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3,749,695

**LUBRICATING OIL ADDITIVES**

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1 Claim

**ABSTRACT OF THE DISCLOSURE**

Lubricating oil compositions are provided containing effective detergents and dispersants which are the reaction products of hydrocarbyl-substituted polyamines or succinimides with alkane sultones.

**BACKGROUND OF THE INVENTION**

**Field of the invention**

The novel lubricating oil compositions of this invention contain additives which are the products of the reaction of hydrocarbyl-substituted polyamines and succinimides with alkane sultones. The hydrocarbyl group is an oil-solubilizing group of relatively high molecular weight composed entirely of carbon and hydrogen atoms.

These compounds are effective detergents and dispersants for use in internal combustion engines. In the internal combustion engine the presence of narrow openings and close tolerances between moving parts provides many opportunities for deposits to form and seriously reduce the operating efficiency of the engine.

The lubricating oil must be capable of maintaining sludge and varnish-forming deposits dispersed in the oil, thus keeping pistons, rings, and other moving parts and openings relatively free of deposits. Sludge formation must be minimized in the crankcase and in areas where valves and gears operate.

In addition, the lubricating oil additives must not produce significant enhancement of the rate of formation of deposits by their own degradation.

**DESCRIPTION OF THE PRIOR ART**

Patents of interest include the following: U.S. Pat. Nos. 3,018,291, 3,018,250, and 3,018,247, which describe the N-dialkylaminoalkyl alkenyl succinimides and their compositions. U.S. Pat. No. 3,565,804 describes polyisobutenyl-substituted polyamines. U.S. Pat. No. 3,017,416 treats quaternary ammonium salts of succinimide. U.S. Pat. Nos. 2,540,800, 3,194,812, 3,272,746 and 3,341,542 are concerned with the succinimide ashless detergents.

**SUMMARY OF THE INVENTION**

Lubricating oil compositions of modified hydrocarbyl-substituted succinimides of alkylene polyamines are provided, wherein the succinimides are modified by reaction with alkane sultones to provide an ionic product of high dispersancy. In the same way, hydrocarbyl-substituted polyamines also are reacted with alkane sultones to yield an ionic product of high dispersancy. The hydrocarbyl radicals are usually polyolefin groups of about 100 to about 50,000 average molecular weight, and are preferably polyisobutenyl. The polyamines have at least 2 amine nitrogens and preferably from 2-10 amine nitrogens.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

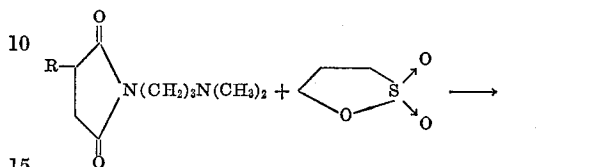
The lubricating oil compositions of this invention contain the reaction product of hydrocarbyl-substituted succinimides or polyamines with alkane sultones. The sultones are cyclic anhydrides of hydroxysulfonic acids. The reaction with amine nitrogens (primary, secondary,

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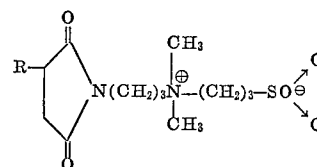
or tertiary) is believed to yield an internal alkyl ammonium sulfonate salt or "zwitterion."

**Succinimides**

The reaction of a hydrocarbyl-substituted succinimide of an alkylene polyamine with 3-hydroxy-1-propanesulfonic acid sultone (propane sultone) is believed to yield a product as follows:



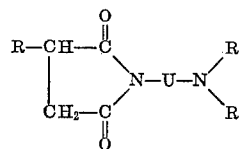
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where R is an oil solubilizing hydrocarbyl radical.

The succinimides of the present invention are monohydrocarbyl-substituted succinimides wherein the hydrocarbyl radical is preferably an alkenyl radical of from 8 to 200 carbon atoms. The succinimide can be represented by the following formula:

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wherein R is a hydrocarbyl radical containing from 8 to about 200 carbon atoms, R<sup>1</sup> and R<sup>2</sup> are H or alkyl radicals, and >N-U-N< is a portion of the polyamine moiety, containing at least 2 nitrogen atoms and preferably from 2 to 10 amine nitrogens. Thus U is alkylene, polyalkylene amine, or polyalkylene polyamine. For example, U may be (CH<sub>2</sub>)<sub>2</sub>, or (CH<sub>2</sub>)<sub>3</sub>, etc. or

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or [(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>]<sub>n</sub>, etc. R<sup>1</sup> and R<sup>2</sup> may be H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, etc. Consequently, the ultimate amine nitrogen in the polyamine chain of the succinimide may be a primary, secondary, or tertiary amine nitrogen.

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It is preferred that the hydrocarbyl group, R, is a polymer of an olefin preferably containing from 2 to 5 carbon atoms, wherein said polymer has an average molecular weight of from about 400 to about 5,000, and more particularly from about 900 to about 1,400. Such olefins are exemplified by ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures thereof. A particularly preferred polymer is polyisobutylene.

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The preparation of the monohydrocarbyl succinimides is effected by reaction of, for example, succinic anhydride with polyamines. Amine reactants for the formation of succinimides include dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminobutylamine, methylaminoethylamine, tetraethylenepentamine, etc. The preparation of certain of the succinimides of the present invention has been described in U.S. Pat. 3,018,291.

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Alternatively, succinic anhydride-substituted hydrocarbon polymers may be used in the preparation of the present invention. These compounds may be prepared in a variety of ways, but generally they are prepared as adducts of maleic anhydride with copolymers of alpha-olefins and polyolefins having an unsaturated group in the alpha position. These compounds, having molecular

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weights in excess of about 10,000, have been described in U.S. Pat. No. 3,197,409. Reaction of the succinic anhydride-substituted hydrocarbon polymers with polyamines, and subsequent reaction with alkane sultones, yields a product within the scope of the present invention.

#### Polyamines

The hydrocarbyl-substituted polyamines of this invention are high molecular weight hydrocarbyl-N-substituted alkylene polyamines. They have an average molecular weight in the range of about 600-10,000, more usually in the range of about 750-5,000.

The hydrocarbyl radical may be aliphatic or alicyclic and, except for adventitious amounts of aromatic structure in petroleum mineral oils, will be free of aromatic unsaturation. The hydrocarbyl groups will normally be branched-chained aliphatic, having 0-2 sites of unsaturation, and preferably from 0-1 site of ethylenic unsaturation. The hydrocarbyl groups are preferably derived from petroleum mineral oil, or polyolefins, either homopolymers or higher order polymers, of 1-olefins of from 2-6 carbon atoms, ethylene being polymerized with a higher homologue.

Illustrative polymers include polypropylene, polyisobutylene, poly-1-butene, etc. The polyolefin group will normally have at least 1 branch per 6 carbon atoms along the chain, preferably at least 1 branch per 4 carbon atoms along the chain, and particularly preferred that there be from 0.5 to 1 branch per carbon atom along the chain. These branched-chain hydrocarbons are readily prepared by the polymerization of olefins of from 3-6 carbon atoms and preferably from olefins of from 3-4 carbon atoms.

In preparing the compositions of this invention, rarely will a single compound be employed. With both polymers and petroleum-derived hydrocarbon groups, the composition is a mixture of materials having various structures and molecular weights. Therefore, in referring to molecular weight, average molecular weights are intended. Furthermore, when speaking of a particular hydrocarbon group, it is intended that the group include the mixture that is normally contained within materials which are commercially available. For example, polyisobutylene is known to have a range of molecular weights and may include small amounts of very high molecular weight materials.

Similarly, commercially available alkylene polyamines are frequently mixtures of various alkylene polyamines having one or two species dominating. Finally, in preparing the compounds of this invention, where the various nitrogen atoms of the alkylene polyamine are not equivalent, the product will be a mixture of the various possible isomers.

Further details of the structure of the hydrocarbyl-substituted polyamines of this invention, and their method of preparation, are given in U.S. Pat. No. 3,565,804.

#### Sultones

The sultones are cyclic anhydrides of hydroxysulfonic acids. Examples of the sultones, finding use within the practice of the present invention, include 3-hydroxy-1-propanesulfonic acid sultone (propane sultone), 4-hydroxy-1-butanefulfonic acid sultone (butane sultone), 5-hydroxy-1-pentanesulfonic acid sultone, 3-hydroxy-1-isobutanefulfonic acid sultone, etc. The propane and butane sultones are preferred, and of these propane sultone is particularly preferred.

The sultones are prepared by sulfonation of alkenes. Five-membered ring sultones can in some cases be obtained in fair yield from the corresponding branched alkene, e.g., 3-methyl-1-butene, 3,3-dimethyl-1-butene, 2,3,3-trimethyl-1-butene, 4-methyl-2-pentene, 4,4-dimethyl-2-pentene, etc., by sulfonation, as well as by sulfonation of certain halogenated compounds, unsaturated ketones, etc. (Sulfonation and Related Reactions, E. E. Gilbert, Interscience Publishers, 1965, New York).

Propane sultone is commercially available (Shell Chemical Company, Distillation Products Industries, and Aldrich Chemical Company) and is prepared by vacuum distilling 3-hydroxypropanesulfonic acid.

#### METHOD OF PREPARATION

The five- and six-membered ring alkane sultones, and their alkyl derivatives, are highly reactive and versatile sulfoalkylating agents. They react readily with many nucleophiles, but propane sultone, with a five-membered ring, reacts more rapidly than butane sultone, which has a six-membered ring.

To prepare the lubricating oil additives of this invention one can proceed by mixing the hydrocarbyl-substituted succinimide or hydrocarbyl-substituted polyamine with an alkane sultone in a suitable hydrocarbon solvent, at room temperature, in the mole ratio of about 1:1 to 2:1, or higher mole ratio of succinimide (or polyamine) to sultone. Alternatively, the alkane sultone can be added dropwise to the constantly stirred reaction mixture at a temperature of about 80-110° C.

#### Example 1

To 2258 grams of polyisobutenyl succinic anhydride (average molecular weight 950) was added 248.5 g. of dimethylaminopropylamine and about 500 cc. of xylene. The mixture was refluxed for 7 hours.

#### Example 2

351 g. of propane sultone was added to the product of Example 1 and refluxed for 6 hours. An additional 51 g. of propane sultone was added to the reaction mixture and stirred for 45 minutes at 80-100° C. 2,150 g. of product were separated with methanol. The product contained 3.91 percent sulfur by weight.

#### Example 3

A 5-liter 3-neck flask was charged with 2,430 g. of polyisobutenyl succinimide of dimethylaminopropylamine (1.17 percent nitrogen by weight and of average molecular weight 1130) in 50 percent concentration in neutral oil. 300 g. of neutral oil having a  $V_{100}$  of 100 SUS was added. The mixture was heated to 93° C. and 121.5 g. of propane sultone was added dropwise over 30 minutes. The mixture was stirred at 93° C. for 90 minutes and filtered slowly while hot.

#### Example 4

To a 200 c. round-bottomed flask was added 25 g. of polyisobutenyl succinimide of dimethylaminopropylamine and 3.5 g. of propane sultone. The mixture was refluxed with xylene for 4 hours. The xylene was evaporated on a rotary evaporator, finally, going to high vacuum at a temperature of 100° C. The product was a thick rubbery residue which was dissolved in hexane, separated with methanol, and redissolved in pentane. After evaporation on a rotary evaporator at 100° C. and high vacuum the product contained 1.49 percent nitrogen and 2.17 percent sulfur by weight.

#### Example 5

A 2-liter, 3-neck, round-bottomed flask was charged with 1000 g. of polyisobutenyl ethylene diamine in 60 percent concentration in neutral oil (average molecular weight 1460 and containing 1.55 weight percent nitrogen) and 73.2 g. of propane sultone. The mixture was refluxed in 450 cc. of xylene for 4 hours. The product was stripped of xylene, redissolved in hexane and separated with methanol.

#### Example 6

To a 200 cc. round-bottomed flask was added 50 g. of polyisobutenyl ethylene diamine, 60 percent concentration in neutral oil and 3.66 g. of propane sultone. The mixture was refluxed in xylene for 4 hours. The xylene was evaporated via a rotary evaporator, finally, going to high vacuum at 100° C. The product was dissolved in

hexane, separated with methanol and stripped in high vacuum at 100° C. 45.6 g. of product was obtained, containing 1.75 percent nitrogen and 1.6 percent sulfur by weight.

The compositions of this invention may be formulated with various lubricating fluids (hereinafter referred to as "oils") which are either derived from natural or synthetic sources. Oils generally have viscosities of about 35–50,000 Saybolt Universal Seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin-base, naphthenic-base, asphaltic-base, and mixed-base oils. Illustrative of synthetic oils are: hydrocarbon oils such as polymers of various olefins, generally of from 2–8 carbon atoms, and alkylated aromatic hydrocarbons; and non-hydrocarbon oils, such as polyalkylene oxide, aromatic ethers, carboxylate esters, phosphate esters, and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic. These oils may be used individually or together whenever miscible or made so by the use of mutual solvents.

When the detergents of this invention are compounded with lubricating oils for use in an engine, the lubricating oil will be a major component of the composition and the detergents will be present in at least about 0.1 weight percent and usually not more than 20 weight percent, more

In order to demonstrate the excellent effectiveness of the compounds of this invention as detergents and dispersants in lubricating oils, several compounds were tested in Caterpillar engines. The tests determine the effect of the lubricant on ring sticking, wear and accumulation of deposits, principally in the piston ring area; thus serving to evaluate detergency at ring temperatures.

The tests used are particularly severe. They are referred to as the 180 BMEP and the 280 BMEP (brake mean effective pressure in p.s.i.) Caterpillar Tests. The 180 BMEP test conditions are for a supercharged Caterpillar test wherein the pressure of the supercharged air is 70 inches Hg abs., the water temperature of the cooling jacket is 190° F., the air temperature is 255° F., the oil temperature of the bearing is 205° F., the sulfur content of the fuel is 0.4 percent, the speed of the engine is 1800 r.p.m. and the rate of fuel input is at a rate which provides 7,460 B.t.u. per minute. The test is carried out for a stated number of hours as indicated in the following tables.

In Tables I and II the rating of groove deposits is based on a range of 0–100, 100 being completely filled grooves. The rating for land deposits is based on a range of 0–800, 800 being completely black. The rating for underhead deposits is based on a range of 0–10, 10 being completely clean.

TABLE I

Composition	Test	Hours	Groove deposit				Land deposit			Underhead
Base oil 1.....	280 BMEP	16	52	14	8.2	0.6	780	465	415	6.3
Composition:										
A <sup>2</sup> .....	280 BMEP	16	25	2.0	0.5	0.5	95	0	0	9.2
B <sup>3</sup> .....	280 BMEP	16	21	2.7	0.1	0.2	80	1.0	0	5.5
C <sup>4</sup> .....	280 BMEP	16	23	3.9	0.4	0.2	75	15	5	5.0

<sup>1</sup> Neutral oil of 480 SUS viscosity at 100° F., containing 1% by weight of 4,4-methylene bis-(2,6-di-tert-butyl phenol) and 20 mM./kg. TCP.

<sup>2</sup> Base oil plus 4% by weight of reaction product of polyisobutenyl succinimide of propylene diamine with propane sulfone. Polyisobutenyl group of average molecular weight 950.

<sup>3</sup> Base oil plus 4% weight of a polyisobutenyl succinimide of triethylene tetramine. Polyisobutenyl group of average molecular weight 950.

<sup>4</sup> Base oil plus 4% by weight of a polyisobutenyl succinimide of tetraethylene pentamine. Polyisobutenyl group of average molecular weight 950.

TABLE II

Composition:	Test	Hours	Groove deposit				Land deposit			Underhead
D <sup>1</sup> .....	180 BMEP	60	67	3.4	0.5	0.5	45	10	15	5.1
B <sup>2</sup> .....	180 BMEP	60	35	2.2	0.5	0.5	105	10	15	6.4
C <sup>3</sup> .....	180 BMEP	60	33	1.5	0.5	0.5	55	10	35	3.9

<sup>1</sup> Base oil consists of a neutral oil with 2.5 mM./kg. of calcium sulfonate, 100 mM./kg. of carbonated, sulfurized, calcium polypropylene phenate and 20 mM./kg. of zinc bis(polypropylene phenyl) dithiophosphate.

<sup>2</sup> Base oil plus 3.0% by weight of the reaction product of polyisobutenyl-ethylene-diamine with propane sulfone. The polyisobutenyl group is of average molecular weight 1,400.

<sup>3</sup> Base oil plus 3.0% by weight of additive of Table I footnote 3.

<sup>4</sup> Base oil plus 1.57% by weight of additive of Table I footnote 4.

usually in the range of about 1–10 weight percent. The compounds can be prepared as concentrates due to their excellent compatibility with oils. As concentrates, the compounds of this invention will generally range from about 10–70 weight percent, more usually from about 20–50 weight percent of the total composition.

Other additives may also be included in the oil such as pour point depressants, oiliness agents, antioxidants, rust inhibitors, etc. Usually, the total amount of these additives will range from about 0.1–10 weight percent, more usually from about 0.5–5 weight percent. The individual additives may vary from about 0.01–5 weight percent of the composition.

A preferred aspect of the use of the compositions of this invention in lubricating oils is to include in the oil from about 1–50 mM./kg. of a dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are from about 4–36 carbon atoms. Usually, the hydrocarbyl groups will be alkyl or alkaryl groups. The remaining valence of the phosphorodithioate will usually be satisfied by zinc, but polyalkyleneoxy or a third hydrocarbyl group may also be used.

The additives of Compositions A and D of Tables I and II, which are examples of the sulfone reaction products of this invention, were also tested in a Vespa Scooter Dynamometer Test. This test measures valve sticking, piston deposits, exhaust port blocking and spark plug fouling in the two-stroke internal combustion engine. Overall performance of both additives was satisfactory.

It is evident from the above results that the compositions of this invention are excellent detergents and dispersants under the hot conditions of a Caterpillar internal combustion engine, even when tested under extremely severe conditions. Furthermore, the compositions are compatible with other additives normally found in compounded lubricating oils.

While the character of this invention has been described in detail with several examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claim.

I claim:

1. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and from about 0.1 to about 10 percent by weight of the reaction product of an alkane sultone with a hydrocarbyl-N-substituted alkylene polyamine, wherein the hydrocarbyl substituent has an average molecular weight in the range from 100 to 10,000 and is an aliphatic or alicyclic branched-chain hydrocarbon radical derived from petroleum hydrocarbons or polyolefins, reacted in a mol ratio of about 1:1 to 1:2 at a temperature of from about room temperature to about 110° C.

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252—47, 51.5 A