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3,465,029

ESTERS OF (3,5-DIHYDROCARBYL-4-HYDROXY-BENZYL)THIO-DICARBOXYLIC ACIDS

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3 Claims

ABSTRACT OF THE DISCLOSURE

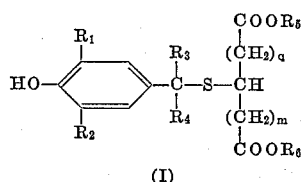
Esters of (3,5-dihydrocarbyl - 4 - hydroxybenzyl)thio-dicarboxylic acids are effective stabilizers for organic material. For example, dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate prolongs the life of polypropylene. Effectiveness is synergistically increased by inclusion of an ester of a thio-dialkanoic acid such as dilaurylthiodipropionate.

This invention relates to antioxidant compositions. In particular, this invention relates to the stabilization of organic material against oxidative degradation with dialkyl-[(3,5-dialkyl-4-hydroxybenzyl)thio]succinate.

It is a common practice to include an antioxidant in organic material normally susceptible to oxidation. Many of the antioxidants employed are either not effective over a long period of time or impart an undesirable color to the organic material being stabilized. The problem is particularly acute with polyolefins, especially polyolefins containing tertiary carbon atoms such as polypropylene, polybutylene, polybutadiene, and the like. These materials are subjected to elevated temperatures during processing, which tends to destroy many antioxidants or to cause them to impart an undesirable color to the polymer.

It is an object of this invention to provide improved antioxidant compositions. It is a further object to provide organic compositions which are resistant to oxidative degradation and which do not color appreciably during long periods of storage.

These and other objects are accomplished by providing a compound having the formula:



wherein m is an integer from 0-12, q is an integer from 0-1, R_1 is selected from the group consisting of alkyl radicals containing from about 1-20 carbon atoms, aryl radicals containing from about 6-20 carbon atoms, aralkyl radicals containing from about 7-20 carbon atoms and cycloalkyl radicals containing from about 6-20 carbon atoms; R_2 is selected from the group consisting of alpha-branched alkyl radicals containing from about 3-20 carbon atoms, alpha-branched aralkyl radicals containing from about 8-20 carbon atoms and cycloalkyl radicals containing from about 6-20 carbon atoms; R_3 and R_4 are selected from the group consisting of hydrogen, alkyl radicals containing from about 1-6 carbon atoms, aryl radicals containing from about 6-12 carbon atoms and aralkyl radicals containing from about 7-12 carbon atoms; and R_5 and R_6 are selected from the group consisting of alkyl radicals containing from about 1-20 carbon atoms, aralkyl radicals containing from about 7-20 carbon atoms, and aryl radicals containing from about 6-20 carbon atoms.

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Some examples of these compounds are:

- dihexyl 3-[(3-isopropyl-4-hydroxy- α , α -5-trimethylbenzyl)thio]glutarate;
- dimethyl[(3-sec-eicosyl-4-hydroxy-5-n-amy- α -hexylbenzyl)thio]malonate;
- dieicosyl 2-[(3-cyclohexyl-4-hydroxy-4-phenylbenzyl)thio]adipate;
- diphenyl 3-[(3,5-di(α -methylbenzyl)-4-hydroxybenzyl)thio]suberate;
- dibenzyl 2-[(3(2,5- α -trimethylbenzyl)-4-hydroxy-5-sec-butylbenzyl)thio]sebacate;
- di(4-octylphenyl)-2-[(3-(2,4-di-tert-butylphenyl)-4-hydroxy-5-(2,4,6-tri-tert-butyl- α -methylbenzyl)- α -phenylbenzyl)thio]brassylate

In a preferred embodiment of a compound of Formula I, R_1 is an alkyl radical containing from 1 to about 20 carbon atoms or an aralkyl radical containing from about 7 to 20 carbon atoms; R_2 is an alpha-branched alkyl radical containing from about 3 to 20 carbon atoms or an alpha-branched aralkyl radical containing from about 8 to 20 carbon atoms; R_3 and R_4 are hydrogen; R_5 and R_6 are alkyl radicals containing from about 1 to 20 carbon atoms; m is 1 and q is 0. These are derivatives of succinic acid and are referred to as dialkyl[(3,5-dialkyl-4-hydroxybenzyl)thio]succinate. Examples of these compounds are:

- dimethyl[(3-isopropyl-5-methyl-4-hydroxybenzyl)thio]succinate;
- dieicosyl 2-[(3-sec-octyl-4-hydroxy-5-propylbenzyl)thio]succinate;
- didecyl 2-[(3-cyclohexyl-4-hydroxy-5-(α -methylbenzyl)benzyl)thio]succinate;
- dicetyl 2-[(3-tert-amyl-4-hydroxy-5-n-amybenzyl)thio]succinate;
- dilauryl 2-[(3,5-di(α -methylbenzyl)-4-hydroxybenzyl)thio]succinate

In a more preferred embodiment of Formula I, R_1 and R_2 are both alpha-branched alkyl radicals containing from 3 to about 20 carbon atoms or alpha-branched aralkyl radicals containing from about 8 to 20 carbon atoms; R_3 and R_4 are hydrogen; R_5 and R_6 are alkyl radicals containing from 6 to 20 carbon atoms; m is 1 and q is 0. Some examples of these compounds are:

- di-n-hexyl-[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate;
- didecyl[(3,5-diisopropyl-4-hydroxybenzyl)thio]succinate;
- dieicosyl[(3,5-di-sec-butyl-4-hydroxybenzyl)thio]succinate;
- dilauryl[(3-tert-eicosyl-4-sec-octyl-4-hydroxybenzyl)thio]succinate;
- dicetyl[(3(α -methylbenzyl)-4-hydroxy-5-tert-nonylbenzyl)thio]succinate

A most preferred antioxidant compound of this invention is dilauryl[(3,5-di-tert-butyl - 4 - hydroxybenzyl)thio]succinate.

The antioxidant compounds of Formula I can be prepared by reacting the appropriate benzyl halide with the proper mercapto derivative of a diester of a dibasic acid. For example, dilauryl[(3,5-di-tert-butyl - 4 - hydroxybenzyl)thio]succinate is formed by the reaction of 3,5-di-tert-butyl - 4 - hydroxybenzyl chloride with dilauryl mercaptosuccinate. The following examples illustrate the preparation of some typical antioxidant compounds of this invention. All parts are parts by weight unless otherwise stated.

Example 1

To a reaction vessel equipped with stirrer and thermometer was added 440 parts of benzene, 12.74 parts (0.05 mole) of 3,5-di-tert-butyl-4-hydroxybenzyl chloride and 24.14 parts (0.05 mole) of dilauryl mercaptosuccinate. Following this, there was added, while stirring, at room temperature, 10.12 parts (0.1 mole) of triethyl amine. A precipitate of triethyl amine hydrochloride formed immediately. The mixture was stirred an additional 2 hours at room temperature and then the precipitate was filtered off. Benzene was distilled from the filtrate, leaving a yellow viscous oil. This material was eluted with benzene through an alumina column and all of the fractions having the same infrared spectrum were combined. The benzene was distilled from this material, leaving 21.4 parts of a yellow viscous liquid. Analysis showed it to contain 73.5 percent carbon and 11 percent hydrogen, which is in good agreement with the theoretical analysis for dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate.

Example 2

To a reaction vessel equipped as in Example 1 is added 1500 parts of toluene, 254.5 parts of 3,5-di-tert-butyl-4-hydroxybenzyl chloride, 332 parts of diphenyl 2-mercaptosuccinate and 202 parts of triethyl amine. The mixture is stirred at 50° C. over a period of 4 hours, and then cooled to room temperature. The triethyl amine hydrochloride precipitate that forms is filtered off and the product recovered employing the procedure of Example 1.

Example 3

To a reaction vessel equipped as in Example 1 is added 3000 parts of toluene, 350.5 parts of 3,5-di(α -methylbenzyl)-4-hydroxybenzyl chloride and 486 parts of dilauryl mercaptosuccinate. Following this, 202 parts of diethyl amine hydrochloride is removed by filtration and the toluene distilled from the filtrate under vacuum to a liquid temperature of 100° C. at 1 mm. The residue is dilauryl[(3,5-di(α -methylbenzyl)-4-hydroxybenzyl)thio]succinate.

Example 4

Using the same procedure as in the above example, 1.0 mole of 3-methyl-4-hydroxy-5-tert-butylbenzyl chloride is reacted with 1.0 mole of dibenzyl-3-mercaptosebacate in the presence of 2 moles of triethyl amine and 3000 parts of benzene, yielding dibenzyl 3[(3-methyl-4-hydroxy-5-tert-butylbenzyl)thio]sebacate.

Example 5

Using the same procedure as in the above examples, 1.0 mole of 3-cyclohexyl-4-hydroxy-5-tert-eicosylbenzyl chloride is reacted with 1.0 mole of diamyl-2-mercaptobrassylate in the presence of 2 moles of triethyl amine and 3000 parts of benzene, yielding diamyl 2[(3-cyclohexyl-4-hydroxy-5-tert-eicosylbenzyl)thio]brassylate.

The compounds that have been described are useful in stabilizing organic material normally subject to oxidative degradation. When used for this purpose they are usually present in amounts from 0.001 to 5 weight percent. Although the preferred amount will vary with the organic material being stabilized and the degree of stability desired, in most cases, adequate protection is obtained when from about 0.1 to 3 percent of the additive compound is included in the organic material.

The present antioxidants can be used in a wide range of organic materials. Some examples of these are liquid hydrocarbon fuels such as gasoline, kerosene and fuel oil. Likewise, liquid hydrocarbon fuels such as gasoline which contain organometallic additives such as tetraethyllead as well as other organometallic compounds which are used as fuel additives attain appreciably increased oxidative stability by the practice of this invention. In addition, lubricant oils and functional fluids, both those derived from naturally occurring hydrocarbons and

those synthetically prepared are greatly enhanced by the practice of this invention. The addition of small quantities of the compounds of this invention to such materials as turbine, hydraulic, transformer and other highly refined industrial oils, soaps and greases; plastics; synthetic polymers such as polyethylene and polypropylene; organometallic compositions where such fluids contain tetraethyllead and tetraethyllead antiknock mixtures as well as other organometallics; elastomers, including natural rubber; lubricating greases; crankcase lubricating oils; and the like, greatly increase resistance to deterioration in the presence of air, oxygen or ozone.

The compounds of this invention are also very useful in protecting petroleum wax—paraffin wax and microcrystalline wax—against oxidative deterioration. They also find use in the stabilization of edible fats and oils of animal and vegetable origin which tend to become rancid, especially during long periods of storage because of oxidative deterioration. Typical representatives of these edible fats and oils are linseed oil, cod liver oil, castor oil, soy bean oil, rape seed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter fat, lard, beef tallow, and the like.

The compounds of this invention are also useful in preventing oxidative deterioration in lubricating oil compositions. The following examples illustrate the preferred lubricating oil compositions of this invention.

Example 6

To 1,000 parts of a solvent refined neutral oil 95 V.I. and 200 SUS at 100° F., containing 6 percent of a commercial methacrylate type VI approver which gives the finished formulation of a V.I. of 140 and a viscosity of 300 SUS at 100° F., is added 5 percent of dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate.

Example 7

To an additive-free solvent refined crankcase lubricating oil having a viscosity index of 95 and an SAE viscosity of 10 is added 0.001 percent of dimethyl[(3-isopropyl-5-methyl-4-hydroxybenzyl)thio]succinate.

Example 8

To 10,000 parts of a petroleum hydrocarbon oil having a gravity of 30.3° API at 60° F., a viscosity of 178.8 SUS at 100° F., a viscosity index of 154.2 and which contains 0.2 percent sulfur, is added 200 parts of dieicosyl 2-[(3-sec-octyl-4-hydroxy-5-propylbenzyl)thio]succinate. The resulting oil possesses greatly enhanced resistance to oxidative deterioration.

Example 9

To 100,000 parts of a commercially available pentaerythritol ester having a viscosity of 100° F. of 22.4 centistokes, and known in the trade as "Hercoflex 600" is added 400 parts (0.4 percent) of didecyl 2-[(3-cyclohexyl-4-hydroxy-5-(α -methylbenzyl)benzyl)thio]succinate. The resulting finished oil possesses markedly improved resistance against oxidative deterioration.

Example 10

To 100,000 parts of dioctyl sebacate having a viscosity of 210° F. of 36.7 SUS, a viscosity index of 159 and a molecular weight of 426.7 is added 250 parts (0.25 percent) of dicetyl 2-[(3-tert-amyl-4-hydroxy-5-n-amylbenzyl)thio]succinate.

The compounds of this invention are also useful as additives to functional fluids and automatic transmission fluids. The primary constituent of a functional fluid is a refined mineral lubricating oil having a carefully selected minimum viscosity of 49 Saybolt Universal Seconds (SUS) at 210° F. and a maximum viscosity of 7,000 SUS at 0° F., generally a distillate oil, lighter than an SAE 10 motor oil. The oil usually amounts to between about 73.5 to about 97.5 percent by weight of the

finished fluid. Preferably, the base oil is selected from a paraffin base distillate such as a Pennsylvania crude.

The fluids usually contain compounds which are characterized by containing one or more organic components which may be alkyl, aryl, alkaryl or aralkyl groups that are bonded to one or more metal atoms through coupling groups such as sulfonate, hydroxyl, carboxyl and mercaptan. The metal atoms may be aluminum, calcium, lithium, barium, strontium, and magnesium. The organic components contain oil solubilizing groups such as high molecular weight straight or branched chain paraffins, aromatic or naphthenic rings, or contain a halogen. These metal compounds are present in the compounded fluid in a concentration range of between about 0.1 to about 5 percent by weight. These compounds include alkaline-earth metal salts or phenyl-substituted long chain fatty acids, alkaline-earth metal salts of the capryl or octyl esters of salicylic acid, the alkaline-earth metal salts of petroleum sulfonic acids, the alkaline-earth metal salts of alkyl-substituted phenol sulfides, the salt of aluminum or the alkaline-earth metals with cetyl phenol, and the metal salts of wax-substituted phenol derivatives. Another class of additives are the so-called overbased phenates and sulfonates, which can be prepared by reaction between an alkyl phenol or alkyl phenyl sulfonate and an alkaline-earth metal oxide or hydroxide at an elevated temperature. The overbased phenate or sulfonate formed from the reaction contains up to two or three times as much metal as the normal phenate or sulfonates.

In addition, functional fluids may contain additional components which improve the properties of the fluid. Typical components include anti-squawk additives, pour point depressants, foam inhibitors, rust preventatives, extreme pressure agents, metal deactivators and viscosity index improvers.

The following examples show typical functional fluids of this invention. The fluids are formed by mixing the ingredients together, while heating the oil to a temperature up to 200° F.

Example 11

A fluid of this invention is prepared by blending 80 parts of a conventionally-refined Pennsylvania mineral oil (99 SUS at 100° F.), 2 parts of dilauryl 2-[[3,5-di (α - methylbenzyl) - 4 - hydroxybenzyl]thio]succinate, 5 parts of barium petroleum sulfonate, 10 parts of a polyacrylate having a molecular weight of approximately 7,000 derived from a fatty alcohol such as cetyl or lauryl alcohol, 0.1 part of a dimethyl silicone polymer anti-foam agent, 2 parts of a dialkyl zinc dithiophosphate and 0.9 part of a dark, viscous liquid having a viscosity of 560 SUS at 210° F., a flash point of 420° F., a pour point of 30° F. and a specific gravity of 60/60° F. of 0.919.

Example 12

Another such fluid consists of 95 parts of a solvent refined, light acid-treated, clay-contacted, solvent dewaxed paraffin base distillate mineral oil (110 SUS at 100° F.); 0.1 part of di-n-propyl-[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate; 0.1 part of calcium octylphenyl sulfonate; 2 parts of a sulfurized sperm oil having a sulfur content between 10-12 percent, a viscosity of 210° F. of 200 SUS and a pour point of 65° F.; 0.3 part of an ester of an aromatic acid and wax-alkylated phenol having a molecular weight of approximately 450; 2.5 parts of a linear pale color isobutylene polymer of a controlled molecular weight having a viscosity of 3,000 SUS at 210° F., a specific gravity of 60/60° F. of 0.875.

Liquid hydrocarbon fuels employed in the operation of spark ignition combustion engines are also vastly improved in their storage stability by the practice of this invention. Table I, below, gives the compositions of a number of typical commercial gasolines which may be

stabilized against oxidative deterioration by the inclusion therein of a compound of this invention.

TABLE I.—GASOLINE COMPOSITIONS

Gasoline	Percent Aromatics	Percent Olefins	Percent Saturates	Gravity ° API
A-----	26.6	20.8	52.6	62.1
B-----	8.6	7.9	83.5	68.5
C-----	20.0	41.2	38.8	62.9
D-----	20.5	32.9	46.6	63.5
E-----	38.1	7.3	54.6	59.3

Example 13

To 1,000 parts of Gasoline A, as described in Table I, is added 10 parts of didecyl[(3,5-diisopropyl-4-hydroxybenzyl)thio]succinate.

Example 14

To 10,000 parts of Gasoline B is added 50 parts of dieicosyl[(3,5 - di - sec-butyl-4-hydroxybenzyl)thio]succinate.

Example 15

To 500 parts of Gasoline C, as described in Table I, is added 10 parts of dilauryl[(3-tert-eicosyl-4-sec-octyl-4-hydroxybenzyl)thio]succinate.

Example 16

To 2,000 parts of Gasoline D is added 15 parts of dicetyl[[3(α - methylbenzyl) - 4 - hydroxy-5-tert-nonylbenzyl]thio]succinate.

Example 17

To 10,000 parts of Gasoline E is added 500 parts of dicetyl[(3,5-diisopropyl-4-hydroxybenzyl)thio]malonate.

Antiknock compositions and spark ignition internal combustion engine fuels containing mixtures of organolead antiknock agents and cyclopentadienyl manganese tricarbonyls are also vastly improved in their storage stability by the practice of this invention. Such compositions are described more fully in U.S. Patent No. 2,818,417.

The following examples illustrate the compositions of this invention and the methods by which they are prepared.

Example 18

To 1,000 gallons of a commercial gasoline having a gravity of 59.0° API, an initial boiling point of 98° F. and a final boiling point of 390° F. are added 3.18 grams per gallon of lead as tetraethyllead, 0.6 theory (based on the lead) of bromine as ethylene dibromide, 1.0 theory (based on the lead) of chlorine as ethylene dichloride, 0.25 gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl and 0.0002 weight percent (based on the gasoline) of dilauryl [(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate. The resultant fuel possesses enhanced stability characteristics.

Example 19

With a gasoline having an initial boiling point of 93° F., a final boiling point of 378° F., an API gravity of 56.2° and a tetraethyllead content equivalent to 0.2 gram of lead per gallon are blended cyclopentadienyl nickel nitrosyl to a concentration of 0.05 gram of nickel per gallon and dicetyl [[3,5 - di(α-methylbenzyl)-4-hydroxybenzyl]thio]succinate to a concentration of 0.005 weight percent (based on the gasoline). The finished fuel so formed possesses improved stability properties.

Example 20

To a gasoline having an API gravity of 51.5°, an initial boiling point of 91° F. and a final boiling point of 394° F. are blended 6.4 grams of lead per gallon as tetrabutyllead, 2 grams of manganese per gallon as octylcyclopentadienyl manganese tricarbonyl and 0.0008 weight percent (based on the gasoline) of diphenyl 2-[(3-methyl-5-tert-octyl-4-hydroxybenzyl)thio]glutarate. The resultant fuel possesses very good stability.

Example 21

With a gasoline having an initial boiling point of 92° F. and a final boiling point of 410° F. are blended 2 grams of lead per gallon as tetraphenyllead, 6 grams of nickel as diethylcyclopentadienyl nickel nitrosyl, 1 theory (based on the lead) bromine as ethylene dibromide and 0.01 weight percent (based on the gasoline) of dibenzyl 3-[3,5-di-sec-butyl-sec-butyl-4-hydroxybenzyl]thio]adipate. The finished fuel has very good storage stability.

This invention also extends to the use in the above fuel compositions containing manganese pentacarbonyl (i.e., dimanganese decarbonyl).

The compounds of this invention are also very effective antioxidants for high molecular weight unsaturated hydrocarbon polymers, such as polybutadiene (including poly-cis-butadiene), methyl rubber, polybutene rubber, natural rubber, butyl rubber, GR-S rubber, GR-N rubber, piperylene rubber, dimethyl butadiene rubber, and the like. Thus, a preferred embodiment of the present invention is a rubber containing as an antioxidant therefor a compound of this invention as defined above. Another part of this invention is the method of preserving rubber which comprises incorporating therein a compound of this invention as defined above. The stabilizer is incorporated into the rubber by milling, Banbury mixing, or similar process, or is emulsified and the emulsions added to the rubber latex before coagulation.

As used in the description and claims, the term "rubber" is employed in a generic sense to define a high molecular weight plastic material which possesses high extensibility under load coupled with the property of forcibly retracting to approximately its original size and shape after the load is removed. It is preferable that the rubber be a sulfur-vulcanizable rubber, such as India rubber, reclaimed rubber, balata, gutta percha, rubbery conjugated diene polymers and copolymers exemplified by the butadiene-styrene (GR-S) and butadiene-acrylonitrile (GR-N or Paracril) rubbers, and the like, although the invention is applicable to the stabilization of any rubbery high molecular weight organic material which is normally susceptible to deterioration in the presence of oxygen, air, or ozone. The nature of these rubbers is well known to those skilled in the art.

Among the definite advantages provided by this invention is that the present rubber compositions possess unusually great resistance against oxidative deterioration. Moreover, these compositions exhibit excellent non-staining and non-discoloration characteristics. Furthermore, the novel stabilizer is relatively inexpensive and easily prepared, and possesses the highly beneficial property of low volatility. As is well known, a highly desirable feature of a rubber antioxidant is that it have a low volatility so that it remains admixed with the rubber during vulcanization and related process steps.

The rubber compositions of the present invention are illustrated by the following specific examples wherein all parts and percentages are by weight.

Example 22

To illustrate the enhanced oxygen resistance of the rubber compositions of this invention and their excellent non-staining and non-discoloration characteristics, a light-colored stock is selected for test. This stock had the following composition:

	Parts by weight
Pale crepe rubber	100.00
Zinc oxide filler	50.00
Titanium dioxide	25.00
Stearic acid	2.00
Ultramarine blue	0.12
Sulfur	3.00
Mercaptobenzothiazole	1.00
	181.12

To the above base formula is added one part by weight of dilauryl [(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate, and the resultant blend cured for 30 minutes at 274° C. The resulting rubber has improved stability.

Example 23

To a synthetic rubber master batch comprising 100 parts of GR-S rubber having an average molecular weight of 60,000, 50 parts of mixed zinc propionate-stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 1.5 parts of mercaptobenzothiazole is incorporated 1.5 parts of diamyl [(3-phenyl-5-tert-cetyl-4-hydroxybenzyl)thio]malonate. This batch is then cured for 60 minutes at 45 p.s.i. of steam pressure.

Example 24

Natural rubber stock is compounded according to the following formula:

	Parts
Thick gristly crepe natural rubber	100
Wax	2
Ultramarine dye	0.1
Zinc oxide	70
Titanium dioxide	20
Sulfur	3
Stearic acid	1.2
Di-2 - ethylhexyl[(3-n-propyl-5-cyclohexyl-4-hydroxybenzyl)-thio]succinate	1
Benzothiazyl disulfide	0.4
Amine activator	0.5

This stock is then vulcanized for 60 minutes at 280° F.

Example 25

A butadiene-acrylonitrile copolymer is produced from butadiene-1,3 and 32 percent of acrylonitrile. Two percent (based on the dry weight of the copolymer) of didecyl [(3,5 - di - cyclohexyl - 4 - hydroxybenzyl)thio]succinate is added as an emulsion in a sodium oleate solution to the latex obtained from emulsion copolymerization of the monomers. The latex is coagulated with a pure grade of aluminum sulfate and the coagulum, after washing, is dried for 20 hours at 70° C.

Each of the above illustrated rubber compositions of this invention possesses greatly improved resistance against oxidative deterioration as compared with the corresponding rubber compositions which are devoid of an antioxidant. Moreover, the light-colored stocks of the above examples exhibit virtually no discoloration or staining characteristics even when subjected to severe weathering conditions and the like. The methods of formulating the improved rubber compositions of this invention will now be clearly apparent to those skilled in the art.

Other rubbers and elastomers which can be prepared according to this invention are the rubbery polymerizates of isoprene, butadiene-1,3 piperylene; also the rubbery copolymer of conjugated dienes with one or more polymerizable monoolefinic compounds which have the capability of forming rubbery copolymers with butadiene-1,3, outstanding examples of such monoolefinic compounds being those having the group $\text{CH}_2=\text{C}<$, exemplified by styrene. Examples of such monoolefins are styrene, vinyl naphthalene, alpha methyl styrene, p-chlorostyrene, dichlorostyrene, acrylic acid, methyl acrylate, methyl methacrylate, methacrylonitrile, methacrylamide, methyl vinyl ether, methyl vinyl ketone, vinylidene chloride, vinyl carbazole, vinyl pyridines, alkyl substituted vinyl pyridines, etc. In fact, excellent stabilization is achieved by incorporating a compound of this invention in any of the well-known elastomers which are normally susceptible to deterioration in the presence of air, such as elastoprenes, elastolenes, elastothiomers, and elastoplastics.

The compounds of this invention are especially effective antioxidants when added to polyolefin compositions normally tending to undergo deterioration in the presence of air or oxygen. The following examples illustrate various embodiments of this aspect of the invention.

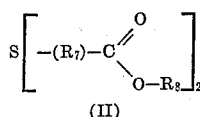
Example 26

To a master batch of high molecular weight polyethylene having an average molecular weight of about 1,000,000, a tensile strength of 6,700 p.s.i., a Shore D hardness of 74 and a softening temperature under low load of 150° C., is added 5 percent of dicetyl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate to prepare a composition of outstanding oxidative stability.

Example 27

A Ziegler polypropylene having a high degree of crystallinity, up to 93 percent, is compounded with 0.005 percent of dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate, and the resulting product has better stabilizing characteristics.

Another embodiment of this invention is a stabilizing composition comprising from 10-90 weight percent of a compound as defined for prior Formula I and 10-90 weight percent of a synergistic compound having the formula:



wherein R_7 is a divalent alkylene radical containing from 1-12 carbon atoms and R_8 is selected from the group consisting of alkyl radicals containing from about 6-20 carbon atoms and aryl radicals containing from about 6-20 carbon atoms. As used in Formula II, a divalent alkylene radical is any divalent hydrocarbon radical having the formula: C_nH_{2n} . The two bonds which connect the radical to the moieties may be on the same or different carbon atoms. Examples of divalent alkylene radicals in which both bonds are on the same carbon atom are: methylene, ethylidene, propylidene; 1-methyl ethylidene, 1-ethylbutylidene, 1-n-propyl-butylidene, and the like. Examples of divalent alkylene radicals in which the bonds are on different carbon atoms are ethylene, 1-methyl ethylene, 1,1-dimethyl ethylene, 1-ethyl ethylene, 1,2-dimethyl ethylene, trimethylene, 1-methyl-trimethylene, 2-methyl-trimethylene, 1-ethyl-trimethylene, 1,1-dimethyl-trimethylene, and the like.

Some examples of synergistic compounds having Formula II are:

dihexylthiodiacetate
diheptylthiodivalerate
di-n-octylthiodibutyrate
di-2-octylthiodicaprate
didecylthiodiacetate
diundecylthiodibutyrate
diheptadecylthiodivalerate
dioctadecylthiodipropionate
dinonadecylthiodibutyrate
dieicosylthiodipropionate

A preferred embodiment of the stabilizing compositions of this invention is a composition comprising from about 10-90 weight percent of a compound having Formula I wherein q is 0, m is 1, R_1 is an alkyl radical containing from about 1-20 carbon atoms or an aralkyl radical containing from about 7-20 carbon atoms, R_2 is an alpha-branched alkyl radical containing from about 3-20 carbon atoms or an alpha-branched aralkyl radical containing from about 8-20 carbon atoms, R_3 and R_4 are hydrogen, and R_5 and R_6 are alkyl radicals containing from about 1-20 carbon atoms; and from about 10-90 weight percent of a compound of Formula II wherein R_7 is a divalent alkylene radical containing from 1-3 carbon atoms and R_8 is an alkyl radical containing from 10-16 carbon atoms.

Some examples of these preferred stabilizing compositions are:

(A)

50% dimethyl[(3-isopropyl-5-methyl-4-hydroxybenzyl)thio]succinate
50% didecylthiodiacetate

(B)

25% dieicosyl 2-[(3-sec-octyl-4-hydroxy-4-propylbenzyl)thio]succinate
75% diundecylthiodibutyrate

(C)

75% didecyl 2-[[3-cyclohexyl-4-hydroxy-5-(α -methylbenzyl)benzyl]thio]succinate
25% didodecylthiodiacetate

(D)

10% dicetyl 2-[(3-tert-amyl-4-hydroxy-5-n-amylbenzyl)thio]succinate
90% dihexadecylthiodiacetate

(E)

90% dilauryl 2-[[3,5-di(α -methylbenzyl)-4-hydroxybenzyl]thio]succinate
10% didodecylthiodi (2-methylacetate)

A more preferred embodiment of the stabilizing compositions of this invention is a composition comprising from 10-90 weight percent of a compound of Formula I in which R_1 and R_2 are alpha-branched alkyl radicals containing from about 3-20 carbon atoms or alpha-branched aralkyl radicals containing from about 8-20 carbon atoms; R_3 and R_4 are hydrogen, m is 1, q is 0 and R_5 and R_6 are alkyl radicals containing from 1-20 carbon atoms; and from 10-90 weight percent of dilaurylthiodipropionate. Some examples of these preferred stabilizing compositions are:

(F)

50% di-n-propyl-[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate
50% dilaurylthiodipropionate

(G)

10% didecyl[(3,5-diisopropyl-4-hydroxybenzyl)thio]succinate
90% dilaurylthiodipropionate

(H)

90% dieicosyl[(3,5-di-sec-butyl-4-hydroxybenzyl)thio]succinate
10% dilaurylthiodipropionate

(I)

25% dilauryl[(3-tert-eicosyl-4-sec-octyl-4-hydroxybenzyl)thio]succinate
75% dilaurylthiodipropionate

(J)

75% dicetyl[[3(α -methylbenzyl)-4-hydroxy-5-tert-nonylbenzyl]thio]succinate
25% dilaurylthiodipropionate

A most preferred embodiment of the stabilizing composition of this invention is the composition comprising from about 10-90 weight percent of dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate and from about 10-90 weight percent of dilaurylthiodipropionate.

The foregoing stabilizing compositions containing the synergistic compounds are useful in stabilizing any of the previously described organic materials normally susceptible to oxidation. These compositions can be formulated as in Examples 6 to 27 by merely substituting a stabilizing composition such as those identified as compositions A through J for the single stabilizer compound shown in the examples.

The stabilizing compositions are especially useful in stabilizing polyolefins against oxidative degradation. Thus, a preferred embodiment is a polyolefin containing from 10-90 weight percent of a compound of Formula I and from 10-90 weight percent of a compound of Formula II. In a more preferred embodiment, the compound of Formula I is either dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate or didodecyl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate and the compound of Formula I is dilaurylthiodipropionate.

In a most preferred embodiment, the polyolefin is a polypropylene and contains a stabilizing quantity of a stabilizing composition comprising about 10-90 weight percent of dialuryl[(3,5-di-tert-butyl-4-hydroxybenzyl)-thio]succinate and about 10-90 weight percent of dilaurylthiodipropionate.

In order to demonstrate the improved stabilization furnished by the antioxidant compounds and stabilizing compositions of this invention, Oven Aging Tests were conducted on polypropylene. These tests are recognized in the plastic industry as a useful guide in determining oxidative stability. In these tests, small specimens of polypropylene are prepared containing the test stabilizer. These test specimens are placed in an air circulating oven maintained at 150° C. Five replicates are made of each polypropylene-stabilizer composition and the test criteria is the time in hours until three of the five replicates show signs of deterioration. Deterioration is evidenced by cracking, discoloration or any visual appearance of change in the specimen.

Test specimens were prepared by mixing the test stabilizers with polypropylene powder for 3 minutes in a Waring Blendor. The mixture was then molded into a 6" x 6" sheet having a thickness of 25 mils. This was accomplished in a molding press at 400° F., under 5000 p.s.i. pressure. Each sheet was then cut into 1/2-inch by 1-inch test specimens in order to obtain the five replicate samples. These samples were then subjected to the Oven Aging Tests.

In one series of tests, the additive compounds of this invention were incorporated into polypropylene samples and compared not only with the unstabilized polypropylene, but with polypropylene stabilized with an equal amount of other recognized antioxidants. Duplicate runs were made on the test stabilizer of this invention in order to provide increased confidence in the results. The results obtained in these tests are shown in the following table.

No.	Additive	Conc. (weight percent)	Hours to Failure
1	None		2.5
2	2,6-di-tert-butyl-4-methylphenol	0.3	16.0
3	2,2'-methylenebis(4-methyl-6-tert-butylphenol)	0.3	112.0
4	4,4'-thiobis(2-tert-butyl-5-methylphenol)	3.3	96.0
5	Dilauryl[3,5-di-tert-butyl-4-hydroxybenzyl]thio)succinate.	0.3	1,224
6	do	0.3	1,114
7	do	0.3	1,000

As the above results show, the additive compounds of this invention (Tests 5-7) provide about a 50-fold increase in polypropylene life over the unprotected polypropylene and a 10-fold increase over the protection afforded by some prior art antioxidant compounds.

Further Oven Aging Tests were conducted to show the effect of the synergistic compounds on the antioxidant compounds of this invention. These tests were carried out

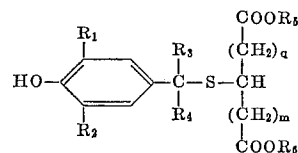
in the same manner as those described above except with different concentrations in order to show the synergistic effect of the sulfur compound. As before, duplicate runs were made to increase the reliability of the results. The results obtained are shown in the following table.

No.	Additive	Cone. (weight percent)	Hours to Failure
10	1-----Dilaurylthiodipropionate.	0.3	288
	2-----Dilauryl[(3,5-di-tert-butyl-4-hydroxy- benzyl)thio]succinate.	0.1	208
	3-----do.	0.1	280
	4-----Dilauryl[(3,5-di-tert-butyl-4-hydroxy- benzyl)thio]succinate dilaurylthio- dipropionate.	0.1 0.2	840
	5-----do.	0.1	808
15		0.2	

As the above results show, although the addition of 0.1 weight percent dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate stabilized the polypropylene for 208 hours (Test 2) and 0.3 weight percent dilaurylthiodipropionate stabilized the polypropylene for only 288 hours (Test 1), the combination of 0.1 weight percent dilauryl[(3,5-di-tert-butyl-4-hydroxybenzyl)thio]succinate and only 0.2 weight percent dilaurylthiodipropionate stabilized the polypropylene on the order of twice the sum of the stability expected from the two components (Tests 4-5).

I claim:

1. A compound having the formula:



wherein m is an integer from 0–12, q is an integer from 0–1, R_1 is selected from the group consisting of alkyl radicals containing from about 1–20 carbon atoms, cyclohexyl radicals and α -methylbenzyl radicals; R_2 is selected from the group consisting of alpha-branched alkyl radicals containing from about 3–20 carbon atoms, cyclohexyl radicals and α -methylbenzyl radicals; R_3 and R_4 are selected from the group consisting of hydrogen and methyl radicals; and R_5 and R_6 are selected from the group consisting of alkyl radicals containing from about 1–20 carbon atoms, benzyl radicals and phenyl radicals.

2. Didodecyl[(3,5-di-*tert*-butyl-4-hydroxybenzyl)thio]succinate.

50 3. Dicetyl[(3,5-di-tert-butyl - 4 - hydroxybenzyl)thio] succinate.

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