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3,556,997

COMPOSITIONS WITH SULFINYL-CONTAINING ALKENYLSUCCINATES

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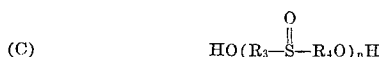
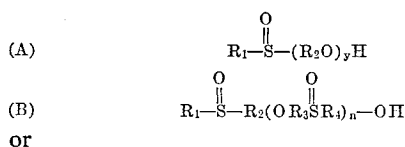
Int. Cl. C01m 1/38

U.S. Cl. 252—48.6

5 Claims

ABSTRACT OF THE DISCLOSURE

The novel sulfinyl-containing alkenylsuccinates of this invention are useful as dispersants, corrosion inhibitors and antiwear agents particularly in lubricating oil and fuel compositions. The novel sulfinyl compounds are prepared by reacting (1) an alkenylsuccinic anhydride, an alkenylsuccinic acid or an alkenylsuccinamic acid and (2) at least one sulfinyl-containing hydroxy compound having the formulas:



wherein

y is an integer from 1 to about 50 or more and n is an integer from 1 to 40,

R₁ is selected from the group consisting of (a) an alkyl radical containing from 1 to 24 carbon atoms, (b) an aryl radical (c) an aralkyl radical wherein the alkyl portion of the radical contains from 1 to 4 carbon atoms and (d) an alkaryl radical wherein the alkyl portion contains from 1 to 24 carbon atoms,

R₂ is an alkylene radical having 2 to 5 carbon atoms, and R₃ and R₄ are alkylene radicals having 2 to 5 carbon atoms, a phenylene radical or a (C₁-C₄) alkyl substituted phenylene radical with the proviso that n is 1 when R₃ and R₄ are phenylene or (C₁-C₄) alkyl substituted phenylene.

This application is a divisional application of my earlier filed and pending application Ser. No. 645,869, filed June 14, 1967, and entitled, "Sulfinyl-Containing Alkenylsuccinates."

BACKGROUND OF THE INVENTION

Internal combustion engines used for vehicles engaged in short run travel (i.e., the so-called stop-and-go driving) do not reach their most efficient operating temperature. Therefore large amounts of undesirable products produced by incomplete combustion of the fuel and oil-insoluble oxidation products from lubricants and other sources accumulate within the internal combustion engine. If these undesirable products deposit on the engine parts, the result is a further reduction of the engine's efficiency. To prevent the accumulation of foreign matter and the deposition of sludge, a dispersant is employed as an additive to the lubricating oil so that the oil-insoluble foreign matter and sludge will remain suspended in the oil and not deposit on any of the vital engine parts.

In addition to the problem of engine deposits, the combustion products of the fuel may cause excessive wear, especially when the engine is operating under relatively

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cold conditions which results in an accumulation of moisture and acid products on the engine surfaces. This accumulation promotes wear on various engine parts.

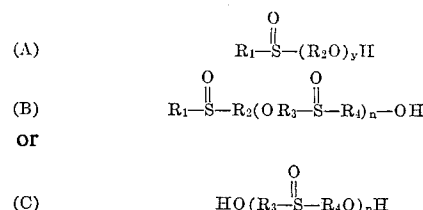
SUMMARY OF THE INVENTION

It is an object of this invention to prepare novel compounds that may be incorporated into lubricating oils or liquid hydrocarbon fuels for the purpose of dispersing sludge, inhibiting corrosion and acting as antiwear agents.

The novel compounds of this invention are prepared by reacting an alkenylsuccinic anhydride, alkenylsuccinic acid or alkenylsuccinamic acid and at least one sulfinyl-containing hydroxy compound. The compounds of this invention are useful as dispersants in lubricating oil and fuel systems. They may be used in the range of about 0.005 to 15% by weight of the oil or fuel composition. The compounds of this invention, as evaluated according to several standard tests, exhibit outstanding activity as dispersants.

DETAILED DESCRIPTION OF THE INVENTION

The novel sulfinyl-containing alkenyl succinates are prepared by reacting (1) an alkenylsuccinic anhydride, an alkenylsuccinic acid or an alkenylsuccinamic acid and (2) at least one sulfinyl-containing hydroxy compound of the following formulas:



wherein y is an integer from 1 to about 50 or more and n is an integer from 1 to 40 or more and preferably from 1 to 10,

R₁ is selected from the group consisting of (a) an alkyl hydrocarbon radical containing from 1 to 24 carbon atoms, (b) an aryl hydrocarbon radical (c) an aralkyl hydrocarbon radical wherein the alkyl portion of the radical contains from 1 to 4 carbon atoms and (d) an alkaryl hydrocarbon radical wherein the alkyl portion contains from 1 to 24 carbon atoms,

R₂ is an alkylene radical having 2 to 5 carbon atoms and having at least 2 carbon atoms extending in a chain between the adjoined S and O atoms,

R₃ and R₄ are alkylene radicals having 2 to 5 carbon atoms and having at least 2 carbon atoms extending in a chain between the adjoined S and O atoms, a phenylene radical or lower alkyl substituted phenylene radical with the proviso that n is 1 when R₃ and R₄ are phenylene or lower alkyl substituted phenylene.

The alkenylsuccinic compound may also be reacted with a mixture of various proportions of the sulfinyl-containing hydroxy compounds described in Formulas A, B and C. Sulfinyl-containing hydroxy compounds within the scope of Formulas A and B, when employed concurrently with one or more Formula C alcohols, will act as chain terminators in the polyester reaction.

Representative R₁ groups are selected from straight chain and branched aliphatic hydrocarbon radicals such as methyl, ethyl, propyl, t-butyl, amyl, isohexyl, octyl, isooctyl, tertiary octyl, nonyl, decyl, dodecyl, t-dodecyl, t-tetradecyl, hexadecyl, t-hexadecyl, eicosyl, tetracosyl, phenyl, naphthyl, tolyl, t-butylphenyl, t-octylphenyl, t-dodecylphenyl, octadecylphenyl, tetrocosylphenyl, benzyl, and phenylethyl.

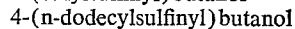
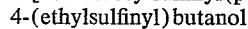
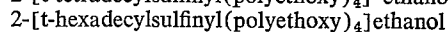
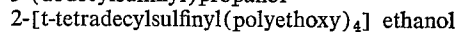
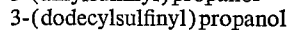
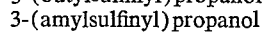
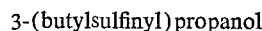
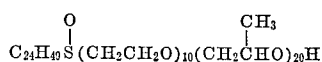
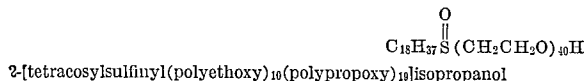
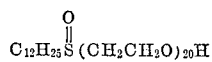
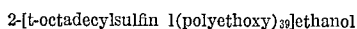
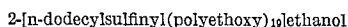
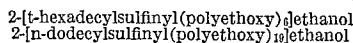
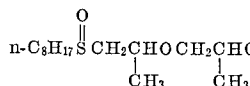
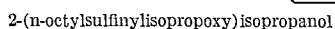
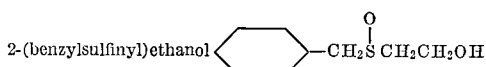
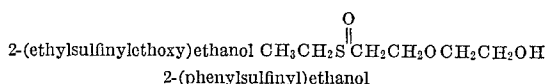
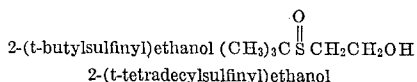
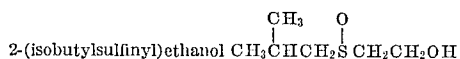
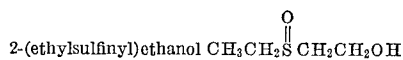
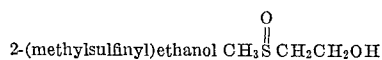
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Typical R_2 alkylene groups are ethylene, propylene and butylene.

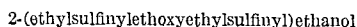
Representative R_3 and R_4 groups are ethylene, propylene, butylene, phenyl, 3,5 dimethylphenyl and 3,5 ditiarybutylphenyl.

Formula A compounds are well known. The R_2 radical of Formula A may represent a mixture of different alkylene groups and these groups may be provided by employing as reactants, in the preparation of the Formula A compound, mixtures of alkylene oxides such as ethylene oxide, propylene oxide and 1,2 butylene oxide. Formula C type compounds are also described in the literature. The sulfides corresponding to the compounds of Formula C are disclosed in U.S. Pat. 2,582,605 and these sulfides may be oxidized to sulfoxides by employing such conventional oxidation agents as hydrogen peroxide and peracids. Representative peracids include peracetic acid, persulfuric acid and perbenzoic acid. Conventional techniques are employed to oxidize the sulfide compound to the equivalent sulfinyl compound. Formula B compounds are prepared by the co-condensation of a Formula A and Formula C compound. The condensation reaction is accelerated by employing a condensation catalyst such as a strong mineral acid, i.e., sulfuric acid.

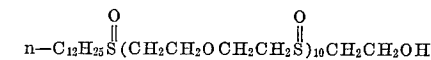
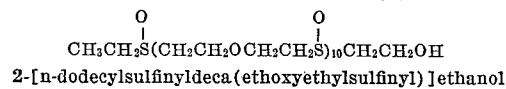
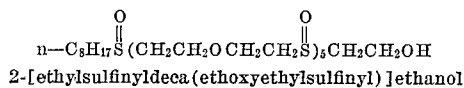
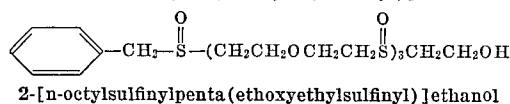
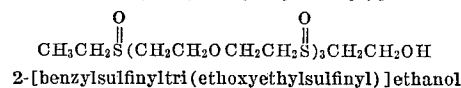
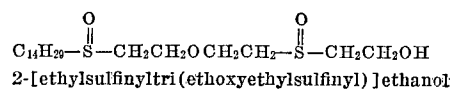
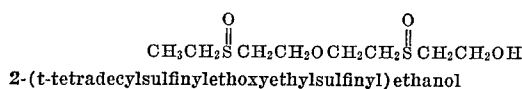
Typical examples of sulfinyl-containing hydroxy compounds within the scope of Formula A are listed below and in certain instances the particular formulas are illustrated.



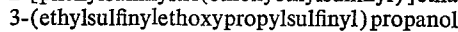
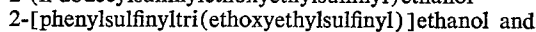
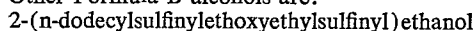
Representative examples of Formula B type sulfinyl-containing hydroxy compounds are:



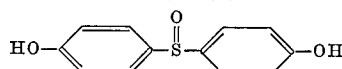
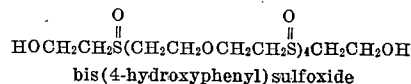
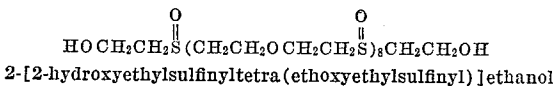
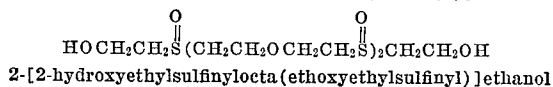
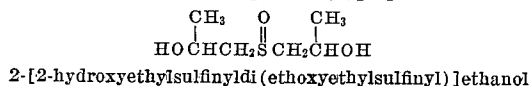
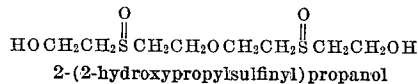
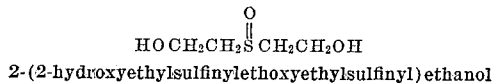
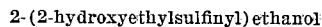
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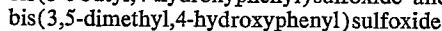
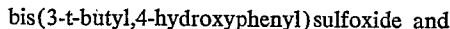
Other Formula B alcohols are:



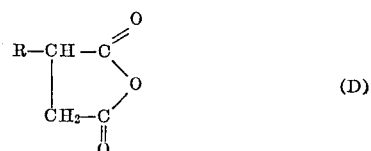
Representative Formula C sulfinyl dihydroxy compounds are:



Other aromatic sulfoxides that may be used include:



The alkenylsuccinic anhydride reactant is of the formula



wherein R represents an alkenyl radical containing about 12 to 200 carbon atoms and preferably from 30 to 200 carbon atoms. Therefore R will have a molecular weight of about 170 to about 2800. This compound is obtained by reacting maleic acid with an appropriate polyolefin.

Other alkenylsuccinic type reactants include alkenylsuccinic acid and alkenylsuccinamic acid wherein the alkenyl group corresponds to the definition of R above.

The alkenylsuccinamic acid is prepared by reacting an alkenylsuccinic anhydride with a compound having the formula:



wherein

A is alkyl of 1 to 24 carbon atoms, phenyl, naphthyl, benzyl or alkyl-substituted phenyl, naphthyl or benzyl in which the total alkyl substituents contain up to 24 carbon atoms, and

B is hydrogen or alkyl of 1 to 24 carbon atoms.

Representative A groups are methyl, ethyl, butyl, t-butyl, octyl, t-octyl, dodecyl, t-octadecyl, tetracosyl, phenyl, naphthyl, butylphenyl, octylphenyl, dodecylphenyl, dioctylphenyl, butylnaphthyl, butylbenzyl, and octylbenzyl. B may be hydrogen, methyl, butyl, octyl, dodecyl, octadecyl, eicosyl, and tetracosyl. Preferably, either A or B represents a t-alkyl radical with the remaining substituent being hydrogen. Each of A and B may represent a single alkyl group or a mixture of alkyl groups. For example, either A or B may represent a mixture of t-alkyl groups containing 12 to 15 carbon atoms averaging 13 carbon atoms or a mixture of 18 to 24 carbon atoms. Another preferred embodiment is when either A or B is a t-butyl radical and the remaining substituent is hydrogen. The reaction between the Formula D and Formula E compounds to produce alkenylsuccinamic acids is conducted at a temperature of about 0° C. to 200° C., and preferably from 60° C. to 120° C.

The R group of Formula D is derived by polymerizing an olefin containing 2 to 18 carbon atoms, preferably 2 to 8 carbon atoms, by addition polymerization from substantially pure olefins. These olefins may be either gaseous or liquid under normal conditions and frequently are obtained from the cracking of petroleum and other hydrocarbons. Fractions containing olefinically unsaturated open-chain hydrocarbons are readily available over a wide range of molecular weights and derived from olefins of 2 to 18 carbon atoms. The preferred olefins are those from 2 to 8 carbon atoms with particular emphasis on the olefin embodiments containing 4 carbon atoms. It is, of course, preferred to employ relatively pure olefins from which sulfur, cyclic compounds and other impurities have been removed.

Mixtures of various olefins, from ethylene to octadecene, may be used or individual embodiments, as desired. Mixtures of specific olefins, from ethylene to pentene, may be advantageously employed. Particularly advantageous for the present purposes are mixtures of the various butenes. Butenes most commonly used comprise both straight and branched chain members. It is also possible, and frequently desirable, to employ a particular isomer, such as isobutylene, but for the purposes of this invention, separation or isolation of particular isomers is not essential. Thus, the mixtures readily available to the chemical industry are especially useful for the purposes of the present invention. The olefinic polymers employed as starting materials vary from rather fluid liquids to rather viscous liquids at normal temperatures.

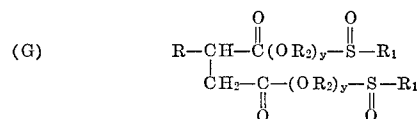
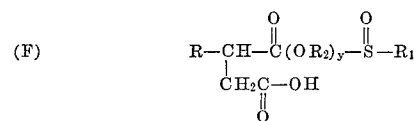
Typical olefinic polymers are those prepared from ethylene, propylene, isobutene, 1-butene, 2-butene, 1-pentene, 2-pentene, 1-hexene, 1-octene, 2-octene, 1-decene, 1-dodecene, 2-dodecene and 1-octadecene.

While the group, R, has been structurally presented as attached to a specific carbon atom with respect to formula (D), it will be understood by those skilled in the art that the R group may be positioned on the other carbon atom that is alpha to the other carbonyl group. The R group enters the molecule concerned by a reaction involving maleic anhydride and, therefore, could be at-

tached to either of the carbon atoms alpha to the carboxyl group. This invention encompasses fully this aspect.

The polyolefin is first reacted with maleic anhydride at temperatures of about 200° to 250° C. for a period of about 6 to 16 hours, as desired. The maleic anhydride is used in excess, preferably about 1.5 to 3 times the stoichiometric amount. The use of excess maleic anhydride tends to maximize yields. The polyolefin reacts with maleic anhydride to form a succinic anhydride derivative which can be separated from the excess maleic anhydride by vacuum distillation or similar treatment. The product can be diluted with xylene or similar solvent and filtered.

The alkenylsuccinates of this invention are prepared by reacting an alkenylsuccinic anhydride, acid or amic acid with either a sulfinyl-containing monohydric alcohol (defined in Formulas A or B), a sulfinyl-containing dihydric compound (defined in Formula C) or mixtures of both. When monohydric sulfinyl-containing alcohols are employed exclusively, the resultant monoester and diester products may be represented by the following formulas:

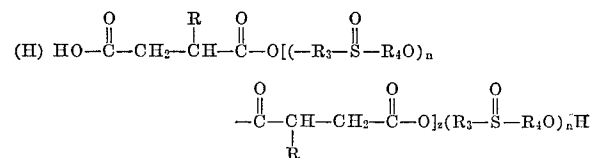


wherein R, R₁, R₂, and y represent the groups defined above.

The acid group in Formula F may be esterified by reaction with any alkanol or phenol according to standard techniques and as described in U.S. application Ser. No. 412,237, filed Nov. 18, 1964.

Formula (F) and (G) esters may be prepared by reacting the alkenylsuccinic anhydride, acid or alkenylsuccinamic acid with the desired Formula (A) or (B) monohydric compound at temperatures of from 25° to 220° C., and preferably from 60° to 150° C. until esterification proceeds to the desired extent. Employing an inert organic solvent in this reaction is discretionary.

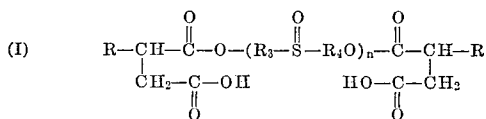
When sulfinyl-containing dihydric compounds are employed, the resultant product is a polyester which may be represented generally by the following formula:



wherein R, R₃, R₄ and n represent the groups defined above and z represents the repeating unit of the polyester and may be an integer from 1 to 50 or more. The reactants of this product may be heated at a temperature range of from 80° to 220° C. and preferably from 120° to 150° C. An inert organic solvent is necessary to azeotrope water from the reaction. Suitable solvents are selected from aromatic hydrocarbons, aliphatic hydrocarbons and halogenated hydrocarbons. The esterification reactions may be conducted in a mineral oil solution or dispersion or in combination with the inert organic solvent. Preferred solvents include benzene, toluene and xylene. Cessation of the evolution of water indicated substantial completion of the reaction.

Another type of product within the scope of this invention is obtained by reacting one equivalent by weight of a dihydric compound as described in Formula C and two equivalents by weight of an alkenylsuccinic anhydride

or acid. This reaction product may be represented by the following formula:



Similarly, one equivalent by weight of a dihydric compound of Formula C may be reacted with two equivalents by weight of an alkenylsuccinamic acid.

In the esterification reactions represented by the above formulas the mole ratio of the alkenylsuccinic anhydride, acid or amic acid to the sulfinyl hydroxy compound may vary from about 1:0.5 to 1:2 or more. Therefore about one-half equivalent to about two moles of sulfinyl hydroxy compound per mole of acid compound is employed.

The compounds of this invention are useful as dispersants in lubricating oil and fuel systems. They may be used in the range of about 0.005 to 15% by weight of the oil or fuel composition and may be incorporated therein according to standard techniques. In fuels, the range is 0.005 to 5%, preferably 0.01 to 2%, by weight of the fuel composition. In lubricants, the range is 0.1 to 15%, preferably 0.1 to 10%, by weight of the lubricant composition. The compounds of the present invention, as evaluated according to several known tests, exhibit outstanding activity as dispersants.

The following describes some of the tests employed in evaluating the compounds of the present invention:

API SERVICE MS SEQUENCE V-A TEST

This test evaluates the sludge dispersant characteristics of a lubricant under low and medium temperature operating conditions. A single cylinder oil test engine is operated under conditions described in ASTM Special Technical Publication No. 315, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

The engine may be rated at any time during the course of the test. The 7 parts rated for sludge (CRC Merit, 10=clean) are the rocker arm assembly, rocker arm cover plate, valve deck, timing gear cover, push rod cover plate, push rod chamber and oil pan.

PANEL COKER TEST

This test is described in the record of the Fifth World Petroleum Congress (1959) in an article by R. N. Jolie, "Laboratory Screening Test for Lubricating Oil Detergents and Dispersants." A sample of a compound under test is dissolved in a 170 SUS Mid-Continent Solvent Extracted Neutral containing 1% of a thermally unstable zinc dialkylidithiophosphate. The blend is placed in a heated sump and is splashed against a heated panel held at 570° F. for 2 hours. Gain in weight of the panel is determined and compared with oil without the test compound.

SUNDSTRAND PUMP TEST

In this test for distillate fuel oils, 1 liter of fuel oil containing 4 grams of synthetic sludge is treated with the additive. The oil is circulated for an hour through a Sundstrand oil burner pump containing a 100-mesh strainer. The sludge deposit is collected and weighed (Nelson, Osterhaut and Schwindeman, Ind. Eng. Chem., 48, 1892 (1956)).

As will be clearly understood in the art, the fuels contemplated are distillate fuels that boil from 75° to 750° F. which includes gasolines, along with jet and diesel fuels and furnace oils. The present compounds are particularly useful in fuels that boil up to about 600° F., that is, the normal gasolines and jet fuels and similar liquid hydrocarbon fuels.

Lubricating compositions of this invention may be based on mineral oils or on synthetic lubricants. The mineral oils may vary over a wide range of viscosity, such as 1 to 25 cs. at 210° F. These oils may be of

naphthenic or paraffinic nature or may be of various mixtures. They may be distillates or mixtures of neutral oils and bright stocks. The lubricants may be bodied or gelled and used as greases, if desired. The oils may vary from spindle oils or hydraulic oils to oils for reciprocating aircraft engines. They include oils for sparking combustion and compression ignition engines, varying from grades identified as S.A.E. 5 to S.A.E. 50. Other types of lubricants are also included, such as hydraulic and automatic transmission fluids.

The synthetic lubricants include esters, such as dioctyl, dinonyl or diisodecyl adipates, azelates or sebacates, polyethers and silicones. When use as hydraulic fluids is contemplated, phosphate esters are included as a base.

In the present composition, there may also be used as a base, a transmission fluid, hydraulic fluid, gear oil or grease.

In the compositions of this invention, there may be used one or more other additives, such as anti-oxidants, antifoam agents, antirust agents, antiwear agents, heavy duty detergents, pour-point depressants, viscosity index improvers, or other type of additive. For example, there may be employed one or more of the dithiophosphates, such as zinc, barium or nickel dialkylidithiophosphate, sulfurized oils, such as sulfurized sperm oil and sulfurized terpenes, phenols, sulfides alkylaryl sulfonates, petroleum sulfonates, whether normal or with alkaline reserve, such as calcium, barium or magnesium petroleum sulfonates, polymers and copolymers from alkyl acrylates, methacrylate, itaconates or fumarates or vinyl carboxylates and mixtures thereof, copolymers of acrylic esters and polar monoethylenically unsaturated compounds, such as N-vinyl-2-pyrrolidone, vinyl-pyridines, amino-alkyl acrylates or methacrylates or polyethylene-glycol acrylic esters, polybutenes, alkylphenoalkylene oxide condensates, alkenylsuccinic anhydrides, various silicones and alkyl or aryl phosphates, such as tricresyl phosphates.

There may also be used 4,4'-methylenebis-2,6-di-tert-butylphenol, trialkylphenols, tris(dimethylaminomethyl) phenol, phenothiazine, naphthylamines, N'-sec-butyl-N, N-dimethyl-p-phenylene-diamine, alkaline earth alkylphenates, alkaline earth salicylates, calcium phenylstearate, alkylamines, especially C₁₂-C₂₄ alkylamines, cyclic amines, alkyl and aryl imidazolines and alkenylsuccinic anhydrides reacted with amines and then with boron compounds, such as boron oxide, boron halides and boron esters.

A turbo prop lubricant may be prepared by blending the compounds of this invention with di-2-ethylhexyl sebacate and a mixture of polyesters formed by condensing 2-ethyl-1,3-hexane-diol and sebacic acid into the polyesters with 2-ethylhexanol, there being an average of about 3 glycol units per molecule. This composition may also contain antioxidant, stabilizer or other useful additives.

The compounds, compositions and method of the present invention may be more fully understood from the following examples which are offered by way of illustration and not by way of limitation. Parts by weight are used throughout.

EXAMPLE 1

A mixture of 409 parts of polybutenylsuccinic anhydride having an anhydride content of 0.502 millimole/gm. (prepared from maleic anhydride and polybutene of molecular weight 1300), 62.6 parts of ethyl sulfinyl ethanol and 400 parts of xylene was heated at 150° C. in a reaction vessel equipped with a stirrer, reflux condenser and water separator. Heating at the reflux temperature was continued for eight hours at which time the theoretical quantity of water had been collected. The final product was obtained after removal of the volatile components and excess reagents by stripping at 150° C./0.5 mm. Hg and filtering. Percent S=2.52 (theory=2.86).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 111 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 31 mg., while the oil without any additive gives 225 mg.

1.6 parts of the above product is blended with 1.0 part of a commercial zinc dialkyl dithiophosphate, 6.0 parts of a commercial polymethacrylate VI improver into 91.4 parts of a 170 SUS Mid-Continent Solvent Extracted Neutral Oil. The viscosity of this blend is 11.2 cSt. at 210° F. and 62.5 cSt. at 100° F. with a viscosity index of 146. The ASTM pour point is -30° F. This blend is evaluated in the Sequence V-A test giving a sludge rating at the end of 75 hours of engine operation of 66.7 (70.0=clean). The value for the reference oil alone is 39.7.

EXAMPLE 2

A mixture of 447 parts of the polybutenylsuccinic anhydride described in Example 1 and 59.2 parts of ethyl sulfinyl polyethoxyethanol (containing an average of 3.2 ethoxy units) was heated with stirring at 70-90° for six hours. At the end of this time the infrared spectrum of the reaction solution showed no anhydride band indicating the reaction to the desired half-acid ester was complete. The final product after filtration contained 1.35% S (theory=1.35).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 56 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 110 mg., while the oil without any additive gives 230 mg.

EXAMPLE 3

The half-acid ester from the polybutenylsuccinic anhydride described in Example 1 and ethyl sulfinyl polyethoxyethanol (containing an average of 10.3 ethoxy units) was made by mixing equimolar quantities of the reactants according to the procedure in Example 2. The final product contained 1.02% S (theory=1.06).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 44 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 16 mg., while the oil without any additive gives 230 mg.

EXAMPLE 4

A mixture of 139 parts of polybutenylsuccinic anhydride with an anhydride content of 0.72 millimole/g. (prepared from maleic anhydride and polybutene of molecular weight 950), 36.8 parts of benzylsulfinyl ethanol and 400 parts of xylene was heated at reflux (about 150° C.) until the theoretical amount of water of reaction was collected in an attached separator. The final product was obtained by vacuum stripping and filtration. Its acidity was 0.02 millimole/g., indicating essentially complete conversion to the diester.

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 32 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 26 mg., while the oil without any additive gives 230 mg.

EXAMPLE 5

A mixture of 362 parts of polybutenylsuccinic anhydride with an anhydride content of 0.276 millimole/gm. (prepared from maleic anhydride and polybutene of molecular weight 2200), 70.2 parts of n-dodecylsulfinyl-

polyethoxyethanol (containing an average of ten ethoxy units) and 150 parts of toluene was stirred and heated at 90-100° C. for twelve hours. At the end of this time, complete reaction to the half-acid ester had been effected as indicated by the complete disappearance of the anhydride band in the infrared spectrum. The final product was obtained by vacuum stripping of the volatile components at 100° C. and filtering.

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 80 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at 0.01 gram in 100 ml. of oil, the weight of sludge is 16 mg., while the oil without any additive gives 230 mg.

3.0 parts of the above product is blended with 1.0 part of a commercial zinc dialkyl dithiophosphate, 6.4 parts of a commercial polymethacrylate VI improver and 2.0 parts of a basic calcium sulfonate (TBN=300) into 87.6 parts of a 150 SUS Mid-Continent Solvent Extracted Neutral Oil. The viscosity of this blend is 11.26 cSt. at 210° F. and 79.3 cSt. at 100° F. with a viscosity index of 143. The ASTM pour point is -40° F. This blend is evaluated in the Sequence V-A test giving a sludge rating at the end of 75 hours of engine operation of 68.2 (70.0=clean). The value for the reference oil alone is 39.7.

EXAMPLE 6

A half-acid ester was made from 391 parts of polybutenylsuccinic anhydride, with an anhydride content of 0.49 millimole/gm. (prepared from maleic anhydride and polybutene of MW 1300), and 137.5 parts of an ethyl polysulfinylether alcohol of Formula B (where R₁ is ethyl, R₂, R₃ and R₄ are ethylene and n is 5), by heating and stirring the components at 130-145° for twelve hours. At the end of this time the homogeneous solution was vacuum stripped and filtered. The product had an acidity of 0.46 millimole/gm. and a sulfur content of 6.73% (theory=7.35).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 63 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 41 mg., while the oil without any additive gives 240 mg.

EXAMPLE 7

A mixture of 500 parts of a polybutenylsuccinic anhydride with an anhydride content of 0.22 millimole/gm. (made from maleic anhydride and polybutene of molecular weight 2400) and 80.2 parts of the sulfinyl alcohol of Example 6 was heated and stirred at 145° for twelve hours. The half-acid ester product was vacuum stripped and filtered. Acidity=0.41 millimole/gm., percent S=3.98 (theory=4.3).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 39 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 18 mg., while the oil without any additive gives 240 mg.

EXAMPLE 8

A half-acid ester was prepared from 491 parts of a polybutenylsuccinic anhydride, with an anhydride content of 0.217 millimole/gm. (made from maleic anhydride and polybutene of molecular weight 2200), and 141 parts of a polysulfinylether alcohol of Formula B (where R₁ is ethyl, R₂, R₃ and R₄ are ethylene and n is 10) by heating and stirring the two reactants at 165° C. for ten hours. The product was vacuum stripped and filtered. Acidity=0.16 millimole/gm.

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In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 82 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 146 mg., while the oil without any additive gives 240 mg.

EXAMPLE 9

An equimolar mixture of 514 parts of the polybutenylsuccinic anhydride of Example 6 and 34.6 parts of sulfinyl diethanol dissolved in 300 parts of xylene was refluxed at 160° for six hours using a water separator. At the end of this time the theoretical amount of water had been collected indicating conversion to the desired polyester was effected. The product was isolated after vacuum stripping at 130° and filtering. Percent S=1.61 (theory=1.60).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 91 mg. The same oil without the additive gives a deposit of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 152 mg., while the oil without any additive gives 240 mg.

EXAMPLE 10

A mixture of 225 parts of the polybutenyl succinic anhydride of Example 1 and 23.8 parts of a dihydric polysulfinylether of Formula C (where R_3 and R_4 are ethylene and n is an average of 3.4) was heated and stirred at 130° C. for 16 hours in order to effect complete reaction to the desired acid-ester. At the end of this time the mixture was completely homogeneous and its infrared spectrum showed essentially no anhydride bands. Analysis of the final product indicated percent S=2.43 (theory=2.33), acidity=0.45 millimole/gm.

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 38 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 9 mg., while the oil without any additive gives 205 mg.

1.6 parts of the above product is blended with 1.0 part of a commercial zinc dialkyl dithiophosphate, 5.9 parts of a commercial polymethacrylate VI improver into 91.5 parts of a 170 SUS Mid-Continent Solvent Extracted Neutral Oil. The viscosity of this blend is 11.06 cst. at 210° F. and 60.65 cst. at 100° F. with a viscosity index of 147. The ASTM pour point is -35° F. This blend is evaluated in the Sequence V-A test giving a sludge rating at the end of 75 hours of engine operation of 65.3 (70.0=clean). The value for the reference oil alone is 39.7.

EXAMPLE 11

A polyester was prepared by refluxing for six hours at 130-140° a toluene solution of 208 parts of the polybutenylsuccinic anhydride of Example 1 and 62.3 parts of a dihydric polysulfinylether of Formula C (where R_3 and R_4 are ethylene and n is an average of 4.8). The system was equipped with a water separator and at the end of the six hour reaction time the theoretical amount of water of reaction had been collected. The reaction mixture was vacuum stripped and filtered and the final product contained 5.5% S (theory=6.05).

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 16 mg. The same oil without the additive gives a deposit weight of 322 mg.

In the Sundstrand Pump Test at .01 gram in 100 ml. of oil, the weight of sludge is 12 mg., while the oil without any additive gives 230 mg.

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EXAMPLE 12

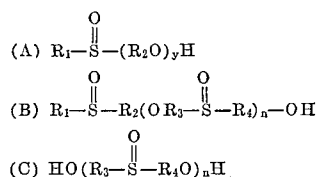
A mixture of 1390 grams of a 90% solution in xylene of polybutenylsuccinic anhydride (prepared from maleic anhydride and polybutene of molecular weight 950), with an anhydride content of 0.720 millimole/gram, and 130 grams of t-octylamine is stirred and heated at 100° C. for 10 hours. Vacuum stripping of the solvents and unreacted t-octylamine produce the intermediate amic acid (percent N=0.90). Equimolar quantities of the amic acid and ethylsulfinyl ethanol are reacted according to the procedure in Example 2 and the final product was vacuum stripped and filtered.

In the Panel Coker Test, a blend containing 1.0% of the above product gives a deposit weight of 85 mg. The same oil without the additive gives a deposit weight of 322 mg.

Similar test results were obtained when Examples 1 and 12 were repeated, except chlorinated polypropene of average number molecular weight of about 900 and a chlorine content of 3.9% was employed in lieu of the polybutene. The polypropenylsuccinic anhydride analyzes 0.91 millimole of anhydride per gram of material.

What is claimed is:

1. A composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient to impart dispersant properties, of the reaction product of (1) a compound selected from the group consisting of an alkenylsuccinic anhydride and an alkenylsuccinic acid and (2) at least one sulfinyl-containing hydroxy compound selected from those of the following formulas:



and wherein

y is an integer from 1 to 50 and n is an integer from 1 to 40,

R_1 is selected from the group consisting of (a) an alkyl hydrocarbon radical containing from 1 to 24 carbon atoms, (b) an aryl hydrocarbon radical (c) an aralkyl hydrocarbon radical wherein the alkyl portion of the radical contains from 1 to 4 carbon atoms and (d) an alkaryl hydrocarbon radical wherein the alkyl portion contains from 1 to 24 carbon atoms.

R_2 is an alkylene radical having 2 to 5 carbon atoms and having at least 2 carbon atoms extending in a chain between the adjoined S and O atoms, and

R_3 and R_4 are alkylene radicals having 2 to 5 carbon atoms and having at least 2 carbon atoms extending in a chain between the adjoined S and O atoms, a phenylene radical or lower alkyl substituted phenylene radical with the proviso that n is 1 when R_3 and R_4 are phenylene or lower alkyl substituted phenylene.

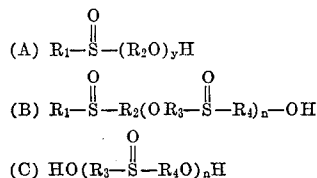
2. A composition according to claim 1 wherein compound (1) is an alkenylsuccinic anhydride and said compound (2) is selected from Formula A.

3. A composition according to claim 1 wherein said compound (1) is an alkenylsuccinic anhydride and said compound (2) is selected from Formula C wherein R_3 and R_4 are ethylene and n is an integer from 1 to 10.

4. A composition comprising a major proportion of a liquid fuel and a minor proportion, sufficient to impart dispersant properties, of the reaction product of (1) a compound selected from the group consisting of an alkenylsuccinic anhydride and an alkenylsuccinic acid (2)

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at least one sulfinyl-containing hydroxy compound selected from those of the following formulas:



and wherein

y is an integer from 1 to 50 and n is an integer from 1 to 40,

R_1 is selected from the group consisting of (a) an alkyl hydrocarbon radical containing from 1 to 24 carbon atoms, (b) an aryl hydrocarbon radical (c) an aralkyl hydrocarbon radical wherein the alkyl portion of the radical contains from 1 to 4 carbon atoms and (d) an alkaryl hydrocarbon radical wherein the alkyl portion contains from 1 to 24 carbon atoms.

R_2 is an alkylene radical having 2 to 5 carbon atoms and having at least 2 carbon atoms extending in a chain between the adjoined S and O atoms, and

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R_3 and R_4 are alkylene radicals having 2 to 5 carbon atoms and having at least 2 carbon atoms extending in a chain between the adjoined S and O atoms, a phenylene radical or lower alkyl substituted phenylene radical with the proviso that n is 1 when R_3 and R_4 are phenylene or lower alkyl substituted phenylene.

5. A composition according to claim 4 wherein said compound (1) is an alkenylsuccinic anhydride and said compound (2) is selected from Formula A.

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