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LUBRICATING OIL COMPOSITIONS CONTAINING N-SUBSTITUTED ALKENYL SUCCINIMIDES IN COMBINATION WITH POLYAMINES

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This invention pertains to lubricating oil compositions having incorporated therein the metal-free detergents, N-substituted alkenyl succinimides, in combination with certain polyamines.

This application is a continuation-in-part of patent applications Serial Nos. 835,390, now Patent No. 3,018,250; 835,391, now Patent No. 3,024,195, and 835,437, filed August 24, 1959.

Alkenyl succinic anhydrides and numerous derivatives thereof are well-known in the art. For example, alkenyl succinic anhydrides in which the alkenyl radical contains from 5 to 20 carbon atoms are taught as corrosion inhibitors in lubricating oil compositions. Also, products obtained by reacting such alkenyl succinic acid anhydrides with monoamines are taught as ferrous corrosion inhibitors for lubricating oil compositions.

However, the above known alkenyl succinimides are not useful as detergents in lubricating oil compositions. In contrast thereto, the N-substituted polyamine alkenyl succinimides which are described herein are new compounds which are useful as detergents in lubricating oil compositions.

Present day internal combustion engines operate at high speeds and high compression ratios. When used in the so-called city stop-and-go driving, which includes the greater part of the driving condition for a large percentage of today's automobiles, the internal combustion engines do not reach the most efficient operating temperature. Under city driving conditions, large amounts of partial oxidation products are formed, and reach the crankcase of the engine by blowing past the piston rings. Most of these partial oxidation products are oil insoluble, tending to form deposits on the various operating parts of the engine, such as the pistons, piston rings, etc. For the purpose of preventing the deposition of these products on the various engine parts, it is necessary to incorporate detergents in the lubricating oil compositions, thus keeping these polymeric products highly dispersed in a condition unfavorable for deposition on metals.

For the most part, the various detergents which are added to crankcase oils to reduce this formation of sludges and varnishes are metal organic compounds, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. Although these metal-containing organic compounds have some effectiveness as detergents for dispersing the precursors of deposits within the oil itself rather than permitting them to form added deposits on the engine parts, they have the disadvantage of forming ash deposits in the engine. These ash deposits lower engine performance by fouling spark plugs and valves, and contributing to preignition.

Lubricating oil compositions containing N-substituted alkenyl succinimides as metal-free detergents are described in the above-noted patent applications Serial Nos. 835,390, Patent No. 3,018,250; 835,391, Patent No. 3,024,195; and 835,437. The addition thereto of certain polyamines markedly improves the effectiveness of such detergents as lubricating oil additives.

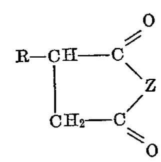
It is a particular object of this invention to provide lubricating oil compositions which are compounded with

a metal-free detergent in combination with certain polyamines.

Therefore, in accordance with this invention, it has been discovered that lubricating oil compositions particularly useful for heavy duty service are obtained by incorporating certain polyamines and N-substituted monoalkenyl succinimides in oils of lubricating viscosity.

By the use of lubricating oil compositions containing the N-substituted alkenyl succinimides in combination with polyamines as described herein, diesel and gasoline engine parts remain remarkably free of deposits and varnish, even under severe operating conditions.

The N-substituted alkenyl succinimides include those of the formula, including the bis derivatives thereof; that is, the di(alkenyl succinimides):



wherein R is a hydrocarbon radical having a molecular weight from about 400 to about 3000; that is, R is a hydrocarbon radical containing about 30 to about 200 carbon atoms; and Z is an amine radical selected from the group consisting of monoalkylene diamine radicals and polyalkylene polyamine radicals. Also included are the bis derivatives of these alkenyl succinimides.

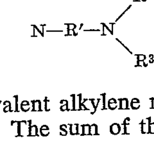
In the alkenyl succinimides, the 2 carbon atoms bonded to the Z in the above formula are actually bonded to a nitrogen atom of the polyamine which Z represents.

The "R" radical of the above formula, that is, the alkenyl radical, is derived from an olefin containing from 2 to 5 carbon atoms. Thus, the alkenyl radical is obtained by polymerizing an olefin containing from 2 to 5 carbon atoms to form a hydrocarbon having a molecular weight ranging from about 400 to about 3000, more preferably, 900 to 1200. Such olefins are exemplified by ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures thereof. Since the methods of polymerizing the olefins to form polymers thereof is immaterial in the formation of the compounds described herein, any of the numerous processes available can be used therefor.

When the Z of the above formula represents a monoalkylene diamine radical, such radicals include those derived from: ethylene diamine, propylene diamine, butylene diamine, octylene diamine, etc.

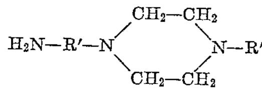
When Z represents polyalkylene polyamine radicals, such radicals include those represented by diethylene triamine, dipropylene triamine, tetraethylene pentamine, pentaethylene hexamine, nonaethylenedecamine, etc.

The polyalkylene polyamine radicals also include dialkylaminoalkylene amines of the formula:



wherein R′ is a divalent alkylene radical, and R^2 and R^3 are alkyl radicals. The sum of the carbon atoms in R′, R^2 and R^3 is preferably 3 to 10; that is, R′, R^2 and R^3 contain a total of no more than 10 carbon atoms. Thus, the resulting dialkylaminoalkylamine radicals are derived from amines exemplified by dimethylaminomethylamine, dimethylaminopropylamine, diethylaminopropylamine, diethylaminobutylamine, dipropylaminobutylamine, etc. It is preferred to use dialkylaminoalkylamines containing a total of 3 to 10 carbon atoms; more particularly, dimethylaminopropylamine.

As polyalkylene polyamine radicals, Z of the above formula also represents aminoalkyl piperazine radicals which include amines of the formula:



wherein R' is an alkyl radical containing from 1 to 3 carbon atoms, and R'' is hydrogen or an alkyl radical containing from 1 to 3 carbon atoms.

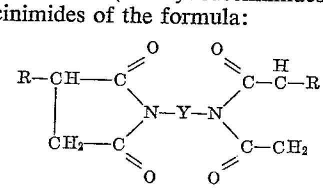
The N-substituted alkenyl succinimides can be prepared by reacting maleic anhydride with an olefinic hydrocarbon, followed by reacting the resulting alkenyl succinic anhydride with the desired polyamine, for example, tetraethylene pentamine.

The reaction between a polyolefin and maleic anhydride is an uncatalyzed addition reaction which should not be confused with a copolymerization reaction such as that obtained with a vinyl monomer and maleic anhydride. This reaction can proceed in a mol ratio of the polyolefin to the maleic anhydride of 1:1 to 1:10, preferably from 1:1 to 1:5. The reaction temperature can vary from 300° F. to 450° F. Because of the greater yield of products obtained thereby, it is preferred to use the high range of temperatures (e.g., 375° F. to 450° F.).

In the reaction between an alkenyl succinic acid anhydride and a polyamine, for example, tetraethylene pentamine, in which reaction the temperatures are from 220° F to 500° F., preferably from 300° F. to 400° F., the yield of the imide is extremely high even though the reactants are used in equal molar ratios. This is surprising, since under the conditions of the reaction there is an excess of secondary amino groups over primary amino groups, and any reaction with the secondary amino groups would lead to amide formation; thus, preventing imide formation.

Since the reaction between the polyolefin and maleic anhydride may not go to completion, the resulting alkenyl succinic anhydride may contain some unreacted polyolefin. As it may not be desirable to separate out this unreacted polyolefin at this stage, the resulting imide formed by reaction of the alkenyl succinic anhydride and the polyamine will contain this polyolefin as an impurity which can be a diluent in the formation of lubricating oil compositions. However, if it is so desired, this unreacted polyolefin can be removed by precipitation, for example, by acetone or methanol from a hydrocarbon solution.

Although the alkenyl succinimide formula hereinabove is directed to mono(alkenyl succinimides), it is intended herein to include the di(alkenyl succinimides), that is, the alkenyl succinimides of the formula:



wherein the R's represent the same as noted hereinabove, and Y represents the remaining portion of the polyamine radical described by Z in the formula hereinabove.

The particular amines which are effective herein in combination with the N-substituted alkenyl succinimides are amines of the formula, including the fatty acid salts thereof,

$$X-\left[CH_2CH_2(CH_2)_n-NH\right]_q-(CH_2)_n-CH_2CH_2-NH_2$$

wherein X is a radical selected from the group consisting of —OH, and —NH_2; n is a number from 0 to 1, and q is a number from 0 to 10.

The particular polyamines and their fatty acid salts are exemplified as follows: ethylene diamine, diethylenetriamine, tetraethylene pentamine, nonaethylenedecamine, dipropylenetriamine, hydroxyethylethylenediamine, ethylenediamine monoacetate, diethylenetriamine monoacetate, ethylenediamine monopropionate, ethylenediamine monobutyrate, tetraethylenepentamine monohexanoate, etc.

The particular fatty acids which can be used in the formation of the fatty acid salts of the polyamines include the fatty acids containing from 2 to 22 carbon atoms, for example, acetic acid, propionic acid, butyric acid, caproic acid, stearic acid, etc.

Lubricating oils which can be used as base oils include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base lubricating oils, other hydrocarbon lubricants, e.g., lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and the mixtures thereof), alkylene oxide-type polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohols, e.g., ethyl alcohol, dicarboxylic acid esters (such as those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkanol succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethyl hexyl alcohol, dodecyl alcohol, etc.), liquid esters of acids of phosphorus, alkyl benzenes (e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc.), and dialkyl benzenes (e.g., n-nonyl 2-ethyl hexyl benzene); polyphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, polymers of silicon (e.g., tetraethyl silicate, tetraisopropyl silicates, tetra(4-methyl-2-tetraethyl) silicate, hexyl(4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxane, poly(methylphenyl) siloxane, etc.). Synthetic oils of the alkylene oxide-type polymers which may be used include those exemplified by the alkylene oxide polymers.

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

The N-substituted alkenyl succinimides can be used in oils of lubricating viscosity as described herein in amounts of 0.1% to 45%, by weight, preferably 0.25% to 5%, by weight.

The polyamines and the salts thereof can be used in amounts of 0.01% to 2%, by weight, preferably 0.02% to 0.5% by weight. The succinimide and the polyamine can be used in amounts such that the succinimide/polyamine weight ratio is from 3:1 to 100:1, preferably 10:1 to 75:1.

The preparation of the N-substituted alkenyl succinimides is illustrated in the following examples.

EXAMPLE I.—PREPARATION OF POLYBUTENYL SUCCINIC ANHYDRIDE

A mixture of 1000 grams (1 mol) of a polybutene having a molecular weight of about 1000 and 98 grams (1 mol) of maleic anhydride was heated at 410° F. in a nitrogen atmosphere with agitation for a period of 24 hours. The reaction mixture was cooled to 150° F. and 700 cc. of hexane added; after which the mixture was filtered under vacuum. After vacuum distillation to remove the hexane from the filtrate, the product was maintained at 350° F. at an absolute pressure of 10 mm. Hg for one hour to remove traces of maleic anhydride. The crude polybutenyl succinic anhydride thus prepared had a saponification number of 79.

EXAMPLE II.—PREPARATION OF TETRAETHYLENEPENTAMINE DERIVATIVE OF THE POLYBUTENYL SUCCINIC ANHYDRIDE OF EXAMPLE I HEREINABOVE

A mixture of 84 grams (0.45 mol) of tetraethylene pentamine and 702 grams (0.45 mol) of the polybutenyl succinic anhydride of Example I hereinabove, was blended with agitation at 125° F. in a nitrogen atmosphere. The temperature was increased to 400° F. during a period of one hour, after which the absolute pressure was reduced to about 200 mm. Hg during a period of 30 minutes to facilitate the removal of water. The reaction mixture was then allowed to reach room temperature at this reduced pressure. The reaction product contained 5.1% nitrogen (theory=5.4%). Infra-red analysis showed that the reaction product was an imide containing a polybutene side chain.

EXAMPLE III.—PREPARATION OF N-DIMETHYL-AMINOPROPYL POLYBUTENYL SUCCINIMIDE

A mixture of 21.3 grams (0.21 mol) of dimethylaminopropylamine and 150 grams (0.09 mol) of the polybutenyl succinic anhydride of Example I hereinabove, was blended with agitation in a nitrogen atmosphere, and the mixture was heated at 500° F. for a period of one hour, after which the absolute pressure was reduced to about 200 mm. Hg at this temperature during a period of 30 minutes to facilitate the removal of water and excess amine. The reaction mixture was then allowed to reach room temperature at this reduced pressure. The reaction product contined 1.7% nitrogen (theory=1.8%). The identity of the N-dimethylaminopropylalkenyl succinimide was established by means of infra-red spectroscopy.

EXAMPLE IV.—PREPARATION OF N-ETHYL-PIPERAZINE POLYBUTENYL SUCCINIMIDE ANHYDRIDE

A mixture of 18 grams (0.14 mol) of N-(β-aminoethyl) piperazine and 200 grams (0.127 mol) of the polybutenyl succinic anhydride of Example I hereinabove was blended with agitation in a nitrogen atmosphere. The mixture was heated at 500° F. for one hour, after which the absolute pressure was reduced to about 200 mm. Hg to facilitate the removal of water and unreacted piperazine. The reaction mixture was then allowed to reach room temperature at this reduced pressure. The reaction product contained 2.59% nitrogen (theory=2.67%). Infra-red analysis showed that the reaction product was an imide containing a polybutene side chain.

Tables I and II hereinbelow present data obtained with lubricating oil compositions containing the combination of polyamines and N-substituted monoalkenyl succinimides.

Alkenyl succinimide "A" was an alkenyl succinimide derived from tetraethylene pentamine wherein the alkenyl radical had a molecular weight of about 1000, which alkenyl radical was a polymer of isobutene.

Alkenyl succinimide "B" was N-dimethylaminopropyl polybutenyl succinimide, wherein the polybutenyl radical had an average molecular weight of about 1000.

The tests were made in a Caterpillar L-1 engine according to Supplement I conditions for a period of 120 hours as described in the Coordinating Research Council Handbook, January, 1946.

The "PD Nos." refer to the piston discoloration rating. After the engine test, the three piston lands are examined visually. To a piston skirt which is completely black is assigned to PD number of 800, to one which is completely clean, a PD number of 0; to those intermediate between completely black and completely clean are assigned PD numbers intermediate in proportion to the extent and degree of darkening.

The base oils were California SAE 30 base oils.

Table I

Additive, Wt. Percent	A	B	C	D	E	F	G	H	I
1. Succinimide A	0.0	1.0	0.0	1.0	1.0	1.0	1.0	1.0	1.0
2. Ethylenediamine	0.0			0.045					
3. Diethylenetriamine	0.0		0.051		0.051				
4. Tetraethylenepentamine	0.0					0.10			
5. Nonaethylenedecaamine	0.0						0.06		
6. Dipropylenetriamine	0.0							0.065	
7. Hydroxyethylethylenediamine	0.0								0.078
Test Results: P.D. No	800, 800, 800	280, 60, 120	570, 235, 375	160, 25,5	0, 0, 0	125, 105, 130	60, 0, 0	125, 0, 10	70, 0, 0

Table II

Additive, Wt. Percent	J	K	L	M	N	O	P	Q
1. Succinimide A	0.0	1.0		0.0	1.0	1.0	1.0	1.0
2. Succinimide B	0.0		2.25	2.25				
3. Diethylenetriamine	0.0			0.51				
4. Tetraethylenepentamine monostearate	0.0				0.177			
5. Triethylenetetramine monocaproate	0.0					0.131		
6. Diethylenetriamine monoacetate	0.0						0.122	
7. Dodecylamine	0.0							0.278
Test Results: P.D. No	800, 800, 800	280,60,120	375, 75, 0	85, 0, 0	135, 15, 50	215, 115, 50	55, 10, 30	610, 330-

It is readily seen from the data set forth hereinabove in Tables I and II that lubricating oil compositions containing the combination of the above defined polyamines and alkenyl succinimides as described herein are superior as lubricating oil compositions for the lubricating of internal combustion engines to the compositions containing only the alkenyl succinimides. On the other hand, it is to be noted that the addition of monoamines, for example dodecylamine, to succinimide-containing oils markedly reduces the effectiveness of the succinimide as a detergent. Thus, monoamines are deleterious to succinimide-containing oils.

In addition to the compositions described hereinabove, lubricating oil compositions may also contain other detergents, viscosity index improving agents, rust inhibitors, oiliness agents, grease thickening agents, etc.

This application is in part a continuation of our U.S. applications Serial Nos. 102,367 and 102,368, both of which were filed April 12, 1961, and both of which are now abandoned.

We claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.1% to 45% by weight of an N-polyamine substituted alkenyl succinimide prepared by reacting an alkenyl succinic anhydride with about an equal molar proportion of a polyamine selected from the group consisting of tetraethylene pentamine and dimethylaminopropylamine at temperatures from 220° F. to 500° F., wherein said alkenyl radical contains from 30 to about 200 carbon atoms, and from 0.01% to 2% by weight of an amine selected from the group consisting of a polyamine of the formula:

$$NH_2\left[CH_2CH_2(CH_2)_n-NH\right]_q(CH_2)_n-CH_2CH_2NH_2$$

wherein n is a number from 0 to 1, and q is a number from 0 to 10, wherein the succinimide/polyamine weight ratio is from 10:1 to 75:1, and fatty acid salts thereof.

2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.1% to 45% by weight of an N-polyamine substituted alkenyl succinimide prepared by reacting an alkenyl succinic anhydride with about an equal molar proportion of tetraethylene pentamine at temperatures from 220° F. to 500° F., wherein said alkenyl radical contains from 30 to about 200 carbon atoms, and from 0.01% to 2% by weight of an amine selected from the group consisting of a polyamine of the formula:

$$NH_2-\left[CH_2CH_2(CH_2)_n-NH\right]_q-(CH_2)_n-CH_2CH_2NH_2$$

wherein n is a number from 0 to 1, and q is a number from 0 to 10, wherein the succinimide/polyamine weight ratio is from 10:1 to 75:1, and fatty acid salts thereof.

3. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.1% to 45% by weight of an N-polyamine substituted alkenyl succinimide prepared by reacting an alkenyl succinic anhydride with about an equal molar proportion of dimethylaminopropylamine at temperatures from 220° F. to 500° F., wherein said alkenyl radical contains from 30 to about 200 carbon atoms, and from 0.01% to 2% by weight of an amine selected from the group consisting of a polyamine of the formula:

$$NH_2-\left[CH_2CH_2(CH_2)_n-NH\right]_q-(CH_2)_n-CH_2CH_2NH_2$$

wherein n is a number from 0 to 1, and q is a number from 0 to 10, wherein the succinimide/polyamine weight ratio is from 10:1 to 75:1, and fatty acid salts thereof.

4. The composition of claim 2, wherein said polyamine is tetraethylene pentamine.

5. The composition of claim 3, wherein said polyamine is tetraethylene pentamine.

6. The composition of claim 2, wherein said polyamine is diethylenetriamine.

7. The composition of claim 2, wherein said polyamine fatty acid salt is tetraethylene pentamine monostearate.

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