promote the formation of salts whereas a relatively high reaction temperature such as above 100° C. tends to promote the formation of imides or amides. A still higher temperature, such as 200° C. or higher, tends to promote the formation of imidazolines or polymeric linear amidines.

The following examples are illustrative of the processes of this invention:

#### EXAMPLE 1

A polyisobutene-substituted succinic anhydride is prepared by the reaction of a chlorinated polyisobutene with maleic anhydride (20% molar excess) at 200° C. The polyisobutenyl radical has an average molecular weight of 850 and the resulting substituted succinic anhydride is found to have an acid number of 113 (corresponding to an equivalent weight of 500). A mixture of 500 grams (1 equivalent) of this substituted succinic anhydride, 189 grams (5 equivalents) of tetraethylene pentamine and 67 grams (1 equivalent) of crotonic nitrile is prepared at room temperature, mixed with 2000 grams of mineral oil, and then heated at 100°-200° C. for 7 hours. The product is an oil solution of the desired nitrogen-containing composition of this invention.

#### EXAMPLE 2

A cyanoethyl-substituted ethylene amine is prepared by mixing 212 grams of acrylonitrile with 216 grams of an ethylene amine mixture consisting of 75% by weight of triethylene tetramine and 25% by weight of diethylene triamine at room temperature and heating the mixture at 110°-130° C. for 5 hours and then to 125° C./30 mm. To a mixture of 1110 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 825 grams of mineral oil there is added at 60° C. 143 grams dropwise of the above cyanoethyl-substituted ethylene amine (having a nitrogen content of 31.8%). The mixture is

heated at 150° C.-160° C. for 5 hours while being purged with nitrogen. A total of 6 cc. of water is removed by distillation. The residue has a nitrogen content of 1.66%.

#### EXAMPLE 3

To 330 parts (by weight) (8 equivalents) of a commercial ethylene amine mixture having a nitrogen content of 34% and having an average composition substantially corresponding to that of tetraethylene pentamine, there is added 318 parts (6 equivalents) of acrylonitrile at 40°-50° C. within a period of 4 hours. An exothermic reaction occurs. The mixture is heated at 50°-55° C. for 2 hours and at the reflux temperature (110°-115° C.) for 2 hours. It is then blown with nitrogen at 125°-130° C. for 2 hours. The residue, 644 parts, is added to 2235 parts of mineral oil and the mass is mixed at 70°-78° C. with 2970 parts (5.3 equivalents) of the polyisobutene-substituted succinic anhydride of Example 1 (having an acid number of 100) and the mixture is heated at 150° C. for 3 hours and blown with nitrogen at 150°-155° C. for 5 hours whereupon 27 parts of water is distilled off. The residue is mixed with a filter-aid and filtered. The filtrate (5580 parts, 96% of the theoretical yield) is a 38.5% oil solution of the nitrogen-containing product and has a nitrogen content of 3%.

#### EXAMPLE 4

To 1020 grams (25 equivalents) of a commercial ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine and having a nitrogen content of 34.3%, there is added dropwise, 1325 grams (25 equivalents) of acrylonitrile at 22°-60° C. An exothermic reaction occurs. The reaction mass is maintained at 22°-60° C. by external cooling during the addition and is then heated at 28° C. for 2 hours, at 108°-115° C. for 3.25 hours and then to 130° C./26 mm. The residue, 2196 grams, is an intermediate product having a nitrogen content of 29.7%. A portion (624 grams) of the intermediate and mineral oil (1456 grams) are placed in a reaction flask and heated to 100° C. To this mixture there is added 1456 grams of mineral oil and 3808 grams (7 equivalents; corresponding to 1 equivalent per equivalent of the ethylene amine in the intermediate product) of the polyisobutene-substituted succinic anhydride having an acid number of 103 and is prepared as described in Example 1 in 4.25 hours at 120°-135° C. The resulting mixture is heated to 150° C. in 5 hours and blown with nitrogen at that temperature for 3 hours. It is mixed with a filter aid and filtered. The filtrate, 6945 grams (95.4% of the theoretical yield), is a 40% oil solution of the desired nitrogen-containing composition of this invention. It has a nitrogen content of 2.2%.

#### EXAMPLE 5

An alkylene amine-alkenyl cyanide intermediate product is obtained by mixing 1060 grams (20 equivalents) of acrylonitrile and 1632 grams (40 equivalents) of the commercial ethylene amine mixture of Example 4 at 45°-55° C. (external cooling required to maintain the temperature range), agitating the mixture at 40° C. for 1 hour, and heating it at 110°-120° C. for 2 hours and then at 120° C./18 mm. to distill off volatile components. The residue is the desired intermediate product having a nitrogen content of 30.8%. A portion (716 grams) of the intermediate product added at 66°-85° C. dropwise to a mixture of 2853 grams of mineral oil and 3626 grams (7 equivalents, corresponding to 1 equivalent per 1.5 equivalents of the ethylene amine in the intermediate product) of the polyisobutene-substituted succinic anhydride having an acid number of 107 and is prepared as described in Example 1. The resulting mixture is heated to 145°-156° C. and then blown with nitrogen at that temperature for 3 hours. It is mixed with a filter aid and filtered. The filtrate, 6693 grams, is a 40% oil solution of the desired product. It has a nitrogen content of 2.8%.

#### EXAMPLE 6

An alkylene amine-alkenyl cyanide intermediate product is obtained as is described in Example 5 from a reaction mixture of 3.1 equivalents of the commercial ethylene amine mixture of Example 4 and 1 equivalent of acrylonitrile. A mixture of 3264 grams (6 equivalents) of the polyisobutene-substituted succinic anhydride having an acid number of 105 and prepared as is described in Example 1, 3100 grams of mineral oil, and 691 grams (12 equivalents of the ethylene amine) of the amine-cyanide intermediate product is prepared at 110°-115° C., blown with nitrogen at 150°-153° C. for 3 hours, mixed with a filter aid and filtered. The filtrate, 6704 grams, is a 44.3% mineral oil solution of the desired product. It has a nitrogen content of 2.9%.

#### EXAMPLE 7

A mixture of 3264 grams (6 equivalents) of the polyisobutene-substituted succinic anhydride of Example 6, 2574 grams of mineral oil, and 651 grams (12 equivalents of the ethylene amine) of an alkylene amine-alkenyl cyanide intermediate product (obtained by reacting 4.1 equivalents of the commercial ethylene amine mixture of Example 4 and 1 equivalent of acrylonitrile) is prepared at 120° C. The mixture is then blown with nitrogen at 150°-157° C. for 3 hours, mixed with a filter aid and filtered. The filtrate (6166 grams, 96% of the theoretical yield) is a 40% oil solution of the desired product. It has a nitrogen content of 3.1%.

#### EXAMPLE 8

A mixture of 3808 grams (7 equivalents) of the polyisobutene-substituted succinic anhydride of Example 6, 2740 grams of mineral oil, and 365 grams (5.22 equivalents of the ethylene amine) of an intermediate product (obtained by the reaction of 2 equivalents of the commercial ethylene amine mixture of Example 4 and 1 equivalent of acrylonitrile) is prepared at 115°-120° C. The mixture is blown with nitrogen at 150°-153° C. for 3 hours, mixed with a filter aid and filtered. The filtrate, 6563 grams, is a 40% oil solution of the desired product. It has a nitrogen content of 1.5%.

#### EXAMPLE 9

An acylated amine intermediate is obtained by reacting 1 equivalent of the polyisobutene-substituted succinic anhydride of Example 1 and 2 equivalents of the commercial ethylene amine mixture of Example 4 at 150°-170° C. A mixture of 265 grams (5 equivalents) of acrylonitrile and 5530 grams (10 equivalents of the ethylene amine) of a 40% oil solution of the acylated amine intermediate is heated at the reflux temperature (105°-145° C.) for 1 hour. The mixture is then heated at 145° C. for 3 hours, cooled to 100° C. and heated to 118° C./18 mm. It is mixed with 144 grams of mineral oil to form a 40% oil solution of the desired product. The solution has the nitrogen content of 3.3%.

#### EXAMPLE 10

An acylated amine intermediate is obtained by reacting one equivalent of the polyisobutene-substituted succinic anhydride of Example 1 and 1.5 equivalents of the commercial ethylene amine mixture of Example 4 at 150°-170° C. A 40% oil solution of the intermediate has a nitrogen content of 2%. A mixture of 424 grams (8 equivalents) of acrylonitrile and 5600 grams (8 equivalents of the ethylene amine) of a 40% mineral oil solution of the acylated amine intermediate is heated at the reflux temperature (94°-118° C.) for 5 hours. The mixture is then heated to 128° C./12 mm. whereupon 238 grams of acrylonitrile is distilled off. The residue is diluted with 103 grams of mineral oil to form a 40% oil solution of the desired product. The solution has a nitrogen content of 2.9%.

## EXAMPLE 11

An acylated amine intermediate is obtained by reacting 4 equivalents of the polyisobutene-substituted succinic anhydride of Example 1 and 3 equivalents of the commercial ethylene amine mixture of Example 4 at about 150°-170° C. A 40% oil solution of the intermediate has a nitrogen content of 1.14%. A mixture of 7368 grams (6 equivalents of the ethylene amine) of the acylated amine intermediate and 159 grams (3 equivalents) of acrylonitrile is heated at the reflux temperature from 125° C. to 145° C. for 1.25 hours, at 145° C. for 3 hours and then at 125° C./18 mm., whereupon 107 grams of acrylonitrile is distilled off. The residue is diluted with 35 grams of mineral oil to form a 40% oil solution of the desired product. It has a nitrogen content of 1.34%.

## EXAMPLE 12

A polyisobutene-substituted succinic acid is prepared by hydrolyzing the substituted succinic anhydride of Example 1 with steam. A mixture of 1 equivalent of the succinic acid, 2 equivalents of hexamethylene diamine, and 1 equivalent of 1-methylvinyl cyanide (alpha-methyl acrylonitrile) is prepared at 25°-60° C. The mixture is heated to 100° C. and maintained at that temperature for 7 hours. It is then mixed with an equal volume of mineral oil and heated at 100° C./1 mm. to distill off volatile components. The residue is filtered. The filtrate is a mineral oil solution of the desired product.

## EXAMPLE 13

A mixture of 2 equivalents of ethylene diamine, 0.2 equivalent of 2,2-dimethylvinyl cyanide, and 1 equivalent of a polypropene (molecular weight of 3000)-substituted succinic anhydride having an acid number of 90 is prepared by carefully mixing the reactants at 25°-80° C. The mixture is then heated at 150° C., mixed with an equal volume of mineral oil and blown with nitrogen at that temperature for 5 hours. The residue is filtered.

## EXAMPLE 14

An alkylene amine-alkenyl cyanide intermediate product obtained by mixing 1 equivalent of trimethylene diamine and 0.1 equivalent of acrylonitrile at 25°-50° C. and heating the mixture at 70° C. for 2 hours. The intermediate is then mixed with 1 equivalent of a polyethylene (molecular weight of 900)-substituted succinic anhydride having an acid number of 60. The mixture is heated at 200° C. and mixed with an equal volume of mineral oil and blown with nitrogen at that temperature for 2 hours. The residue is filtered.

## EXAMPLE 15

A 75% mineral oil solution of a polyisobutene (molecular weight of 60,000)-substituted succinic anhydride having an acid number of 50 (1 equivalent) is added to an alkylene amine-alkenyl cyanide intermediate product obtained by reacting 2 equivalents of N-aminoethyl piperazine and 0.5 equivalent of acrylonitrile at 50°-120° C. The resulting mixture is blown with nitrogen at 150°-250° C. for 5 hours and then filtered.

## EXAMPLE 16

An alkylene amine-alkenyl cyanide intermediate product is obtained by reacting 2 equivalents of N-octadecyl propylene diamine and 1 equivalent of 1,2,2-triethylvinyl cyanide at 25°-120° C. To this intermediate there is added 1 equivalent of a 60% mineral oil solution of an isobutene-styrene copolymer (95:5 weight ratio of isobutene to styrene) (molecular weight of 1500)-substituted succinic anhydride having an acid number of 100. The resulting mixture is blown with nitrogen at 150°-180° C. for 6 hours and filtered.

## EXAMPLE 17

To 1 equivalent of 1-methyl-2-dodecylvinyl cyanide there is added 1 equivalent of octamethylene diamine at 25°-50° C. To this reaction mixture there is then added 0.5 equivalent of a 90% mineral oil solution of an isobutene-piperylene copolymer (98:2 molar ratio of isobutene to piperylene) (molecular weight of 1000)-substituted succinic anhydride having an acid number of 60. The resulting mixture is heated at 120°-180° C. for 8 hours and filtered.

## EXAMPLE 18

A 60% mineral oil solution of the polyisobutene-substituted succinic anhydride of Example 1 (1 equivalent) is added dropwise to a mixture of 8 equivalents of heptamethylene octamine and 0.2 equivalent of 1-hexylvinyl cyanide at 50°-75° C. within a period of 2 hours. The resulting mixture is heated at 140°-220° C. for 8 hours and then filtered.

The principal utility of the compositions of this invention is as additives in hydrocarbon compositions and lubricants to improve their detergent properties and to reduce their tendency to form harmful deposits. Examples of hydrocarbons and lubricants in which the compositions of this invention are useful are gasolines, burner fuel oils, cutting oils, hydraulic fluids and lubricating oils. The lubricating oils may be of synthetic, animal, vegetable or mineral origin. Mineral lubricating oils are preferred by reason of their availability, general excellence and low cost. For certain applications oils belonging to one of the other three groups may be preferred. For instance, synthetic polyester oils such as didodecyl adipate and di-2-octyl sebacate are often preferred as jet engine lubricants. Ordinarily, the lubricating oils preferred will be fluid oils ranging in viscosity from about 40 Saybolt Universal seconds at 100° F. to about 200 Saybolt Universal seconds at 210° F.

The concentration of the compositions of this invention as additives in lubricants usually ranges from about 0.1% to about 10% by weight. The optimum concentrations for a particular application depend to a large measure upon the type of service to which the lubricant is to be subjected. For example, lubricants for use in gasoline internal combustion engines may contain from about 0.5% to about 5% of the additive whereas lubricating compositions for use in gears and diesel engines may contain as much as 10% or even more of the additive. Gasolines or burner fuel oils may contain as little as 0.001% of the composition of this invention.

The compositions of this invention are especially useful in lubricants which may be subjected to contamination by water as they are present in engines such as internal combustion engines of automobiles and trucks. In such engines lubricants containing an ashless detergent often have a tendency to cause rusting of metal parts. The compositions of this invention are unique in that they not only impart detergent properties to lubricants but also are effective to prevent rusting of the metal parts being lubricated. The effectiveness of the compositions of this invention to impart oxidation-inhibiting, corrosion-inhibiting and detergent properties is illustrated by the results obtained from a test in which a 350 cc. sample of a lubricant containing 1.5% by weight of the additive to be tested is heated at 300° F. for a specified period in a 2 x 15 (inch) borosilicate tube. A 1½ x 5½ (inch) SAE 1020 steel panel is immersed in the lubricant. Air is bubbled through the lubricant at a rate of 10 liters per hour. The oxidized sample is allowed to cool to 120° F. and homogenized with 0.5% of water and allowed to stand at room temperature. The sample is filtered through two layers of No. 1 Whatman filter paper under slightly reduced pressure. The precipitate is washed with naphtha, dried and weighed. The quantity of the sludge precipitate (reported as milligrams per 100 ml. of the lubricant) is an indication of the ability of the additive to prevent the

formation of harmful deposits in the lubricant. Thus, the greater the weight of the precipitate, the less effective the additive. The base oil of the lubricant is a Mid-Continent, conventionally refined mineral oil having a viscosity of 180-200 Saybolt Universal seconds at 100° F. The results of the test are shown in Table I below.

TABLE I

Additive Tested	Test Period (Hours)	Test Result mg. of sludge/100 ml. of lubricant
None.....	96	800-1,000
Do.....	144	1,800-2,000
Product of Example 4.....	96	5.3
	144	7.9
Product of Example 5.....	96	3.5
	144	6.0
Product of Example 6.....	96	3
Product of Example 7.....	96	3.4
Product of Example 9.....	96	2.6

The rust inhibiting properties of the compositions of this invention are shown by a rust test by a modified ASTM procedure D665-54. This test involves immersing a steel rod in 300 mls. of a test lubricant containing 5 mls. of "acidified" water (acidified by dissolving 10 grams of glacial acetic acid and concentrated sulfuric acid per liter of solution), agitating the lubricant at 140° F., removing the rod and cleaning it by dipping in benzene and acetone, drying the rod, coating the rod with a clear lacquer to fix the rust, then inspecting the rod for rusting. The tendency of the lubricant to cause rust is rated on a scale of from 0 to 10, 0 representing heavy rust on the entire surface of the rod and 10 representing no rust. The base oil of the test lubricant is a Mid-Continent mineral oil having a viscosity of 207 Saybolt Universal seconds at 100° F. and a viscosity index of 98 and containing 4.5% (by volume) of a polyacrylic acid ester viscosity index improving agent, 0.25% of a polyacrylic acid ester pour point depressing agent, 1% of a zinc dialkyl phosphorodithioate additive and 5% of the composition of this invention. The results of the test are shown in Table II below.

TABLE II

Additive tested:	Test result (rating)
Acylated amine intermediate from 1 equivalent of the polyisobutene-substituted succinic anhydride of Example 1 and 1 equivalent of the ethylene amine mixture of Example 3.....	0
Product of Example 3.....	10
Product of Example 5.....	10
Product of Example 6.....	9
Product of Example 7.....	9
Product of Example 8.....	8
Product of Example 9.....	10
Product of Example 10.....	10

The utility of the dispersant additives of the invention is shown by the results and evaluation of a modified version of the CRC-EX-3 engine test (ordinarily this engine test lasts for 96 hours; the modified version lasts for 144 hours). The test is recognized in the lubricating field as an important test by which lubricants can be evaluated for use under light duty service conditions. In this particular test, a lubricant is used in the crankcase of a 1954, 6-cylinder Chevrolet Powerglide engine for 144 hours under recurring cycling conditions. Each cycle consists of the following: (A) 2 hours at an engine speed of 500±25 r.p.m. under 0 load at an oil sump temperature of 100°-125° F., and an air-fuel ratio of 10:1; (B) 2 hours at an engine speed of 2500±25 r.p.m. under a load of 40 brake horsepower at an oil sump temperature of 160-170° F., and an air-fuel ratio of 16:1; (C) 2 hours at an engine speed of 2500±25 r.p.m. under a load of 40 brake horsepower at an oil sump temperature of 240°-250° F., and an air-fuel ratio of 16:1.

At the end of the test, the engine is dismantled and inspected for sludge and varnish in accordance with a rating system based on (1) the extent of piston ring filling, (2) the amount of sludge formed in the engine (on a scale of 80-0, 80 being indicative of no sludge and 0 being indicative of extremely heavy sludge), and (3) the total amount of engine deposits, i.e., sludge and varnish, formed in the engine (on a scale of 100-0, 100 being indicative of no deposits and 0 being indicative of extremely heavy deposits). The effectiveness of the compositions of the invention as lubricant additives is shown by the following results.

TABLE III

Test Lubricant (percent by weight)	Test Result		
	Percent Ring Filling	Sludge Rating	Total Deposit Rating
20 A. Lubricant containing 0.41% of the reaction product of the polyisobutene-substituted succinic anhydride of Example 1 (1 equivalent) an amine mixture (1 equivalent) consisting of 78% of triethylene tetramine and 25% of diethylene triamine, and acrylonitrile (0.67 equivalent).....	2	75.4	92.8

The compositions of this invention are useful in lubricants in which there are present other additives such as supplemental detergents of the ash-containing type, viscosity index improving agents, pour point depressant agents, anti-foam agents, extreme pressure agents, rust inhibiting agents, oxidation inhibiting agents and corrosion inhibiting agents. These additives may be present in the lubricant at concentrations ranging from 0.1% to about 20% by weight.

The ash-containing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium, and barium.

The term "basic salt" is used to designate the metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involves heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature about 50° C. and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthal, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent, a phenolic promoter compound, and a small amount of water and carbonating the mixture at an elevated temperature such as 60°-200° C.

A supplemental ashless detergent may likewise be used in the lubricating compositions. It is preferably an acylated polyamine such as is described in co-pending applica-

tion Ser. No. 802,667, filed Mar. 30, 1959. The acylated polyamine may be formed by the reaction of a high molecular weight hydrocarbon-substituted succinic acid or anhydride, i.e., one having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent, with at least about 0.5 equivalent of an alkylene polyamine such as ethylene diamine or a polyethylene polyamine. Especially useful in the lubricating compositions of this invention is an acylated polyamine obtained by heating at 100°-250° C. a polyisobutene (molecular weight of from about 700 to 5000)-substituted succinic anhydride and about an equivalent amount of a polyethylene polyamine having from two to about eight amino groups.

Extreme pressure agents and corrosion-inhibiting and oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene; phosphorusulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl substituted phenyl phosphite; metal thiocarbamates such as zinc dioctyl-dithiocarbamate, and barium heptylphenyl dithiocarbamate: Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl) phosphorodithioate, cadmium dinonylphosphorodithioate, and zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

The following examples are illustrative of the lubricating compositions of this invention (all percentages are by weight):

#### EXAMPLE I

SAE 20 mineral lubricating oil containing 0.5% of the composition of Example 1.

#### EXAMPLE II

SAE 30 mineral lubricating oil containing 0.75% of the composition of Example 2 and 0.1% of phosphorus as the barium salt of di-n-nonylphosphorodithioic acid.

#### EXAMPLE III

SAE 30 mineral lubricating oil containing 5% of the composition of Example 5, 0.1% of phosphorus as the zinc salt of a mixture of equimolar amounts of di-isopropylphosphorodithioic acid and di-n-decylphosphorodithioic acid, and 2.5% of sulfate ash as a basic barium detergent prepared by carbonating at 150° C. a mixture comprising mineral oil, barium di-doceylbenzene sulfonate and 1.5 moles of barium hydroxide in the presence of a small amount of water and 0.7 mole of octylphenol as the promoter.

#### EXAMPLE IV

SAE 10W-30 mineral lubricating oil containing 6% of the composition of Example 6, 0.075% of phosphorus as zinc di-n-octyl-phosphorodithioate, and 5% of the barium salt of an acidic composition prepared by the reaction of 1000 parts of a polyisobutene having a molecular weight of 60,000 with 100 parts of phosphorus pentasulfide at 200° C. and hydrolyzing the product with steam at 150° C.

#### EXAMPLE V

SAE 20 mineral lubricating oil containing 3% of an acylated polyamine obtained by heating at 150°-200° C. 1 equivalent of a polyisobutene (molecular weight of

1000)-substituted succinic anhydride and 1 equivalent of an ethylene amine mixture having an average composition corresponding to tetraethylene pentamine, 1% of zinc dioctylphosphorodithioate and 2% of the composition of Example 1.

What is claimed is:

1. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient to impart detergency thereto, of a nitrogen-containing composition prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of a hydrocarbon-substituted succinic acid-producing compound having at least about 50 aliphatic carbon atoms in the hydrocarbon substituent with at least about 0.5 equivalent, per equivalent of the hydrocarbon-substituted succinic acid-producing compound, of an amine selected from the class consisting of alkylene polyamines, and at least about 0.1 equivalent, per equivalent of the hydrocarbon-substituted succinic acid-producing compound, of an alkenyl cyanide.

2. The composition of claim 1 wherein the amine is a polyethylene polyamine.

3. The composition of claim 1 wherein the hydrocarbon substituted succinic acid-producing compound is an olefin polymer-substituted succinic anhydride.

4. The composition of claim 1 wherein the hydrocarbon substituted succinic acid-producing compound is a polyisobutene-substituted succinic anhydride, the amine is a polyethylene polyamine, and the alkenyl cyanide is a vinyl cyanide.

5. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient to impart detergency thereto, of a nitrogen containing composition prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of an isobutene polymer-substituted succinic acid or anhydride in which the isobutene polymer substituent has a molecular weight of from about 750 to about 5000 with at least about 0.5 equivalent, per equivalent of the substituted succinic acid or anhydride, or an alkylene polyamine and at least about 0.1 equivalent, per equivalent of the substituted succinic acid or anhydride, of a vinyl cyanide.

6. The composition of claim 5 wherein the alkylene polyamine is a hydroxy alkyl-substituted polyethylene polyamine.

7. The composition of claim 5 wherein the isobutene polymer substituent is a polyisobutene group having a molecular weight of about 1000.

8. The composition of claim 5 wherein the alkylene amine is a polyethylene polyamine having up to about 10 amino groups and the vinyl cyanide is acrylonitrile.

9. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient to impart detergency thereto, of a nitrogen-containing compound prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of a polyisobutene-substituted succinic anhydride wherein the polyisobutene substituent has a molecular weight from about 750 to 5000 with from about 0.5 to 5 equivalents, per equivalent of the polyisobutene-substituted succinic anhydride, of a polyethylene polyamine and from about 0.5 to 4 equivalents, per equivalent of the polyisobutene-substituted succinic anhydride, of acrylonitrile.

10. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient to impart detergency thereto, of a nitrogen-containing compound prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of a polyisobutene-substituted succinic anhydride in which the polyisobutene substituent has a molecular weight of about 1000 with from about 1 to 2 equivalents, per equivalent of the iso-

butene-substituted succinic anhydride, of a polyethylene polyamine having an average composition corresponding to that of tetraethylene pentamine and from about 0.5 to 2 equivalents, per equivalent of the isobutene-substituted succinic anhydride, of acrylonitrile.

11. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion sufficient to impart detergency thereto of a product prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of one equivalent of a polyisobutene-substituted succinic anhydride wherein the polyisobutene substituent has a molecular weight from about 750 to 5000 with from about 0.5 to 5 equivalents of a polypropylene polyamine and from about 0.5 to 4 equivalents of acrylonitrile.

12. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion sufficient to impart detergency thereto of a product prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of one equivalent of a polyisobutene-substituted succinic anhydride wherein the polyisobutene substituent has a molecular weight from about 750 to 5000 with from about 0.5 to 5 equivalents of a polyalkylene polyamine and from about 0.5 to 4 equivalents of acrylonitrile.

13. A lubricating composition comprising a major pro-

portion of a lubricating oil and a minor proportion sufficient to impart detergency thereto of a product prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of one equivalent of an olefin polymer-substituted succinic anhydride wherein the olefin polymer substituent is derived from a copolymer of isobutene and a diolefin and has a molecular weight from about 750 to 5000 with from about 0.5 to 5 equivalents of a polyalkylene polyamine and from about 0.5 to 4 equivalents of acrylonitrile.

14. A lubricating composition comprising a major proportion of a lubricating oil and a minor proportion sufficient to impart detergency thereto of a product prepared by the process comprising the reaction at a temperature between about 80° C. and below the decomposition temperature of one equivalent of an olefin polymer-substituted succinic anhydride wherein the olefin polymer substituent is derived from a copolymer of isobutene and a styrene and has a molecular weight from about 750 to 5000 with from about 0.5 to 5 equivalents of a polyalkylene polyamine and from about 0.5 to 4 equivalents of acrylonitrile.

No references cited.

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