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SULFONATE SALTS OF ALKENYL SUCCINIMIDES

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No Drawing. Continuation-in-part of application Ser. No. 420,775, Dec. 23, 1964. This application Oct. 10, 1969, Ser. No. 865,529

Int. Cl. C10m 1/40

U.S. Cl. 252—33 13 Claims

ABSTRACT OF THE DISCLOSURE

A composition, useful as a lubricating oil additive, is obtained by first reacting a C_{20}–C_{400} aliphatic hydrocarbon succinic acid or derivative thereof which is capable of forming carboximide bonds with a C_2–C_{30}, N_2–N_{10} akylene polyamine to form a carboximide, and then reacting the carboximide with a C_{12}–C_{40} hydrocarbon sulfonic acid.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 420,775, filed Dec. 23, 1964, and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention is directed to novel sulfonate salts. More particularly, the invention is concerned with novel salts formed by reacting hydrocarbon sulfonic acids with the carboximides produced by reacting aliphatic hydrocarbon-substituted succinic acid or its derivatives with alkylene polyamines. The invention is further concerned with lubricant compositions containing these salts.

One of the principal problems associated with present-day crankcase lubricants is that posed by the inevitable presence in the crankcase of foreign particles such as dirt, soot, water and decomposition products resulting from breakdown of the lubricating oil. Perhaps the most important of these contaminants is water because it seems to be responsible for the deposition of a mayonnaise-like sludge. It appears that if there were no water present the solid components of the mayonnaise-like sludge would circulate with the oil and be removed by the oil filter. It will be readily appreciated that the deposition of the sludge presents a serious problem with respect to the efficient operation of the engine and that it is desirable to prevent such deposition of sludge-like material. Consequently modern engine lubricant compositions commonly contain dispersants to help prevent deposit of the sludge. The compositions of this invention are highly effective as such dispersants.

DESCRIPTION OF THE PRIOR ART

Pertinent to this invention are U.S. Pats. 3,018,250; 3,018,291; 3,172,892; 3,189,544; 3,202,678; 3,219,666; and 3,272,743; which disclose various types of succinimide compounds, and U.S. Pat. 3,442,161, which discloses an unsymmetrical hydrocarbon sulfonic acid.

SUMMARY OF THE INVENTION

The present invention is a new dispersant having rust-inhibiting properties and comprising the product formed by reacting hydrocarbon sulfonic acid with the carboximide reaction product of the reaction between an aliphatic hydrocarbon-substituted succinic acid or derivative thereof and an alkylene polyamine. Embodiments of the invention are lubricating oils containing these salts.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions which find use in this invention are the combination of a first reaction product which is obtained by the reaction of an aliphatic hydrocarbon substituted succinic acid or a derivative thereof with an alkylene polyamine under conditions wherein carboximide formation occurs and then combining the first reaction product with hydrocarbon sulfonic acid to form a salt as the claimed second reaction product. In preparing the first reaction product, the aliphatic hydrocarbon substituted succinic acid will normally be used as its anhydride, although other acid derivatives which are capable of forming carboximide bonds may be employed. The reaction will be carried out so that at least one imide is formed. The alkylene polyamine which is employed will have at least two carbon atoms and at least two nitrogen atoms, the nitrogen atoms being separated by at least two carbon atoms. Normally, the alkylene polyamine will not be of more than 10 nitrogen atoms, and not more than 30 carbon atoms.

The polyamine and succinic acid compounds are combined in a mol ratio of at least 0.1:1 to about 1.5:1, more usually from about 0.1:1 to about 1.2:1. The conditions of reaction are such that as imide formation is obtained, the water of reaction is removed. While mixtures are obtained, the reaction product will normally be an imide with other minor products also present such as amides, imidazolines, amine salts, etc. There will be at least one full equivalent of amine nitrogen in excess over the number of mols of succinic compound, and preferably at least two equivalents in excess. That is, at least one basic amine nitrogen will be present per molecule, so that the basic amine nitrogen is available to form a salt with the hydrocarbon sulfonic acid.

The first reaction product and the hydrocarbon sulfonic acid are then combined to form a salt wherein the hydrocarbon sulfonic acid is employed in an amount of from one mol per mol of first reaction product up to but usually less than the number of basic titratable amine nitrogen atoms in the first reaction product.

The first reaction product will have at least 36 carbon atoms and not less than 72 carbon atoms, preferably having at least 56 carbon atoms.

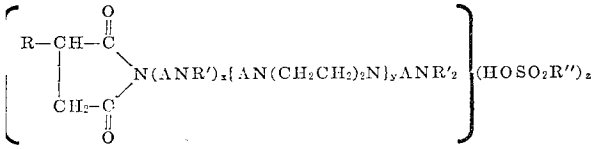
The succinic compound, usually the succinic anhydride, will be combined with the polyamine at a temperature in the range of about 200–500° F., more usually 225–400° F. The time for the reaction will generally be from about one-half hour to 24 hours, more usually in the range of about 1 to 12 hours.

Conveniently, the reactants may be combined in an inert reaction medium such as a hydrocarbon, e.g., mineral lubricating oil. The concentration of the reactants may range from about 1 to 90% by weight, but will usually be from about 25 to 75% by weight of the total reaction mixture. Preferably, the water formed during the reaction is removed either by distillation or, if convenient, subatmospheric pressures may be employed.

The sulfonic salt may then be prepared directly by adding the hydrocarbon sulfonic acid either at room or

elevated temperatures to the first reaction product to form the desired salt. The reaction may be carried out neat or in an inert medium, such as that employed in preparing the first reaction product.

When a 1:1 ratio of succinic compound to polyamine is employed, the composition for the most part will be comprised of a product of the formula:

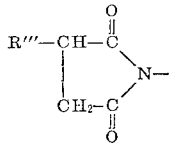


wherein R is an aliphatic radical of from about 20 to 400 carbon atoms; A is an alkylene radical containing from about 2 to 6 carbon atoms; R′ is hydrogen or an alkyl radical containing from about 1 to 5 carbon atoms; x is a number from 0 to 10; y is a number from 0 to 2; the total of x plus y is a number of from 1 to 10; z is a number from 1 to the number of titratable amine nitrogens; and R″ is a hydrocarbon radical containing from about 12 to 40 carbon atoms. The above formula is intended to represent symbolically the number of atoms present in the molecule, but not to represent the actual structure of the molecule. Thus, the alkylene amine and alkylene piperazine components need not be present in any particular order but may be interspersed among one another. Similarly, the hydrocarbon sulfonic acid portion of the molecule in the above formula is intended to include ionic structures.

Preferred compositions have the following formula:

$$X(A'NH)_nAX\cdot(HOSO_2R'')_{z'}$$

wherein X is either of the radicals:



or amino (—NH_2), with at least one X being the former radical; R‴ is a branched chain aliphatic radical of from 50 to 200 carbon atoms, having at least one branch of one carbon atom for each two carbon atoms along the chain and not more than one branch per one carbon atom along the chain; A′ is alkylene of from 2 to 3 carbon atoms; n is 0 to 5 when one X is amino and 1 to 5 when neither X is amino; R″ is as defined previously; and z' is at least 1 and not greater than about 2, and in no case is z' greater than n.

The aliphatic radical substituent R‴ is readily obtained by polymerizing monoolefins of from 2 to 5 carbon atoms, such as ethylene, propylene, n-butene, isobutylene, or pentene, and mixtures thereof. Methods of polymerization are well known in the art, as are methods of substituting the aliphatic chain onto the succinic anhydride structure.

The polyamine with which the aliphatic hydrocarbon-substituted succinic anhydride is reacted contains 2 to 30 carbon atoms, 1 to 10 nitrogen atoms, and preferably, 1 to 6 nitrogen atoms as its only hetero atoms. It is free of unsaturation. The nitrogen atoms in the secondary amino groups are joined by alkylene or piperazine groups of from 2 to 6 carbon atoms and, more usually, of from 2 to 3 carbon atoms. These nitrogen atoms may be substituted with hydrogen or lower alkyl of 1 to 6 carbon atoms, preferably of from 1 to 3 carbon atoms.

The polyamine reactant has the following formula

$$H_2N(ANR')_x\{AN(CH_2CH_2)N\}_yANR'_2$$

wherein A is an alkylene radical containing from about 2 to 6 carbon atoms; R′ is hydrogen or alkyl radicals containing from about 1 to 6 carbon atoms; x is a number from 0 to 10; y is a number from 0 to 2; and the total of x plus y is a number from 1 to 10.

Preferred polyamines have the general formula

$$H_2N(A'NH)_mH$$

wherein A′ is an alkylene radical of from 2 to 3 carbon atoms, and m is an integer from 1 to 10, preferably from 1 to 6. Illustrative alkylene polyamines and polyalkylene polyamines of the foregoing types are ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene, hexamine, nonaethylene decamine, dipropylene triamine, dimethylamino propylamine, N-aminoethyl piperazine, etc.

The hydrocarbon sulfonic acids have the general formula

$$HOSO_2R''$$

wherein R″ is a hydrocarbon radical containing from about 12 to 40 carbon atoms, preferably 12 to 30 carbon atoms. The hydrocarbon radical may be aliphatic or aromatic, or may be a structure combining both aromatic and aliphatic components. Included are the "petroleum" or "mahogany" sulfonic acids. These sulfonic acids are conveniently prepared in accordance with methods well known in the art. For example, a dodecylbenzene sulfonic acid having the dodecyl group derived from propylene tetramer is readily prepared by sulfonating the dodecylbenzene with concentrated sulfuric acid. Generally, about 1 mol of the hydrocarbon sulfonic acid will be combined with 1 mol of the acylated polyamine. However, it is obviously possible to combine the acylated polyamine with as many hydrocarbon sulfonic acid groups as there are basic titratable amino nitrogen atoms in the polyamine.

A particularly preferred group of sulfonic acids are the unsymmetrical dialkylbenzene sulfonic acids, including those derived from the materials described in aforesaid U.S. Pat. No. 3,422,161. These materials are unsymmetrical dialkylbenzene mixtures having an average molecular weight in the range of 300 to 500, and in which the alkyl groups contain from 3 to 21 carbon atoms, and for the mixture the average carbon atom content of the two chains varies by at least four. It is further preferred that the two alkyl chains be dissimilar; i.e., that one be a straight chain alkyl group and the other be a branched chain alkyl group.

In the finished lubricating oils of the invention, the hydrocarbon sulfonate salt of alkenyl succinimide is employed in amounts sufficient to improve the detergent characteristics and/or inhibit rusting. Ordinarily, amounts of from about 0.1 to about 15 percent by weight are satisfactory for both of these purposes. In view of the excellent solubility characteristics of the hydrocarbon sulfonic acid salt of alkenyl succinimide, a further feature of the invention lies in the preparation of lubricating oil concentrates containing higher percentages of the salt up to about 75 percent by weight.

The base oil in the lubricant composition of the invention is any oil of lubricating viscosity. Thus, the base oil can be a refined paraffin-type base oil, a refined naphthenic-type base oil, or a synthetic hydrocarbon or synthetic nonhydrocarbon oil of lubricating viscosity. As synthetic oils, suitable examples include oils obtained by polymerization of lower molecular weight alkylene oxides, such as propylene oxide and/or ethylene oxide employing alcohol or acid initiators, such as lauryl alcohol or acetic acid. Still other synthetic oils include esters, e.g., di-(2-ethylhexyl)-sebacate, tricresylphosphate and silicate esters, such as tetra-(2-ethylhexyl)-orthosilicate and hexa-(2-ethylbutoxy)-disiloxane. For present purposes the mineral lubricating oils are preferred, since they show the greatest improvement.

Lubricant compositions within the scope of the present invention may also contain still other additives of conventional types, such as pour point depressants, oiliness and extreme pressure agents, anti-oxidants, dyes, blooming agents, and the like.

Illustrative lubricant compositions may include, for example, from about 0.1 to about 10 percent by weight of alkaline earth metal higher alkyl phenate detergent and wear-reducing agents such as the calcium alkylphenate having mixed alkyl groups of 12 to 15 carbon atoms. They may also include from about 0.1 to 10 percent by weight of organic thiophosphate corrosion and high-temperature oxidation inhibitors, such as the reaction product of pinene and P_2S_5, the reaction product of polybutene and P_2S_5, and the bivalent metal dihydrocarbon dithiophosphates, zinc butyl hexyl dithiophosphate and zinc di-(tetradecylphenyl) dithiophosphate. Metal salt detergents in amounts from about 0.1 to 10 percent which may also be used are the calcium petroleum sulfonates of the oil-soluble mahogany type and the calcium naphthenates.

Further illustrations of the preparation of the hydrocarbon sulfonates of alkenyl succinimides of this invention are given in the following examples. The proportions are on a weight basis unless otherwise specified.

EXAMPLE 1

Sulfonate salt produced by reacting tetrapropenyl benzene sulfonic acid with the reaction product of polyisobutenyl succinic anhydride and tetraethylene pentamine

2460 g. (1 mol) of a 50 percen stolution in lubricating oil of the reaction product of a polymer of ethylene diamine approximating tetraethylene pentamine and polyisobutenyl succinic anhydride, in which the polyisobutenyl radical has a molecular weight of about 850, and 326 g. (1 mol) of tetrapropylene benzene sulfonic acid were mixed and vigorously stirred on a hot plate at a temperature of about 80° C. for 2 hours. The resulting solution was a very viscous liquid.

EXAMPLE 2

Sulfonate salt produced by reacting tetrapropenyl benzene sulfonic acid with the reaction product of polyisobutenyl succinic anhydride and diethylene triamine

This experiment was conducted as in Example 1, except that the ethylene diamine polymer was diethylene triamine, and the polyisobutenyl radical had a molecular weight of about 350. One mole of each reactant was used.

EXAMPLE 3

Sulfonate salt produced by reacting unsymmetrical dialkylbenzene sulfonic acid with the reaction product of polyisobutenyl succinic anhydride and tetraethylene pentamine

This experiment was conducted as in Example 1, except that the sulfonic acid was a mixture of unsymmetrical dialkylbenzene sulfonic acids, prepared according to the procedures in U.S. Pat. 3,422,161. The average branched alkyl chain contained six carbon atoms, and the average straight alkyl chain contained nineteen carbon atoms; the average difference in carbon content between the chains was thirteen carbon atoms. The average molecular weight of the mixed sulfonic acids was about 405.

Table I presents data obtained on an oil containing the sulfonate salt of Example 1 tested in a Caterpillar 1–H Engine Test for 120 hours. In this test an uncompounded oil will not run for 120 hours, so in the table a comparison is made with a base oil run under the much milder conditions of the MIL–L–2104 test. These test data show that the sulfonate salt of tetraethylene pentamine is an effective detergent.

In the tests, a solvent-refined paraffinic base Mid-Continent SAE 30 weight mineral lubricating oil was used as the base oil. The Caterpillar 1–H Engine Test was run under MIL–L–3104 conditions. The "PD Nos." refer to the piston discoloration rating. After the engine tests, the three piston lands were examined visually. To a piston skirt 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.

TABLE I.—1–H CATERPILLAR ENGINE TESTS

	A	B
Additive: Example 1, percent	0	6.5
Test results:		
GDS Nos.	38, 18, 10, 10	50, 6, 2, 1, 0
Land PD Nos.	800, 800, 800	260, 40, 5, 0

Table II presents data obtained in the MS Sequence II Rust Test. This test is described in a report of January 22, 1962, published by Section G–IV Tech. Comm. B. of ASTM Committee D–2. The test is a cycling test in a 1960 V–8 Oldsmobile engine, each cycle consisting of 3 hours run and 3 hours down, and the total test being 10 cycles. The rating is on a scale of 10 (no rust) to 0 (heavy rust). In addition to the additive of Example 2, the test oil contained the N-(triethylenetetraminoethyl)-polyisobutenyl succinimide described in Example 1 (called succinimide) and two thiophosphates. Thiophosphate A was the zinc salt of a dialkyl dithiophosphoric acid in which the alkyl groups were derived from a mixture of butyl alcohol and amyl alcohol. Thiophosphate B was the zinc salt of a dialkylphenyl dithiophosphoric acid in which the alkyl radicals were branched-chain averaging about 12 carbon atoms each. The data show that the additive of Example 2 is an effective rust inhibitor.

TABLE II.—MS SEQUENCE II RUST TEST

	A	B
Additive:		
Example 2, percent	0	0.19
Succinimide, percent	1	0.85
Thiophosphate A, mm./kg.	10	10
Thiophosphate B, mm./kg.	2	2
Test results:		
Valve lifter rating	3.9	7.7
Overall rating	4.1	7.2

Table III presents data from the Caterpillar 1–G Engine Test, which is defined in Federal Test Methods Standards No. 791a, Method No. 341–2. The terms "Pd Nos." and "GD Nos." are as previously defined. "Underhead" refers to the deposits on the underside of the piston head. A rating of 0 indicates a completely black underhead and 10 indicates a completely clean underhead. In addition to the additive described in Example 3, the test oil contained the succinimide and thiophosphate B, described above, as well as a carbonated calcium alkylphenate, containing dispersed calcium carbonate, and in which the alkyl radicals were branched chain averaging 12 carbon atoms each. These data show that the additive of Example 3 is an effective detergent additive.

TABLE III.—1–G CATERPILLAR ENGINE TESTS

	A	B
Additive:		
Example 3, concentration in mm./kg.	0	35
Succinimide, percent	2	2
Thiophosphate B, mm./kg.	20	20
Calcium alkylphenate, mm./kg.	40	40
Test results:		
GD Nos.	20, 4, 0.5, 0.5	15, 1, 0.2, 0.1
Land PD Nos.	210, 100, 20	65, 5, 0
Underhead	6.8	9.2

The above data and discussion clearly illustrate the detergency and rust inhibition character of the claimed salts. The lubricants containing these salts are highly effective as engine lubricants.

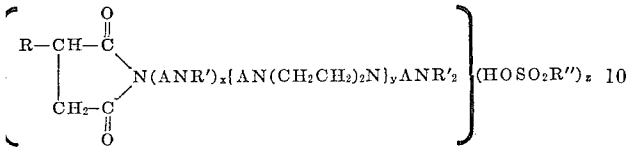
What is claimed is:

1. The product obtained by first reacting a C_{20}–C_{400} aliphatic hydrocarbon substituted succinic acid or a derivative thereof which is capable of forming carboximide bonds with a C_2–C_{30}, N_2–N_{10} alkylene polyamine to form

a carboximide and then reacting said carboximide with a C_{12}–C_{40} hydrocarbon sulfonic acid.

2. The product claimed in claim 1, further characterized in that it is derived from an aliphatic hydrocarbon substituted succinic anhydride.

3. The product claimed in claim 2, having the formula



wherein R is an alkyl or alkenyl radical of from about 20 to 400 carbon atoms; A is an alkylene radical containing from about 2 to 6 carbon atoms; R' is hydrogen or an alkyl radical containing from about 1 to 5 carbon atoms; x is a number from 0 to 10; y is a number from 0 to 2; the total of x plus y is a number from 1 to 10; z is a number from 1 to the number of titratable amine nitrogens; and R'' is a hydrocarbon radical containing from about 12 to 40 carbon atoms.

4. The product claimed in claim 3, wherein R'' is mixture of dialkylbenzene radicals having an average molecular weight in the range of 300 to 500 molecular weight units wherein each alkyl substitutent contains from 4 to 21 carbon atoms; and wherein the average carbon contents of the two alkyl substituents on each dialkylbenzene molecule differ by at least four carbon atoms.

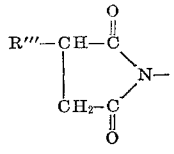
5. The product claimed in claim 4, further characterized in that the alkyl substituents consist of one straight-chain alkyl radical and one branched-chain alkyl radical.

6. The product claimed in claim 3, wherein R is an alkyl or alkenyl radical of from about 25 to 400 carbon atoms.

7. The product claimed in claim 3 having the formula

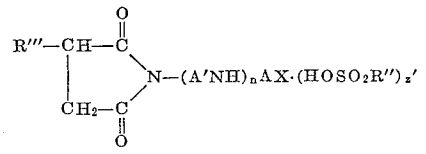
$$X(A'NH)_nAX\cdot(HOSO_2R'')_{z'}$$

wherein X is —NH_2 or



with at least one X being the latter radical; R''' is a branched-chain aliphatic radical of from 50 to 200 carbon atoms, having at least one branch of one carbon atom for each two carbon atoms long the chain and not more than one branch per one carbon atom along the chain; A' is alkylene of from 2 to 3 carbon atoms; n is 0 to 5 when one X is —NH_2 and 1 to 5 when neither X is —NH_2; and z' is at least 1 and not greater than about 2, and in no case is z' greater than n.

8. The product claimed in claim 7 having the formula



9. The product claimed in claim 8, wherein R'' is a mixture of dialkylbenzene radicals having an average molecular weight in the range of 300 to 500 molecular weight units wherein each alkyl substituent contains from 4 to 21 carbon atoms; and wherein the average carbon contents of the two alkyl substituents on each dialkylbenzene molecule differ by at least four carbon atoms.

10. The product claimed in claim 9, further characterized in that the alkyl substituents consist of one straight-chain alkyl radical and one branched-chain alkyl radical.

11. A lubricating oil composition comprising a major proportion of oil of lubricating viscosity and a minor proportion sufficient to improve the detergent properties thereof of the product claimed in claim 1.

12. A lubricating oil composition comprising a major proportion of oil of lubricating vicsosity and a minor proportion sufficient to improve the detergent properties thereof of the product claimed in claim 3.

13. A lubricating oil composition comprising a major proportion of oil of lubricating viscosity and a minor proportion sufficient to improve the detergent properties thereof of the product claimed in claim 7.

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