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(54) Method for lubricating an alkanol-fueled spark ignition internal combustion engine.

(57) Improved lubrication of an alkanol fueled spark ignition internal combustion engine is achieved by employing a lubricant composition which includes a dispersant additive derived from the reaction of a succinic compound and a branched polyamine.

METHOD FOR LUBRICATING AN ALKANOL-FUELED SPARK IGNITION INTERNAL COMBUSTION ENGINE

BACKGROUND OF THE INVENTION

This invention relates to a method for lubricating an alkanol-fueled spark ignition internal combustion engine. Metal corrosion in internal combustion engines operating on conventional hydrocarbon fuels such as gasoline is generally not much of a problem because such fuels are inherently non-corrosive. However, with the use of fuels based in whole or in part on alkanols, e.g., gasohol (a mixture of gasoline and alkanol) or straight alkanol fuels, particularly methanol and ethanol, excessive engine wear has become a major problem because such fuels are relatively quite corrosive. Much of the wear which is caused by a fuel of this type, such as methanol, is thought to take place on the piston rings and upper cylinder areas of the engine. This wear results from a "washing away" of the lubricant film and direct chemical attack of the fuel and its corrosive combustion products on the metal surfaces of the cylinder liner. Fuel blow by into the lubricant, i.e., fuel and its combustion products which blow past the rings, and the resulting reaction with lubricant additives can also lead to a general increase in engine wear where alkanol fuels are concerned.

The use of various additives in alkanol-fuels has been widely investigated as a potential solution to the problem of excessive engine wear associated with these fuels. U.S. Patent No. 4,375,360 describes alkanol fuel additives such as fatty alcohols, alcohol ethoxylates, fatty acids and ethoxylates, esters including mono-, di, polyol and phosphate esters and polyalkylene glycols. A number of organic acid alkanol fuel additives are disclosed in U.S. Patent Nos. 4,177,768; 4,185,594; 4,242,099; 4,248,182; and, 4,305,730. Still other alkanol fuel additives are described in U.S. Patent Nos. 4,198,931 (n-hydroxy hydrocarbonamide); 4,204,481 (fatty acid amides or esters of diethanol amine); 4,208, 190 (straight chain aliphatic primary amines); 4,385,904 (cyclized alkenyl succinic acid anhydride); 4,509,951 and 4,511,366 (combination of a polymerized polyunsaturated monocarboxylic acid and a polyalkylenepolyamine derivative); 4,549,882 (combination of a monoalkylenesuccinic acid and an alkanolamide); and, 4,609,376 (ester of a carboxylic acid and a polyhydric alcohol).

Fuel and lubricant additives based on polyalkylene polyamine derivatives are known, inter alia, from U.S. Patent Nos. 3,172,892; 3,200,106; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,259,578; 3,272,746; 3,509,052; 3,804,763; 3,948,800; 4,105,571; and, 4,234,435. In particular, aforecited U.S. Patent Nos. 3,200,106, 3,259,578 and 4,234,435 describe lubricating oil additives resulting from the reaction of a branched polyamine and an acylating agent such as an alkenyl succinic acid/anhydride.

SUMMARY OF THE INVENTION

It has now been discovered that the lubrication requirements of an alkanol-fueled spark ignition internal combustion engine can be more effectively met by utilizing a lubricant composition which includes as a dispersant the reaction product of a branched polyamine and a hydrocarbon-substituted succinic acid together with one or more other known and conventional lubricant additives.

Compared to lubricant compositions of similar overall composition but containing an essentially linear polyamine derivative as dispersant, lubricant compositions containing a branched polyamine derivative in accordance with this invention have been found to perform much more effectively in the lubrication of alkanol-fueled engines.

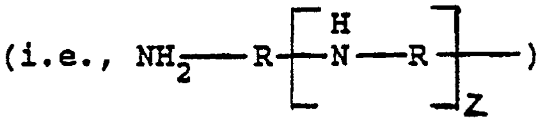
The lubrication compositions employed in the practice of the lubrication method of this invention are themselves known materials, having been disclosed in, among others, U.S. Patent No. 4,234,435, supra. No claim of invention is made herein to the lubrication compositions per se.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

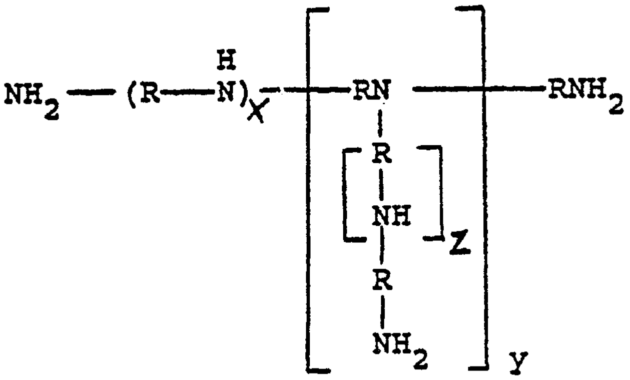
The lubrication method of the present invention is applicable to the operation of any spark ignition internal combustion engine which employs an alkanol type fuel including gasoline-alkanol mixtures (i.e., "gasohol") as well as essentially straight-alkanol type fuels. Useful alkanols include methanol, ethanol, n-propanol, isopropanol, isobutanol, etc., and their mixtures.

As previously indicated, the branched polyamine derivative component of the lubricating oil used in the practice of the present invention is obtained by reacting a branched polyamine with a hydrocarbon-substituted succinic acid and/or hydrocarbon-substituted succinic acid anhydride, e.g., as described in U.S.

Patent Nos. 3,200,106, 3,259,578 and 4,234,435, supra, the contents of which are incorporated by reference herein. The branched polyamines are polyalkylene polyamines wherein the branched group is a side chain containing on the average at least one nitrogen-bonded aminoalkylene (i.e., $NH_2-R\left[\overset{H}{N}-R\right]_z-$) group per nine amino units present on the main chain, for example, 1-4 of such branched chains per nine units on the main chain, but preferably one side chain unit per nine main chain units. Thus, these polyamines contain at least three primary amino groups and at least one tertiary amino group.



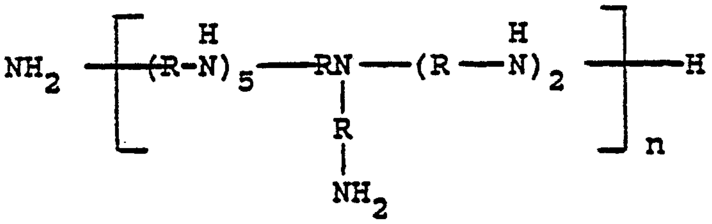
These branched polyamines can be represented by the formula:



$$NH_2-(R-\overset{H}{N})_x-\left[\underset{\substack{|\\ \left[\substack{R\\|\\NH}\right]_z \\ | \\ R \\ | \\ NH_2}}{RN}\right]_y-RNH_2$$

wherein R is an alkylene group such as ethylene, propylene, butylene and other homologues (both straight chained and branched), etc., but preferably ethylene; and x, y and z are integers, x being for example, from 4 to 24 or more but preferably from 6 to 18, y being, for example, from 1 to 6 or more but preferably from 1 to 3, and z being, for example, from 0 to 6 but preferably 0 or 1. The x and y units can be sequential, alternative, orderly or randomly distributed.

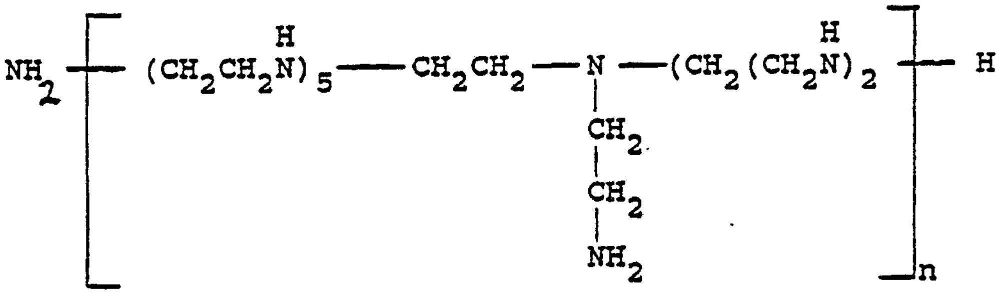
The preferred class of branched polyamines includes those of the formula:



$$NH_2-\left[(R-\overset{H}{N})_5-\underset{\substack{|\\R\\|\\NH_2}}{RN}-(R-\overset{H}{N})_2\right]_n-H$$

wherein n is an integer, for example, from 1-20 or more but preferably from 1-3, wherein R is preferably ethylene, but may be propylene, butylene, etc. (straight chained or branched).

The preferred branched polyamines can be represented by the formula:



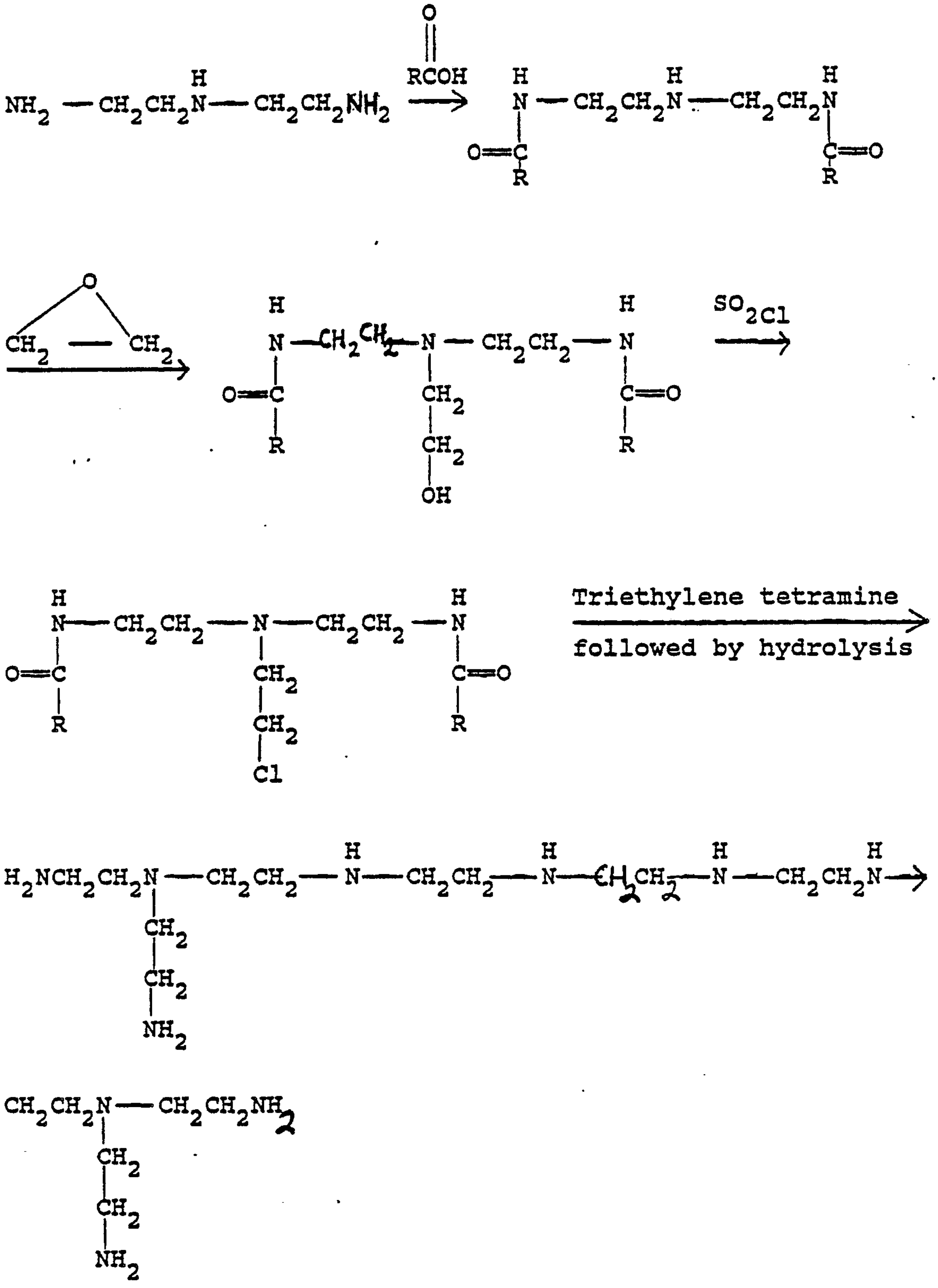
$$NH_2-\left[(CH_2CH_2\overset{H}{N})_5-CH_2CH_2-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\NH_2}}{N}-(CH_2(CH_2\overset{H}{N})_2\right]_n-H$$

wherein n is 1 to 3.

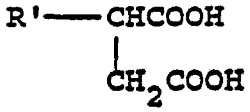
The radicals in the brackets can be joined in a head-to-head or in a head-to-tail fashion. Compounds embraced by this formula wherein n is 1-3 are manufactured and sold as Polyamines N-400, N-800, N-1200, etc. Polyamine N-400 conforms to the above formula wherein n is 1.

These compounds can be prepared by a variety of methods. One method comprises the reaction of ethanolamine and ammonia under pressure over a fixed bed of a metal hydrogenation catalyst. By controlling the conditions of the reaction, one can obtain varying amounts of piperazine and polyamines as well as the foregoing branched polyamines.

These branched polyamines can also be prepared by the following reactions:

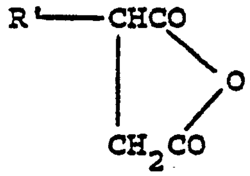


To provide the dispersant additive of the lubrication composition employed in the method of this invention, one or more of the foregoing branched polyamine reactants is acyclated with a substituted succinic compound selected from the group consisting of substituted succinic acids having the structural formula



$$\begin{array}{ll} R'\text{—} & CHCOOH \\ & | \\ & CH_2COOH \end{array}$$

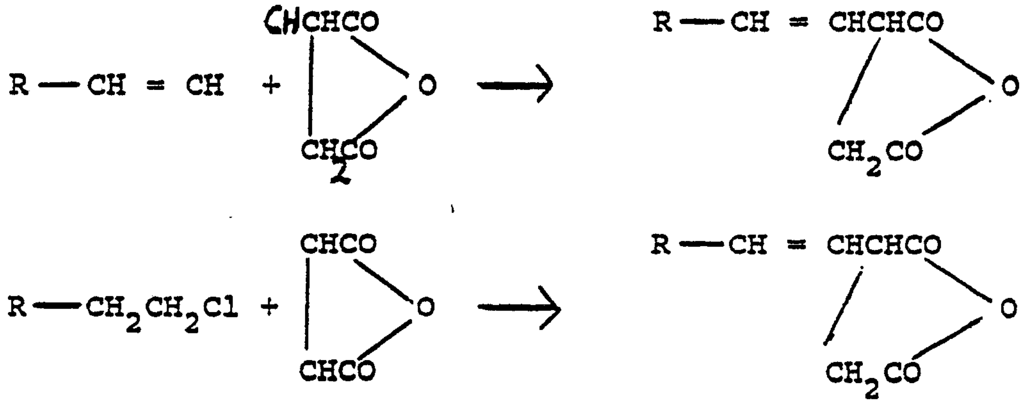
and substituted succinic anhydrides having the structural formula



in which structural formulas R′ is a large, substantially aliphatic hydrocarbon radical having at least about 50 carbon atoms. This reaction can result in a simple acyclic diamide, a cyclic diamide, a polymeric amide or a combination of any of these types of products. The amide groups have the capability for reacting further to form imide groups, a substantial number of which may indeed result from the foregoing acylation reaction. There may also be present in the acylated product an appreciable proportion of amine carboxylate salt.

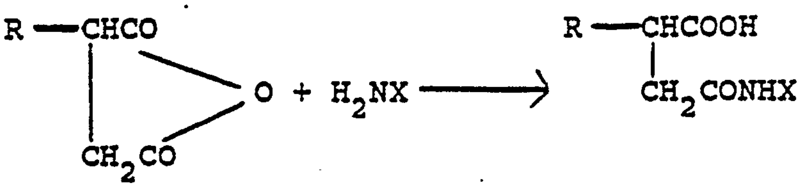
Substituent R′ in the succinic compounds, supra, is selected from amongst substantially aliphatic hydrocarbon radicals including both alkyl and alkenyl radicals. Such radicals are commonly derived from polyolefins such as polyethylene, polypropylene, polybutylene, etc., although they can be derived from any substantially aliphatic hydrocarbon.

The foregoing substituted succinic anhydrides can be obtained by reacting maleic anhydride with a high molecular weight olefin or a chlorinated high molecular weight olefin. The product from such a reaction is the corresponding alkenyl succinic anhydride. The reaction involves merely heating the two reactants at a temperature of about 150-200°C. The reactions in each case are illustrated by the following equations.

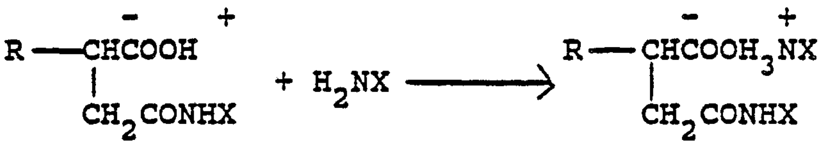


It will be appreciated that the reactions might not conform precisely to that indicated in the above equations, especially with respect to the particular carbon atom of the olefin or chloride reactant which ultimately becomes attached to the maleic acid or anhydride reactant. Furthermore, although the product of this reaction has been indicated as being an alkenyl succinic anhydride it is apparent that similar products can be prepared by this process in which the substituent is something other than an alkenyl group. For the purposes of this invention this substituent should, however, be a substantially aliphatic group and in most cases, of course, it will be an alkyl or alkenyl group. In some cases, however, it may well be desirable to employ a substituted succinic anhydride in which the substituent is derived from a copolymer of styrene and isobutylene, or of a substituted styrene and some other aliphatic olefin. In these latter cases, the copolymer will be substantially aliphatic, that is, the composition of the copolymer will be predominantly aliphatic, e g., more than 90% of the monomeric units will be those of the aliphatic monomer.

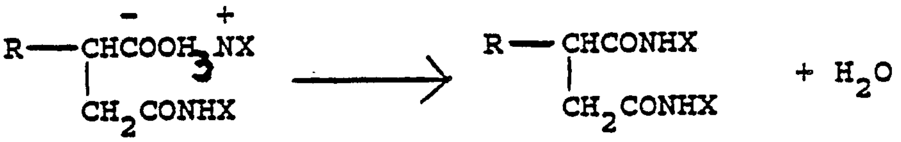
The most commonly used sources of these substantially aliphatic hydrocarbon substituents are the polyolefins. These are illustrated by polyethylene, polypropylene, polyisobutylene, etc. A particularly preferred polyolefin for this use is polyisobutylene. Thus, for example, the condensation of a polyisobutylene having a molecular weight of about 750 with maleic anhydride yields an alkenyl succinic anhydride which upon further reaction with a branched polyamine produces an especially effective lubricating oil dispersant. The reaction of branched polyamine and succinic compound involves a splitting out of water and the reaction conditions are such that this water is removed as it is formed. Presumably, the first principal reaction which occurs, following salt formation, is the formation of a half amide



followed by salt formation (X = branched organoamine residue)



and finally involving dehydration of the salt to form the product



The first two of these reactions appear to take place spontaneously (when a substituted succinic anhydride is used) upon mixing but the third requires heating. Temperatures within the range of about 80°C. to about 200°C. are generally satisfactory and within this range it is preferred to use a reaction temperature of from about 100°C. to about 160°C. A useful method of carrying out this step is to add some toluene to the reaction mixture and to remove the water by azeotropic distillation.

The foregoing acylated branched polyamine dispersant can be added to conventional base oils in widely varying amounts, for example, from about 0.001 to about 25% by weight of base oil. Preferably, however, the dispersant is used in amounts ranging from about 0.01 to 15%, and more preferably in amounts ranging from about 0.1 to 10%, by weight of the total composition.

In addition to the foregoing branched polyamine derivatives, other known and conventional lubricating oil additives can be utilized. These additives include, for example, detergents of the ash-containing type, dispersants of the ashless-type, viscosity index improving agents, pour-point depressing agents, anti-foam agents, rust-inhibiting agents oxidation and corrosion inhibiting agents, and various mixtures of these materials in various proportions. More particularly, the ash-containing detergents can be illustrated by the oil soluble neutral and basic salts of the alkali or alkaline earth metals of the sulfonic acids, carboxylic acids, or the organic phosphorus acids. Calcium and magnesium sulfonates are preferred.

The term "basic salt" is intended to include the metal salts where the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts comprises heating a mineral oil solution of the acid with a stoichiometric excess of a metal neutralizing agent, e.g., a metal oxide, hydroxide, carbonate, bicarbonate, sulfide, etc., at temperatures above about 50°C. In addition, various promoters can be used in the neutralizing process to aid in the incorporation of the large excess of metal. These promoters are presently known and include such compounds as the phenolic substances, e.g., phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol and the various condensation products of formaldehyde with a phenolic substance, e.g., alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, Carbitol, ethylene glycol, stearyl alcohol and cyclohexyl alcohol; and, amines such as aniline, phenylenediamine, phenothiazine, phenyl-beta-naphthylamine and dodecyl amine, etc. A particularly effective process for preparing the basic salts comprises mixing the acid with an excess of the basic alkaline earth metal in the presence of the phenolic promoter and a small amount of water and carbonating the mixture at an elevated temperature, e.g., 60°C. to about 200°C.

Extreme pressure agents, 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, phosphosulfurized 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, 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 dioctyldithiocarbamate and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)-phosphorodithioate, cadmium dinonylphosphorodithioate and zinc salts of a phosphordithoic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

Detergent additives derived from the partial or complete esterification of a polyhydric alcohol with any of the succinic compounds described herein can also be incorporated into the base lubricating oil. Suitable polyhydric alcohols include glycols such as ethylene glycol, diethylene glycol, triethylene glycol, butylene glycol, glycerol, sorbitol, pentaerythritol, and the like.

The lubricating compositions employed in the method of this invention can also contain metal detergent additives in amounts usually within the range of from about 0.001% to about 15% by weight.

The lubricant base oils utilized herein include those of the solvent-refined or acid-refined mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale or also useful base oils. The synthetic lubricating oils include the hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, propyleneisobutylene copolymers, chlorinated polybutylenes, etc.) alkyl benzenes (e.g., dodecylbenzene, tetradecylbenzene, dinonylbenzene, di-(2-ethylhexyl)benzene, etc.) polyphenyls (e.g., bi-phenyls, terphenyls, etc.), and the like. The alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., comprise another class of synthetic lubricating oils which are useful herein. These are exemplified by the oils prepared by polymerization of ethylene oxide, propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500 to 1000, diethyl ether of polypropylene glycol having a molecular weight of 1000 to 1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_3 fatty acid esters, or the C_{13}Oxo acid diester of tetraethylene glycol.

Another class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, pentaerythritol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)-sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisoctyl azelate, dii odocyl azelate, dioctyl phthalate, didecyl phthalate, dieicoxyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of 2-ethyl-hexanoic acid, and the like.

Silicone-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl-silicate, tetraisopropyl-silicate, tetra-(2-ethylhexyl)-silicate, tetra-(4-methyl- 2-tetraethyl)silicate, tetra(p-tert-butylphenyl)-silicate, hexyl-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)-siloxanes, poly(methylphenyl)-siloxanes, etc.). Other synthetic lubricants include the liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decane phosphonic acid, etc.), polymeric tetrahydrofurans, and the like.

EXAMPLE 1

This example illustrates the lubricating method of the present invention which utilizes a known lubricating oil composition containing a branched polyamine component (Lubricating Oil A) and compares the performance of such lubricating oil composition with three other known lubricating oil compositions which lack such branched polyamine component (Lubricating Oils B, C and D).

The lubricating oils were tested for 16 hrs. operation in a conventional 2.3 liter 4 cylinder engine whose carburetor was modified in a known manner to permit operation of the engine on the partially vaporized methanol/air mixture used for the tests.

For the test, the engine was charged with 5 quarts of lubricating oil with 4 ounces of the oil being reserved as a control. The engine was operated at 2500 rpm, 135°F water temperature, 125°F oil temperature and a load of 52 ft.-lbs. 2 Oz. samples of oil were taken at 1, 15, 30, 45 and 60 minutes of engine operation and 4 oz. samples were taken at 4, 8, 12 and 16 hours of engine operation. Fresh oil was added after each sampling to maintain the original oil level.

The lubricating oil compositions were formulated with the same 300 SEN base oil and contained similar additive packages except that Lubricating Oil A contained a dispersant derived from the reaction of polyisobutylene succinimide and a branched polyamine and Lubricating Oils B, C and D contained a dispersant derived from the reaction of polyisobutylene succinic acid and a linear amine.

Table I below sets forth the properties of each lubricating oil and the amount of engine wear observed during the 16 hour test.

	Lubricating oil			
Lubricating Oil Properties	A	B	C	D
Vis, 210° F, cSt.	14.87	9.3	10.04	12.69
Vis, 100° F, cSt.	132.56	81.11	91.56	123.46
TAN	4.893	5.954	4.048	4.733
TBN D 2896	15.061	11.197	15.105	27.804
Ash, SO4, wt.%	2.151	1.777	1.711	3.515
Zn, wt.%	0.22	0.26	0.12	0.25
P	0.19	0.21	0.1	0.25
S	0.79	0.67	0.63	---
N ppm	452	219	1000	1900
Ca, wt.%	0.5	0.41	0.51	1.42
Mg, ppm	12	7	13	51
Metal Wear Rate				
(Fe ppm/hr.)	1.5			
0-4 hr.	0.2	2.6	3.8	4.8
4-8	0.2	1.4	1.2	0.8
8-12	0.2	0.9	0.9	0.4
12-16	0.1	0.6	0.7	0.3

As these data show, Lubricating Oil A resulted in far less engine wear after 16 hrs. of continuous engine operation than any of Lubricating Oils B, C and D.

EXAMPLES 2-5

Lubricating Oil A was tested for 64 continuous hours under conditions similar to those of the 16 hr. test of Example 1 except that the methanol fuel was not partially vaporized. The measured engine wear (parts per million of iron per hour) was as follows:

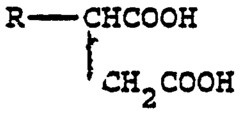
EXAMPLE (Fe ppm)				
Hours	2	3	4	5
0- 4	9.5	6.4	5.5	4.2
4- 9	2.5	0.3	1.9	1.7
8-12	1.8	0.3	1.4	1.2
12-16	1.4	0.3	1.2	1.1
16-20	1.2	0.3	1.0	0.9
20-24	1.1	0.3	0.9	0.8
24-28	0.9	0.3	0.8	0.8
28-32	0.9	0.4	0.7	0.7
32-36	0.8	0.4	0.7	0.7
36-40	0.7	0.4	0.7	0.6
40-44	0.7		0.6	0.6
44-48	0.6	0.4	0.6	0.6
48-52	0.6	0.5	0.6	0.5
52-56	0.6	0.5	0.5	0.5
56-60	0.6	0.5	0.5	0.5
60-64	0.5	0.5	0.5	0.5

These data, taken at four times the duration of engine opration of the comparative test of Example 1, are fully consistent with the excellent lubricating performance observed for Lubricating Oil A as shown in that example.

Claims

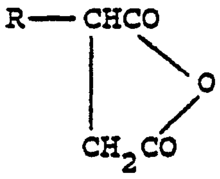
1. A method for lubricating an alkanol fueled spark ignition internal combustion engine which comprises applying to working surfaces of the engine a lubricating amount of a lubricating oil composition comprising a major portion of lubricating oil and a minor portion of a branched polyamide derivative obtained from the reaction of:

a) a substituted succinic compound selected from the group consisting of substituted succinic acid of the general formula:



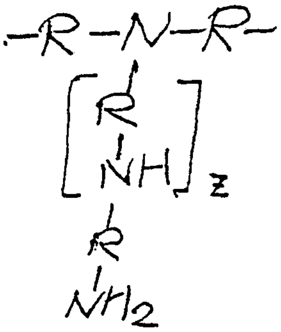
$$R-\underset{|}{C}HCOOH \quad CH_2COOH$$

and substituted succinic anhydride of the general formula



wherein R is a large, substantially aliphatic hydrocarbon radical having at least about 50 carbon atoms, with

b) a branched polyamine containing at least three primary amino groups and at least one tertiary amino group having the formula

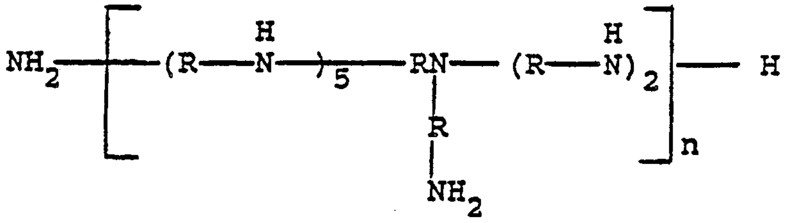


wherein R is an alkylene group having at least two carbon atoms, z is an integer of 0 to 6.

2. The method of Claim 1 wherein the engine is fueled with methanol.

3. The method of Claim 1 wherein radical R of succinic compound (a) is derived from a polybutylene.

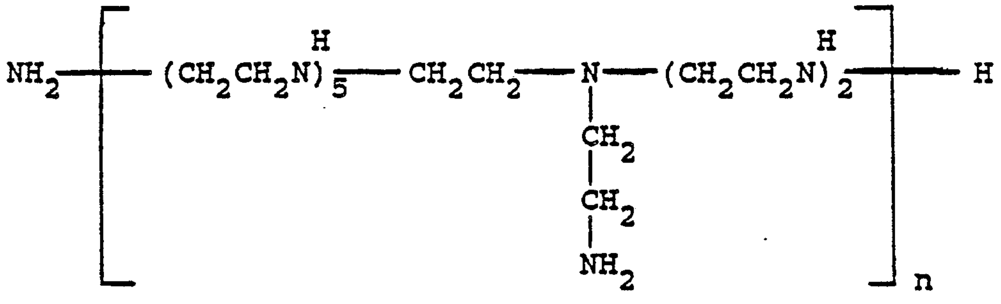
4. The method of Claim 1 wherein the branched polyamine (b) possesses the general formula



$$NH_2-\left[(R-\overset{H}{N})_5-\underset{\substack{|\\R\\|\\NH_2}}{RN}-(R-\overset{H}{N})_2\right]_n-H$$

wherein n is from 1 to 20 and R is ethylene, propylene, or butylene.

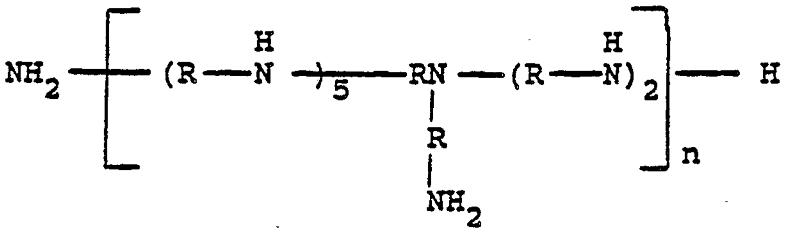
5. The method of Claim 1 wherein branched polyamine (b) possesses the general formula



$$NH_2-\left[(CH_2CH_2\overset{H}{N})_5-CH_2CH_2-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\NH_2}}{N}-(CH_2CH_2\overset{H}{N})_2\right]_n-H$$

wherein n is 1 to 3.

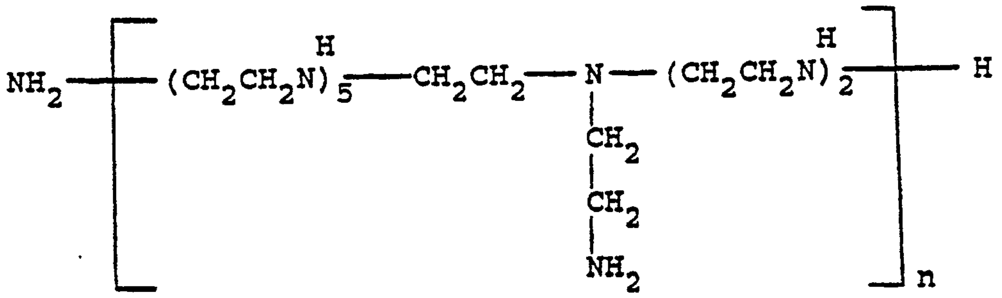
6. The method of Claim 1 wherein radical R of succinic compound (a) is derived from a polyisobutylene and branched polyamine (b) possesses the general formula



$$NH_2-\left[(R-\overset{H}{N})_5-\underset{\substack{|\\R\\|\\NH_2}}{RN}-(R-\overset{H}{N})_2\right]_n-H$$

wherein n is from 1 to 20 and R is ethylene, propylene, or butylene.

7. The method of Claim 1 wherein radical R of succinic compound (a) is derived from a polyisobutylene and branched polyamine (b) possesses the general formula



$$NH_2\left[(CH_2CH_2\overset{H}{N})_5-CH_2CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_2\\ |\\ NH_2}}{N}-(CH_2CH_2\overset{H}{N})_2\right]_n H$$

wherein n is 1 to 3.

8. The method of Claim 1 wherein the lubricating oil composition further comprises individually minor amounts of one or more other materials selected from the group consisting of detergent, antioxidant, corrosive-inhibiting agent, dispersant, viscosity control agent, pour point depressing agent, anti-foam agent and mixtures thereof.

9. The method of Claim 1 wherein the lubricating oil further comprises a minor amount of dihydrocarbyl dithiophosphate.

10. The method of Claim 1 wherein the lubricating oil further comprises a minor amount of zinc dihydrocarbyl dithiophosphate.

11. The method of Claim 1 wherein the lubricating oil further comprises a minor amount of an ester derived from the reaction of succinic compound (a) and a polyhydric alcohol.

12. The method of Claim 1 wherein the lubricating oil further comprises a minor amount of an ester derived from the reaction of succinic compound (a) in which R is derived from a polyisobutylene and pentaerythritol.

13. The method of Claim 1 wherein the lubricating oil further comprises a sulfonate.

14. The method of Claim 1 wherein the lubricating oil further comprises an alkaline earth metal sulfonate.

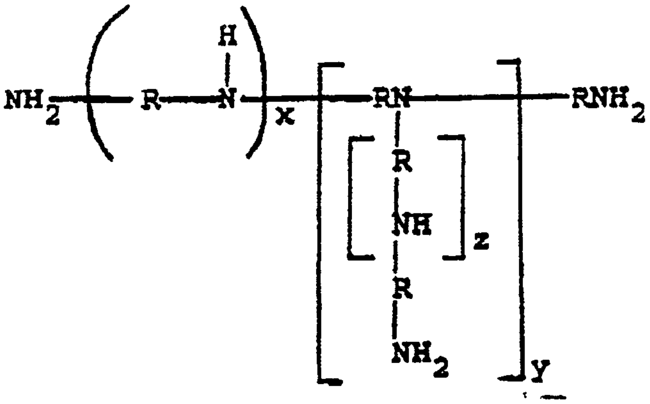
15. The method of Claim 1 wherein the lubricating oil composition further comprises individually minor amounts of one or more other materials selected from the group consisting of metal dihydrocarbyl dithiophosphate; ester derived from the reaction of succinic compound (a) and a polyhydric alcohol; sulfonate; and, mixtures thereof.

16. The method of Claim 1 wherein the lubricating oil composition further comprises individually minor amounts of one or more other materials selected from the group consisting of zinc dihydrocarbyl dithiophosphate; ester derived from the reaction of succinic compound(a) in which R is derived from a polyisobutylene and pentaerythritol; alkaline earth metal sulfonate; and, mixtures thereof.

17. The method of Claim 1 wherein the engine is fueled with methanol, R in the succinic compound is derived from a polyisobutylene and the lubricating oil composition further comprises individually minor amounts of one or more other materials selected from the group consisting of metal dihydrocarbyl dithiophosphate; ester derived from the reaction of succinic compound (a) and a polyhydric alcohol; sulfonate; and, mixtures thereof.

18. The method of Claim 1 wherein the engine is fueled with methanol, R in the succinic compound is derived from a polyisobutylene and the lubricating oil composition further comprises individually minor amounts of one or more other materials selected from the group consisting of zinc dihydrocarbyl dithiophosphate; ester derived from the reaction of succinic compound(a) in which R is derived from a polyisobutylene and pentaerythritol; alkaline earth metal sulfonate; and, mixtures thereof.

--19. The method of claim 1 wherein the branched polyamine (b) possesses the general formula



wherein R is an alkylene group having at least two carbon atoms, x is an integer of 4 to 24, y is an integer of 1 to 6, and z is an integer of 0 to 6.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 89 30 9605

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WO-A-8 605 501 (THE LUBRIZOL CORP.) * Page 9, line 19 - page 10, line 14; page 22, line 19 - page 23, line 2; page 31, lines 30-35; page 34, line 36 - page 35, line 9; page 36, lines 9-21; claims 7,8,22,34 * ---	1-10,15-19	C 10 M 133/56 C 10 M 141/10 C 10 M 163/00 // (C 10 M 141/10 C 10 M 129:95 C 10 M 133:56 C 10 M 137:10) (C 10 M 163/00 C 10 M 129:95 C 10 M 133:56 C 10 M 137:10 C 10 M 159:24) C 10 N 40:25
D,X	US-A-4 234 435 (N.A. MEINHARDT) * Column 19, lines 18-47; column 24, line 40 - column 25, line 40; column 42, lines 60-67; column 44, lines 30-41; claims 1,12 *	1,3-8,19	
Y	 ---	9-11,13-16	
Y	EP-A-0 067 002 (THE LUBRIZOL CORP.) * Page 8, lines 9-14; page 13, line 21; page 17, example A *	9-11,13-16	
A	 -----	12,17,18	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
			C 10 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-11-1989	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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