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POLYPIPERAZINYL SUCCINIMIDES IN LUBRICATING OILS

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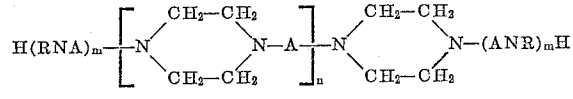
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6 Claims. (Cl. 252—51.5)

This invention pertains to lubricating oil compositions having incorporated therein metal-free detergents.

For the most part, the various detergents which are added to crankcase oils to reduce the 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 contribute to preignition.

It is a particular object of this invention to provide lubricating oil compositions which are compounded with metal-free detergents.

Therefore, in accordance with this invention, it has been discovered that lubricating oil compositions particularly useful for heavy duty service are obtained by incorporating reaction products of alkenylsuccinic acid compounds selected from the class consisting of alkenylsuccinic acids, alkenylsuccinic anhydrides, alkenylsuccinic halides and lower alkyl esters of alkenylsuccinic acids, in which the alkenyl group contains from 30 to 400 carbon atoms, with polypiperazinyl alkylenes having the formula:

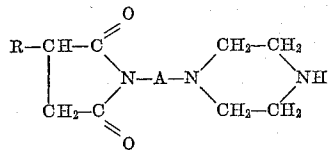


in which R is selected from the class of hydrogen or lower alkyl, A is selected from the class of alkylene, hydroxyalkylene and ketoalkylene radicals containing from 2 to 4 carbon atoms, *m* is selected from the class of 0 and 1, and *n* is an integer from 1 to 5. These reaction products are amides or imides. When the terminal nitrogen atom, which reacts with the alkenylsuccinic derivative, is a primary amine group the principal product of reaction is an imide and when the nitrogen atom is in the form of a secondary amine group the product is an amide in oils of lubricating viscosity. For the sake of brevity herein, these compounds will be termed, "polypiperazinyl succinic derivatives."

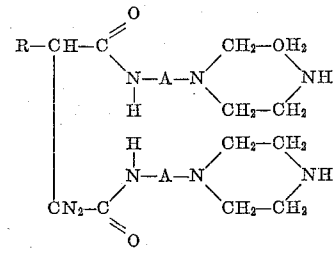
By the use of lubricating oil compositions containing the polypiperazinyl succinic derivatives described herein, diesel and gasoline engine parts remain remarkably free of deposits and varnish, even under severe operating conditions.

These polypiperazinyl succinic acid derivatives can be prepared by several methods, as follows.

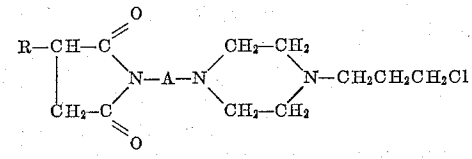
(A) An N-aminoalkylpiperazine can be reacted with an alkenylsuccinic anhydride (or the acid, halide or lower ester) to form an amide or imide as exemplified by the formula:



and



in which R is an alkenyl group containing 30 to 400 carbon atoms and A is an alkylene group containing 2 to 4 carbon atoms. This imide or amide can be reacted with a dihaloalkane containing two different halogen atoms on different carbon atoms such as 1-bromo-3-chloropropane to form the N-haloalkyl derivative of the imide or amide. In the case of the imide this would have the formula:



This chloro-derivative can then be reacted with piperazine or a piperazine derivative such as N-methyl piperazine to eliminate hydrogen chloride and form a derivative containing two piperazine radicals. As long as the terminal piperazine nitrogen (or alkyleneamine nitrogen) contains a hydrogen atom this reaction can be repeated stepwise by further addition of the dihaloalkane. It is preferred that the dihaloalkane contain two different halogen atoms of differing reactivity so that the reaction can proceed stepwise. If both halogen atoms are the same the reaction can terminate by approximately simultaneous reaction of the two halogen atoms with two amino radicals. An arylsulfonate radical can be substituted for one of the halogen atoms with equally good results.

(B) A polyalkylene polypiperazine can first be prepared by reacting piperazine with dihaloalkane and this polyalkylenepolypiperazine can be reacted with an alkenylsuccinic acid compound to form compounds of the invention. It is important in the reaction of the piperazine with the dihaloalkane to have a terminal nitrogen atom containing at least one hydrogen atom to provide a reacting link with the alkenylsuccinic acid compound. This can be done by removing the final halogen with an alkylene diamine such as ethylene diamine.

(C) A haloepoxyalkane such as epichlorohydrin can be reacted first with either a piperazine derivative or with the reaction product of the piperazine derivative and an alkenylsuccinic acid compound. This product can be further reacted with a piperazine derivative or the reaction product of a piperazine derivative and an alkenylsuccinic acid compound derive materials conforming to the invention. These compounds contain piperazine rings connected by hydroxyalkylene radicals resulting from opening of the epoxy-ring.

(D) In place of the haloepoxyalkanes other compounds containing two reactive groups may be used to provide different connecting radicals for the piperazine rings. Thus esters of chloroaliphatic acids (e.g. ethyl β-chloropropionate) will react to provide a ketoalkylene connecting radical. Esters of acrylic acid will react in a similar manner. Esters of epoxyalkanecarboxylic acids will react to yield connecting alkylene radicals containing both a hydroxy and a keto group. Acid halides may be used in place of the esters.

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, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc., liquid esters of acids or phosphorus; alkyl benzenes, e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc. and dialkyl benzenes, e.g., n-nonyl 2-ethylhexyl benzene; polyphenyls, e.g., biphenyls and terphenyls; alkyl biphenyl ethers; silicon esters, e.g, tetraethyl silicate, tetraisopropyl silicate, hexa-(4-methyl-2-pentoxy) disiloxane, etc.

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 polypiperazinyl succinimides can be used in oils of lubricating viscosity in amounts of 0.1% to 10% by weight, preferably 0.25% to 5% by weight. Concentrates containing up to 60% or higher are also within the scope of the invention.

The preparation of the polypiperazine succinimides described herein is illustrated in the following example.

EXAMPLE I. — PREPARATION OF N-METHYL PIPERAZINYL TRIMETHYLENE-N-PIPERAZINYLETHYL POLYISOBUTENYL-SUCCINIMIDE.

A mixture of 1400 grams (50% conversion in base oil) of N-piperazinylethyl polyisobutenyl succinimide wherein the polyisobutenyl radical had a molecular weight of about 850, and 100 grams trimethylenechlorobromide was blended at room temperature. This blend is herein identified as "Blend A."

A mixture of 700 grams of Blend A and 74 grams of N-methylpiperazine was agitated at room temperature for 15 minutes, then heated, with agitation, at 150° C. for 2 hours.

The resulting mixture diluted in hexane was washed with dilute ethanol and potassium carbonate solution. After drying, the hexane was removed by final heating at 80° C. at reduced pressure.

EXAMPLE II. — PREPARATION OF N-METHYL-PIPERAZINYL-2-HYDROXYTRIMETHYLENE - N-PIPERAZINYLETHYL POLYISOBUTENYLSUCCINIMIDE

A mixture of 1500 grams of a 50% solution in lubricating oil of N-piperazinylethyl polyisobutenyl succinimide wherein the polyisobutenyl radical had molecular weight of about 850 and 62 grams of epichlorohydrin was heated at 50° C. for one hour. 67 grams of N-methylpiperazine was added to the reaction mixture and was heated at 150° C. for several hours. The product was washed and dried as in Example I. The nitrogen content of the reaction product was 2.33% with a basic nitrogen content of 1.32%.

EXAMPLE III.—PREPARATION OF THE REACTION PRODUCT OF A MIXTURE OF 1-N-METHYL-PIPERAZINYL - 3 - AMINOETHYLPIPERAZINYL-2-PROPANOL AND 1-N-METHYLPIPERAZINYL-3 - PIPERAZINYLETHYLAMINO - 2 - PROPANOL WITH POLYISOBUTENYLSUCCINIC ANHYDRIDE

In this example the mixture of substituted isopropanols was first prepared and this mixture was further reacted with polyisobutylsuccinic anhydride.

(A) *Preparation of mixture of 1-N-methylpiperazinyl-3-aminoethylpiperazinyl-2-propanol and 1-N-methylpiperazinyl-3-piperazinylethylamino-2-propanol*

A solution of 80 grams of N-methylpiperazine in 200 ml. of ethanol was heated to reflux and 74 grams of epichlorohydrin was added as rapidly as control of the reaction would permit. Upon completion of the addition 95 grams of N-aminoethylpiperazine was charged quickly to the reaction mixture. The product was permitted to stir overnight. The solution was treated with an equivalent amount of saturated potassium carbonate solution to liberate the free base from the hydrochloride salt resulting from the reaction of the epichlorohydrin. After removal of the precipitated potassium chloride, the solution was washed to assure removal of salts. The product was subjected to distillation to remove solvent and any volatile amines. The product was a white semi-solid weighing about 100 grams.

(B) *Reaction of the mixture of substituted isopropanols with polyisobutenylsuccinic anhydride*

A solution of 100 grams of the mixture of substituted isopropanols in 260 grams of absolute alcohol was heated to 70° C. and mixed with 463 grams of polyisobutenylsuccinic anhydride, wherein the polyisobutenyl radical had a molecular weight of about 850. The polyisobutenylsuccinic anhydride had a temperature of 85° C. at the time it was added and the addition took 15 minutes. The ethanol was removed by distillation and the mixture was heated to 150° C. for about 30 minutes. It was finally heated for one hour at 150° C. under vacuum.

EXAMPLE IV.—PREPARATION OF THE REACTION PRODUCT OF A MIXTURE OF 1,3-DI-(AMINOETHYLPIPERAZINYL) - 2 - PROPANOL; 1,3-DI - (PIPERAZINYLETHYLAMINO) - 2 - PROPANOL AND 1-PIPERAZINYLETHYLAMINO-3-AMINOETHYL - PIPERAZINYL - 2 - PROPANOL WITH POLYISOBUTENYLSUCCINIC ANHYDRIDE

In this example the mixture of the three substituted isopropanols was first prepared and this mixture was further reacted with polyisobutenylsuccinic anhydride.

(A) *Preparation of the mixture of isopropanols substituted in the 1,3-positions with N-aminoethylpiperazine*

2.3 liters of N-2-aminoethylpiperazine was heated to 125° C. and 200 grams of epichlorohydrin was added dropwise. The addition was completed in 2 hours and the final temperature was 140° C. The mixture was heated to 150° C. and held at this temperature with stirring for about 16 hours. Excess N-2-aminoethylpiperazine was removed by distillation under vacuum and the residue was treated with a solution of 85 grams of sodium hydroxide in 100 ml. of water to liberate the free base from the hydrochloride salt.

(B) *Reaction of the mixture of substituted isopropanols with polyisobutenylsuccinic anhydride*

24.5 grams of the mixture of substituted isopropanols was dissolved in 50 ml. of the dimethyl ether of diethylene glycol and the solution was heated to 100° C. To this was added 315 grams of preheated (100° C.) polyisobutenylsuccinic anhydride in which the polyisobutenyl radical had a molecular weight of about 850. The reaction mixture was heated to 150° C. while stirring and held at this temperature for about 1 hour. Volatile material was then removed by continuing heating at 150° C. for ½ hour under vacuum. The nitrogen content of the product was 1.80% and the basic nitrogen content 1.11%.

EXAMPLE V.—PREPARATION OF THE REACTION PRODUCT OF A MIXTURE OF N-(AMINOETHYLPIPERAZINOACETYL) - N' - AMINOETHYLPIPERAZINE, N - (AMINOETHYLPIPERAZINOACETYLAMINOETHYL) PIPERAZINE, N-(PIPERAZINYLETHYLAMINOACETYL)- N'-AMINOETHYLPIPERAZINE AND N-(PIPERAZINYLETHYLAMINOACETYLAMINOETHYL) PIPERAZINE WITH POLYISOBUTENYLSUCCINIC ANHYDRIDE

In this example the mixture of the four acetyl derivatives was first prepared and this mixture was further reacted with polyisobutenylsuccinic anhydride.

(A) *Preparation of mixture of acetyl derivatives*

199 grams of chloroacetyl chloride was slowly added with stirring to 2200 ml. of N-aminoethylpiperazine. Warming occurred and after the mixing was complete the temperature was raised to 150° C. and the mixture was stirred for 19 hours. After cooling to 70° C. a 30% aqueous solution of 141 grams of sodium hydroxide was added. Water was removed by distillation and excess aminoethylpiperazine was then distilled off under a pressure of 4 mm. of mercury. The residue was filtered free of sodium chloride. The yield was 457 grams. The nitrogen content was 27.50% (theory 28.2%).

(B) *Reaction of mixed acetyl derivatives with polyisobutenylsuccinic anhydride*

160 grams of the mixed acetyl derivatives from A was mixed with 1600 grams of polyisobutenylsuccinic anhydride, in which the polyisobutene radical had a molecular weight of about 850 at a temperature of 100° C. The product was stripped of volatile matter by heating at 150° C. under a pressure of 3 mm. of mercury. The yield was 1745 grams and the nitrogen content was 2.60%.

EXAMPLE VI.—PREPARATION OF N-(β-N'-METHYLPIPERAZINOPROPIONYL)- PIPERAZINYLETHYL POLYISOBUTENYLSUCCCINIMIDE

41 grams (0.20 moles) of ethyl β-N-methylpiperazinopropionate was added to 500 grams (0.20 moles) of a 50% oil solution of an N-piperazinylethyl polyisobutenylsuccinimide having a molecular weight of 2551. The mixture was stirred and heated to 200° C. The product was stripped of volatile materials under a pressure of 3 mm. of mercury at a temperature of 100° C. for two hours. The nitrogen content was 2.33%.

Table I hereinbelow presents data obtained with a lubricating oil composition containing the additives of the invention previously described. Metal dithiophosphates were included in some of the formulations to inhibit corrosion. The concentration of the dithiophosphates is expressed in millimols per kilogram of finished composition (based on the metal) that is, mM./kg.

Dithiophosphate A was a zinc salt of a mixed dialkyl dithiophosphate wherein one of the alkyl radicals contained 4 carbon atoms and the other alkyl radical contained 6 carbon atoms. Dithiophosphate B was a zinc di-(alkylphenyl) dithiophosphate.

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 land discoloration rating. After the engine test, the three piston lands are examined visually. To a piston land which is completely black is assigned a 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 "GD Nos." refer to the percentage deposits in the piston ring grooves; a 0 evaluation being a clean groove; and a number of 100 being a groove full of deposits.

The base oils were solvent refined Mid-Continent SAE 30 base oils.

TABLE I.—ENGINE TESTS

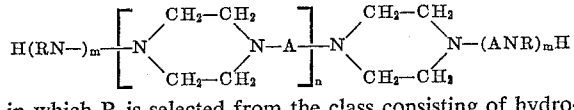
	A	B	C	D	E	F	G	H
Additive:								
Example I, Wt. Percent	0.0	2.0						
Example II, Wt. Percent	0.0		1.5					
Example III, Wt. Percent	0.0			1.5				
Example IV, Wt. Percent	0.0				1.5	1.5		
Example V, Wt. Percent	0.0						1.5	
Example VI, Wt. Percent	0.0							1.5
Dithiophosphate A, mM./kg	0.0	10		8	8	8	8	8
Dithiophosphate B, mM./kg	0.0	2						
Test results:								
GD No	[1] 38, 18, 10, 10	1, 0, 0, 0	6, 2, 0, 0	2, 0. 85, 0, 0	5, 1, 0, 0	2, 0. 2, 0, 0	5, 2, 0. 3, 0	5, 2, 0. 2, 0
PD No	800, 800, 800	20, 0, 0	80, 10, 0	25, 2, 0	65, 5, 0	10, 3, 2	115, 2, 0	105, 3, 0

[1] These test results were obtained in a Caterpillar L-1 test under the MIL-L-2104 conditions. Thus under the more severe Supplement-1 conditions these GD Nos. would be considerably higher.

In addition to the dithiophosphates described hereinabove, lubricating oil compositions containing the polypiperazinyl succinic derivatives of this invention may also contain other detergents, oxidation inhibitors, viscosity index improving agents, rust inhibitors, oiliness agents, etc.

We claim:

1. The product of the process which comprises reacting alkenyl succinic acid compounds selected from the class consisting of alkenyl succinic acids, alkenyl succinic anhydrides, alkenyl succinic halides and lower alkyl esters of alkenyl succinic acids, in which the alkenyl group contains from 30 to 400 carbon atoms with polypiperazinyl alkylenes having the formula:

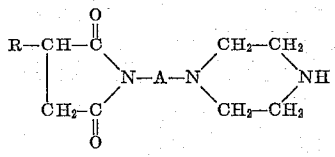


in which R is selected from the class consisting of hydrogen or lower alkyl, A is selected from the class consisting of alkylene, hydroxyalkylene and ketoalkylene radicals containing from 2 to 4 carbon atoms, *m* is selected from the class of 0 and 1 and *n* is an integer from 1 to 5 to form at least one member of the group consisting of alkenyl succinimide and alkenyl succinamide of said polypiperazine.

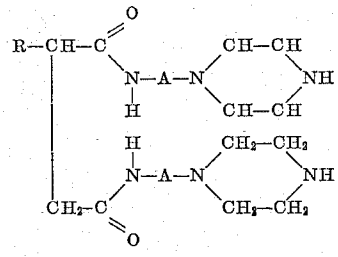
2. A lubricant composition comprising a major proportion of an oil of lubricating viscosity and a minor proportion sufficient to enhance the detergent characteristics of the product of claim 1.

3. The product of the process which comprises reacting N-aminoalkylpiperazines with alkenyl succinic acid compounds selected from the class consisting of alkenyl succinic acids, alkenyl succinic anhydrides, alkenyl succinic halides and lower alkyl esters of alkenyl succinic

acids to form a reaction product having formulae selected from the group consisting of:



and



in which R is an alkenyl group containing 30 to 400 carbon atoms and A is an alkylene group containing 2 to 4 carbon atoms, reacting said reaction product with a dihaloalkane containing two different halogen atoms on two different carbon atoms to provide an N-haloalkyl substituent and reacting said haloalkyl substituted reaction product with a piperazine.

4. A lubricant composition comprising a major proportion of an oil of lubricating viscosity and a minor proportion sufficient to enhance the detergent characteristics of the product of claim 3.

5. The product of the process which comprises reacting N-piperazinylethyl polyisobutenyl succinimide, wherein the isobutenyl radical has from 30 to 400 carbon atoms, with epichlorohydrin, followed by reaction with N-methylpiperazine.

6. The product of the process which comprises reacting epichlorohydrin with N-2-aminoethylpiperazine followed by reaction with polyisobutenyl succinic anhydride, when the polyisobutenyl radical has from about 30 to 400 carbon atoms to form at least one member of the group consisting of polyisobutenyl succinimide and polyisobutenyl succinamide of the reaction product of epichlorohydrin and N-2-aminoethyl-piperazine.

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JOSEPH R. LIBERMAN, *Examiner.*