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LUBRICANT CONTAINING ALKENYL SUCCINIMIDE AND HYDROXYPOLYAMINE

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4 Claims. (Cl. 252—51.5)

This application is a continuation-in-part of Frank A. Stuart and Robert G. Anderson, U.S. application Serial No. 102,366, filed April 12, 1961, now abandoned.

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

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 composition. 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 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 temperatures. 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.

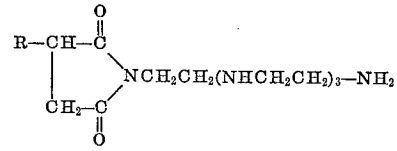
Lubricating oil compositions containing N-substituted polyamine alkenyl succinimides as metal-free detergents are described in Frank A. Stuart, Robert G. Anderson and Alan Y. Drummond copending application Serial No. 835,437, filed August 24, 1959. The addition thereto of certain polyamines markedly 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 hydroxypolyamines.

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 hydroxyalkylalkylenepolyamines and N-substituted monoalkenyl succinimides derived from tetraethylene pentamine in oils of lubricating viscosity.

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

The monoalkenyl succinimides of tetraethylene pentamine have the formula



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.

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 new compound described herein, any of the numerous processes available can be used therefor.

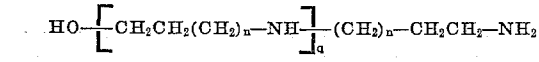
These alkenyl succinimides of tetraethylene pentamine can be prepared by reacting maleic anhydride with an olefinic hydrocarbon, followed by reacting the resulting alkenyl succinic anhydride with tetraethylene pentamine.

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 mole 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 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, 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 diamine 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.

The particular hydroxyalkylalkylenepolyamines which are effective herein in combination with alkenyl succinimides of tetraethylene pentamine are of the formula



wherein n is a number from 0 to 1, and q is a number from 1 to 10.

The particular polyamines are exemplified as follows: hydroxyethylethylene diamine, hydroxyethyldiethylene triamine, hydroxyethyltetraethylene pentamine, hydroxyethylnonaethylene decamine, 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-ethylhexyl 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., non-nonyl 2-ethylhexyl benzenes); polyphenyls (e.g., biphenyls and terphenyls), alkyl biphenyl ethers, polymers of silicon [e.g., tetraethyl silicate, tetraisopropyl silicate, 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 combinations thereof, wherever miscible or wherever made so by the use of mutual solvents.

The alkenyl succinimides of tetraalkylene pentamine 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 can be used in amounts of 0.01% to 2%, by weight, preferably 0.02% to 0.5% by weight. It is preferred that the succinimide and the polyamine be used in amounts such that the succinimide/polyamine mole ratio is from 3:1 to 100:1, preferably from 10:1 to 75:1.

The preparation of the alkenyl succinimides of tetraalkylene pentamine is illustrated in the following examples.

EXAMPLE 1.—PREPARATION OF POLYBUTENYL SUCCINIC ANHYDRIDE

A mixture of 1000 g. (1 mole) of a polybutene, having a molecular weight of about 1000, and 98 g. (1 mole) 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 umber of 79.

EXAMPLE 2.—PREPARATION OF TETRAETHYLENE PENTAMINE DERIVATIVE OF THE POLYBUTENYL SUCCINIC ANHYDRIDE OF EXAMPLE 1 HEREINABOVE

A mixture of 84 g. (0.45 mole) of tetraethylene pentamine and 702 g. (0.45 mole) of the polybutenyl succinic anhydride of Example 1 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.

The alkenyl succinimides described herein are more effective as detergents than alkenyl succinimides having fewer nitrogen atoms in the amine portion of the molecule, and more effective than succinimides having less than 30 carbon atoms in the alkenyl radical. The use of amyl amine, for example, in place of tetraethylene pentamine in the preparation of the succinimide, results in a product which is ineffective as a detergent in lubricating oil compositions.

Table I hereinbelow presents data obtained with lubricating oil compositions containing the combination of hydroxyalkylalkylenepolyamines and N-substituted monoalkenyl succinimides derived from tetraethylene pentamine.

The monoalkenyl succinimide used was an N-substituted succinimide derived from tetraethylene pentamine wherein the alkenyl radical had a molecular weight of about 1000, which alkenyl radical was a polymer of isobutene.

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.

Table I

	A	B	C	D	E	F	G	H
Additive, wt. percent:								
Succinimide	0.0	1.0	0.0	1.0	1.0	1.0	1.0	1.0
Diethylene triamine	0.0		0.051	0.051				
Tetraethylene pentamine	0.0				0.10			
Hydroxyethylethylene diamine	0.0					0.078		
Diethylene triamine monoacetate	0.0						0.122	
Dodecylamine	0.0							0.278
Test results:								
P.D. No.	800, 800, 800	280, 60, 120	340, 130, 40	0, 0, 0	125, 105, 130	70, 0, 0	55, 10, 30	610, 330, 25

The "P.D. 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 a P.D. number of 800; to one which is completely clean, a P.D. number of 0; to those intermediate between completely black and completely clean are assigned P.D. numbers intermediate in proportion to the extent and degree of darkening.

The base oils were California SAE 30 base oils.

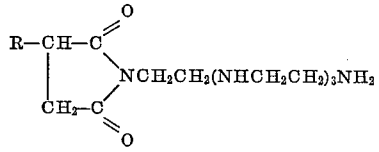
It is readily seen from the data set forth hereinabove in Table I that lubricating oil compositions containing the combination of the above-defined hydroxypolyamines

and alkenyl succinimides of tetraethylene pentamine as described herein are superior as lubricating oil compositions for the lubricating of internal combustion engines to the compositions containing only the alkenyl succinimides of tetraethylene pentamine. On the other hand, it is noted that monoamines, for example, dodecylamine, have a detrimental effect on the described succinimides as ashless detergents in lubricating oil compositions.

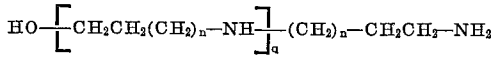
In addition to the compositions described hereinabove, lubricating oil compositions may also contain other detergents, viscosity index improving agents, rust inhibitors, oiliness agents, grease thickening agents, etc.

We claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.1 to 45 percent by weight of an alkenyl succinimide of tetraethylene pentamine having the following formula:

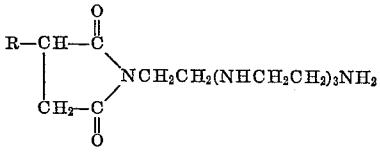


wherein R is a hydrocarbon radical containing from 30 to about 200 carbon atoms, and from 0.01 percent to 2 percent by weight of a hydroxypolyamine of the formula:

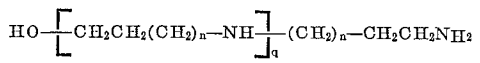


wherein *n* is a number from 0 to 1, and *q* is a number from 1 to 10, wherein the succinimide/polyamine mol ratio is from 10:1 to 75:1.

2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from 0.25 to 5 percent by weight of an alkenyl succinimide of tetraethylene pentamine having the following formula:

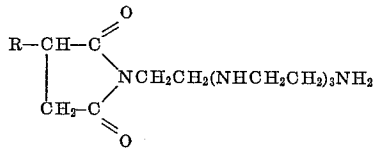


wherein R is a hydrocarbon radical containing from 30 to about 200 carbon atoms, and from 0.2 percent to 0.5 percent by weight of a hydroxypolyamine of the formula:



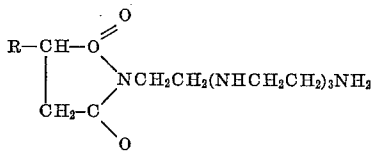
wherein *n* is a number from 0 to 1, and *q* is a number from 1 to 10, wherein the succinimide/polyamine mol ratio is from 10:1 to 75:1.

3. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil, and from about 0.25 percent to about 5 percent by weight of an alkenyl succinimide of the formula:



wherein R is a polymer of isobutene having a molecular weight of about 1,000, and from 0.02 percent to 0.5 percent by weight of N-(2-hydroxyethyl) ethylene diamine.

4. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, from 0.1 percent to 45 percent by weight of an alkenyl succinimide of tetraethylene pentamine having the following formula:



wherein R is an hydrocarbon radical containing from 30 to about 200 carbon atoms, and from 0.01 percent to 2 percent by weight of N-(2-hydroxyethyl)ethylene diamine, wherein the succinimide/diamine mol ratio is from 10:1 to 75:1.

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DANIEL E. WYMAN, *Primary Examiner.*