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THIOBIS(2,6-DIALKYLANILINE) COMPOUNDS

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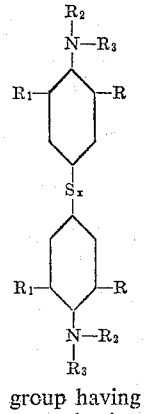
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This invention relates to novel chemical compounds which are outstanding as antioxidants in a wide variety of oxygen sensitive organic material. More particularly the invention relates to sulfur-containing alkyl substituted aromatic amines.

Certain aromatic amine compounds are known to possess antioxidant activity in some oxygen sensitive organic material. However, many of these compounds suffer from a low order of antioxidant activity in many organic substrates.

It is an object of the present invention to provide organic compounds containing aromatic amine moieties which are outstanding antioxidants. A further object of this invenion is to provide methods of preparing these novel compounds. Another object of this invention is to provide lubricants characterized by greatly increased resistance to oxidative deterioration, particularly at elevated temperatures. Other objects will become apparent from the following description of the invention.

The objects of this invention are accomplished by a 4,4'-thiobis[2,6-di(lower alkyl) aniline] compound. In general the compounds of this invention have the formula:



wherein R is an alkyl group having from 2 to 4 carbon atoms, R_1 is an alkyl group having from 1 to 4 carbon atoms, R_2 and R_3 are each selected from the class consisting of hydrogen and lower alkyl groups having from 1 to about 8 carbon atoms, and x ranges from 1 to 4 inclusive. Although all of the compounds within the scope of the above formula are excellent antioxidants, those compounds where R_2 and R_3 are hydrogen are preferred because of their antioxidant activity. Representative of compounds of this invention are 4,4'-thiobis-(2,6 - diethylaniline), 4,4'-dithiobis(2-methyl-6-sec-butyl aniline), 4,4'-trithiobis(2-isopropyl-6-ethylaniline), 4,4'-tetrathiobis(2,6-diethylaniline), 4,4'-dithiobis(2-methyl-6-ethylaniline), and 4,4' - thiobis(2 - isopropyl-6-tert-butyl aniline).

Another preferred group of compounds of this invention are those in which R and R_1 in the above formula are alkyl groups having from 1 to 2 carbon atoms. These compounds are especially preferred since they are easily prepared from readily available starting materials and have been found to have excellent antioxidant properties. A still further preferred group of compounds of this invention are those in which x in the above formula is 2, that is, the 4,4'-dithiobis compounds of this invention. These compounds are especially preferred since they are

prepared readily from the acid salts of the 2,6-dialkyl anilines employed as starting materials and, in addition, are outstanding antioxidants. The most particularly preferred compound of this invention is 4,4'-dithiobis(2,6-diethylanaline) which is a superior antioxidant for lubricating oil.

The compounds of this invention are solids with melting points in excess of about 70° C. They are soluble in many organic solvents and insoluble in water. They are compatible with organic material in which they may be incorporated as antioxidants.

A variety of methods are available for preparing the compounds of this invention depending upon the particular compound desired. Each of these preparations starts with a 2,6-dialkyl analine (which may have N-alkyl substitutents). In one embodiment of the invention the dialkyl aniline or acid salt is reacted with a sulfur halide such as sulfur dichloride (SCl_2) or sulfur monochloride (S_2Cl_2) in the presence of an inert solvent. When the nitrogen is substituted with a single alkyl group or has no alkyl substitutents, it is preferred to react the amine as the acid salt to prevent reaction of the solvent halide with the nitrogen portion of the molecule. However, when the aniline used as a starting material is an N,N-dialkylaniline, it may be employed without first forming an acid salt. This embodiment of the invention leads to compounds of the above formula where x is 2, that is, to the 4,4'-dithiobis(2,6-dialkylaniline) compounds.

In this process temperatures from about 0° C. to the reflux temperature of the particular solvent employed may be used. Reaction times of from about one half-hour to ten hours or longer have been found to be satisfactory.

Among the solvents employed in this process are halogenated aliphatic and aromatic compounds such as ethylene dichloride and chlorobenzene, nitro hydrocarbons such as nitrobenzene and nitromethane, inert hydrocarbons such as hexane, benzene and toluene and highly polar solvents such as carbon disulfide.

The following examples in which all parts are by weight illustrate this process, which is the preferred process of this invention since the compounds prepared in this manner have been found to be outstanding antioxidants.

EXAMPLE 1

To a solution of 560 parts of 2,6-diethylaniline hydrochloride in 3000 parts of chloroform was added dropwise with stirring a solution of 145 parts of S_2Cl_2 in 750 parts of chloroform. The mixture was heated at 40–50° until no more hydrogen chloride evolved, then refluxed at about 65° C. for one hour. The solid precipitate which formed on cooling was collected on a filter, washed with chloroform and dried to give 441 parts of a finely divided tan solid. This solid was treated with 2000 parts of 10 percent sodium carbonate solution to free the amine. The organic portion was extracted with ether, washed with water and dried. Evaporation of the ether left a dark brown semi-crystalline mass which was freed of oils on a suction filter and recrystallized from n-hexane to obtain 43.3 of yellow crystalline 4,4'-dithiobis(2,6-diethylaniline) having a melting point of 103.5–104.5°. Calculated sulfur content for the compound is 17.8 percent, 18.2 percent sulfur was found on analysis.

EXAMPLE 2

A solution of 675 parts of sulfur monochloride in 1498 parts of chloroform was added dropwise at 20° C. to a stirred solution of 2,6-diethylaniline (1490 parts—as the hydrochloride) in 7490 parts of chloroform. The solution became dark and after 20 minutes precipitated a solid which was filtered and washed with n-hexane. After

standing, the chloroform n-hexane mother liquids deposited 320 parts of a yellow solid. Regeneration of the free base from this material and recrystallization of the residue gave about 100 parts of 4,4'-dithiobis(2,6-diethylaniline).

Further concentration of the chloroform n-hexane mother liquids yielded 1100 parts of an orange solid. Regeneration of this solid gave an oil which was partially insoluble in n-hexane and could not be caused to crystallize.

EXAMPLE 3

Fifty-six parts of 2,6-diethylaniline hydrochloride (prepared in ether) was suspended in 300 parts of chloroform and 18.9 parts of sulfur monochloride in 75 parts of chloroform was added slowly over a period of one hour at 5°. The reaction mixture was warmed to 50° and stirred for 3 days. The solid in the reaction mixture was filtered off and divided into two portions. One portion was suspended in a mixture of ether and saturated aqueous sodium carbonate and stirred until there were two clear layers. The ether layer was dried and stripped to yield 30 parts of crude 4,4'-dithiobis(2,6-diethylaniline). The second portion of solid (24 parts) was regenerated as above and the resulting residue was recrystallized from isooctane-ethanol to give pure 4,4'-dithiobis(2,6-diethylaniline), melting point: 100–102°.

EXAMPLE 4

A solution of 256 parts of N-methyl-2,6-di-tert-butylaniline hydrochloride in 250 parts of nitrobenzene is stirred at 20–25° while a solution of 68 parts of SCl_2 in 50 parts of nitrobenzene is added dropwise over a period of two hours. The reaction is completed by stirring an additional one hour at 25°, then 0.5 hour at 40–45°, after which time hydrogen chloride no longer evolves from the reaction mixture. The nitrobenzene solution is washed with 10 percent sodium carbonate solution to free the amine. The solution is then dried, and nitrobenzene is stripped at reduced pressure. The residue is recrystallized from n-hexane to obtain 4,4'-dithiobis(N-methyl-2,6-di-tert-butylaniline).

EXAMPLE 5

To a refluxing solution of 382 parts of N,N-dimethyl-6-tert-butyl-o-toluidine in 1900 parts of ethylene dichloride is added dropwise a solution of 135 parts of sulfur monochloride in 200 parts ethylene dichloride. The addition requires three hours, after which the mixture is heated at reflux for an additional hour, then cooled to 30° and washed with a solution of 10 percent aqueous Na_2CO_3. The mixture is separated into a water and organic phase. The organic layer is dried, and the ethylene dichloride is stripped to obtain as residue 4,4'-dithiobis(N,N-dimethyl-6-tert-butyl-o-toluidine).

EXAMPLE 6

A suspension of 213.5 parts of 2,6-diisopropylaniline hydrochloride in 1200 parts of dry toluene is stirred vigorously at 20° while a solution of 57 parts of sulfur dichloride in 100 parts of toluene is added portionwise over a period of one hour. Stirring is continued at 20° for four hours after the addition is completed, then at 95° for one hour. The free amine is obtained by treatment of the reaction mixture with a 5 percent solution of sodium hydroxide. The free amine is completely dissolved in the toluene layer, which is stripped of volatiles at reduced pressure leaving as residue 4,4'-dithiobis(2,6-diisopropylaniline).

In the above examples the di-substituted anilines were reacted with a sulfur halide in the absence of a catalyst to prepare dithiobis compounds of this invention. To prepare the monothiobis compounds of this invention the above process may be conducted in the presence of a suitable catalyst such as for example the Friedel Crafts catalyst aluminum chloride. Reaction conditions for this process are generally the same as those employed in preparing the dithiobis compounds as illustrated by the following examples.

EXAMPLE 7

A suspension of 37 parts of 2,6-diethylaniline in hydrochloride and 100 parts of ethylene dichloride is stirred at 0°, and a solution of 2 parts anhydrous aluminum chloride in 10 parts of ethylene dichloride is added. While maintaining a reaction temperature of 0–10° a solution of 13.5 parts of sulfur monochloride in 15 parts of ethylene dichloride is added portionwise over a period of one-half hour. Stirring is continued at 10–20° for two additional hours. Then the reaction mixture is treated successively with 150 parts of ice water and 200 parts of 10 percent sodium carbonate with vigorous stirring. The organic layer is separated, filtered to remove sulfur formed in the reaction, dried, and stripped of solvent to obtain a residue of 4,4'-thiobis(2,6-diethylaniline).

Reaction mixtures containing primarily the monothiobis compounds of this invention are also prepared by reacting sulfur with a suitable 2,6-di-substituted aniline at temperatures ranging from 50 to about 200° in the presence of a suitable catalyst, preferably without a solvent. As catalyst in this process, iodine, sodium, polysulfide, phosphorus pentasulfide, and ammonium polysulfide may be employed. The following examples illustrate this process.

EXAMPLE 8

A mixture of 300 parts of 2,6-diethylaniline, 67 parts of powdered sulfur and 4 parts of phosphorus pentasulfide catalyst are heated with stirring to 155–165°. Hydrogen sulfide is evolved vigorously at first, then more slowly as the reaction nears completion. When the rate of evolution of hydrogen sulfide drops so that it darkens moist lead acetate paper only very slowly, the mixture is cooled and extracted with n-hexane. The extract is filtered to remove unreacted sulfur and other insolubles and the hexane is distilled. The residue consists essentially of 4,4'-thiobis(2,6-diethylaniline). It can be purified by recrystallization from n-hexane.

EXAMPLE 9

A mixture of 30 parts of 2,6-diethylaniline, 14.5 parts of powdered sulfur and 0.07 part of idoine crystals were stirred at 170°–180°. After 7.5 hours evolution of H_2S was at the minimum rate observed for the reaction period, the mixture was cooled and extracted with three portions of 100 parts of chloroform each. The extract was washed with a 5 percent solution of sodium thiosulfate, filtered, dried, and the solvent stripped. This left as residue 34.8 parts of a resinous material consisting of mixed thiobis(2,6-diethylaniline). Extraction of the resinous mixture with n-hexane followed by fractional crystallization gives the 4,4'-thiobis(2,6-diethylaniline).

EXAMPLE 10

A mixture of 60 parts of 6-isopropyl-o-toluidine, 29 parts of sulfur and 5 parts of 40 percent aqueous sodium tetrasulfide is stirred at 110–115° until hydrogen sulfide evolution is no longer detectable. The reaction mixture is cooled and extracted with four portions of 150 parts of hot n-hexane. The hexane solution is filtered and stripped of volatiles to obtain a material which is primarily 4,4'-thiobis(6-isopropyl-o-toluidine).

A somewhat more complex preparation is required for the tri- and tetra-thio compounds of this invention. One method consists of first preparing the dithiobis compound and hydrogenating to split the compound into two molecules of the thiol such as 2,6-diethylaniline-4-thiol. This hydrogenation is conducted under hydrogen pressure in the presence of a suitable hydrogenation catalyst. The hydrogenation may also be carried out by use of zinc and acetic acid, metallic sodium and alcohol or by employing a metal hydride such as lithium aluminum hy-

dride. The thiol thus produced is converted to a metal salt such as the sodium salt by the addition of sodium hydroxide and alcohol. The alcohol is then removed, the system dehydrated and the resulting thiol salt is again reacted with a sulfur halide. When sulfur dichloride is employed the products are primarily the trithiobis compounds of this invention. On the other hand when sulfur monochloride is reacted with the thiol salt the products are predominantly the tetra thiobis compounds of this invention. This process for preparing the tri- and tetrathiobis compounds of this invention and the thiol and thiol salts is illustrated by the following examples.

EXAMPLE 11

A product obtained essentially as described in Example 1 and consisting of relatively pure crystalline 4,4'-dithiobis(2,6-diethylaniline) (360 parts) is dissolved in 1800 parts of toluene and hydrogenated in a stirred autoclave using a molybdenum disulfide catalyst. The hydrogenation is carried out at 150–160° and a hydrogen partial pressure of 800 p.s.i.g. When hydrogen is no longer absorbed, the mixture is cooled, filtered and the toluene distilled at atmospheric pressure. The residue is 2,6-diethylaniline-4-thiol.

Other 2,6-dialkyl aniline-4-thiol compounds which may be prepared by hydrogenation of a 4,4-dithiobis(2,6-dialkyl aniline) of this invention include 2,6-di-sec-butyl aniline-4-thiol, 2-methyl-6-isopropyl aniline-4-thiol, 2,6-diisopropyl aniline-4-thiol, N,N-2,6-tetra-ethyl aniline-4-thiol, N-methyl - N - octyl-2,6-diethyl aniline-4-thiol, and the like.

EXAMPLE 12

The sodium mercaptide of 2,6-diethylaniline-4-thiol is prepared by dissolving 90 parts of the thiol in 250 parts of absolute alcohol and adding portionwise with stirring at 20° a solution of 19 parts of sodium hydroxide in 200 parts of absolute alcohol. The reaction is carried out in an inert atmosphere of nitrogen. The dry solid sodium mercaptide is obtained by stirring volatiles at reduced pressure using a water aspirator and heating on the steam bath. The dry solid sodium mercaptide (45 parts, 10 percent excess) is suspended in 250 parts of dry toluene by stirring vigorously, and a solution of 10 parts of sulfur dichloride in 20 parts of toluene is added slowly while maintaining the temperature at 20–25°. When the addition is complete the mixture is stirred until the reddish color of sulfur dichloride is no longer observed. The reaction mixture is filtered to move the by-product sodium chloride and excess mercaptide, and then toluene is stripped at reduced pressure on the steam bath. The residue is 4,4'-trithiobis (2,6-diethylaniline).

EXAMPLE 13

A solution of 181 parts of 2,6-diethylaniline-4-thiol in 1000 parts of dry benzene is treated with dry hydrogen chloride gas until no further precipitation of 2,6-diethylaniline-4-thiol hydrochloride occurs. This requires between about 36 and 40 parts of hydrogen chloride, which allows for an excess of hydrogen chloride to insure completion of the reaction. The resulting mixture of the aniline hydrochloride in benzene is stirred vigorously and a solution of 68 parts of sulfur monochloride in 100 parts of benzene is added dropwise over a period of one hour while maintaining a temperature of 25–30°. When the addition is completed the mixture is heated slowly to reflux to drive off hydrogen chloride formed by the reaction. The mixture is then cooled to about 30° and stirred with about 600 parts of 10 percent sodium carbonate solution to free the amine, which dissolves in the benzene layer. This layer is separated and all volatiles distilled at water aspirator pressure and steam temperature. The residue is 4,4'-tetrathiobis(2,6-diethylaniline).

EXAMPLE 14

To illustrate the outstanding benefits obtained by the practice of this invention, a standard oil oxidation test is used. The equipment and test procedure described by Kroger et al., Erdöl and Kohle, 2, page 398 (1949), served as a basis for the tests. The equipment and procedures are slightly modified in order to make the oxidizing conditions more strenuous. In this manner, the test lubricants are subjected to severe oxidizing conditions in order to conclusively establish the effectiveness of additives under very adverse conditions. Furthermore, the modifications are found to provide results which correlated extremely well with test results of other standard procedures, including actual engine tests.

The equipment consists of a reaction cell connected with an open end manometer whereby the total uptake of oxygen by the oil is determined by noting the drop in height of the mercury in the manometer. The test oil sample is placed in the reaction cell which is then flushed with oxygen and the temperature is then raised and held at that selected for the test (300° F.) until the substrate oil undergoes catastrophic oxidation which is shown by a rapid oxygen uptake. In all cases, the test oil is deliberately contaminated with iron hexoate as an oxidation promoter. In tests of this nature, the oxidation stability of a test lubricant is ordinarily determined by measuring its induction period, that is, the time required for catastrophic deterioration under the above outlined conditions. The longer the induction period, the more stable the lubricant. In tests of this nature employing a highly refined additive-free mineral oil having a viscosity index of 106.5 and a density of 0.85, the preferred compound of the invention, 4,4' - dithiobis(2,6 - diethylaniline) was shown to be an unexpectedly outstanding antioxidant. The oil with no added antioxidant had an induction time of only three minutes. However, when 1.0×10^{-2} moles of 4,4' - dithiobis(2,6 - diethylaniline) (0.424 weight percent) was added to the oil, the induction period was 2145 minutes. This shows the compound to be an outstanding antioxidant.

As noted above the compounds of this invention are excellent antioxidants. Thus, an embodiment of this invention is an organic material normally susceptible to deterioration in the presence of air, oxygen or ozone protected against such deterioration by the inclusion therein of a small antioxidant quantity, up to about 5 percent, of a compound of this invention.

Depending upon the material to be protected and the severity of oxidation to be encountered, various concentrations of the compound of this invention may be employed as antioxidants. Generally, from about 0.001 percent by weight of the compound to about 5 percent is employed. However, in many instances, concentrations of antioxidant well below the latter figure give adequate protection. Thus, lubricating oil concentrations of from 0.01 to 2 percent by weight of the compound are usually adequate. Generally speaking, it is preferred to use from 0.05 to about 3 percent by weight of the additive compound since it is found that concentrations within this range provide adequate antioxidant protection.

The compounds of this invention find important utility as antioxidants in a wide variety of oxygen sensitive materials; thus, liquid and solid products derived from petroleum crude are found to possess greatly increased storage stability by the use of an antioxidant of this invention. For example, gasoline jet fuel, kerosene, fuel oil, turbine oils, insulating oils, motor oils and various waxes have increased oxidative stability when they contain an antioxidant of this invention. Likewise, liquid hydrocarbon fuels which contain organometallic additives such as tetraethyllead and other organometallic compositions which are used as fuel additives attain appreciably increased oxidative stability by the practice of this invention. Furthermore, such fuels which contain halogen and phosphorus-containing scavengers for these organometallic compounds are benefited by the practice of this invention. In addition to increased storage stability,

lubricating oils and functional fluids, such as automatic transmission and hydraulic fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, achieve a high degree of resistance to oxidation during use at elevated temperatures by the practice of this invention. It has been found that lubricating oils may be employed at extremely high temperatures without undergoing oxidative degradation when protected by an antioxidant of this invention. The addition of small quantities of the compounds of this invention to such materials as hydraulic, transformer and other highly refined industrial oils as well as crankcase lubricating oils and lubricating greases prepared from these oils by the addition of metallic soaps, greatly increase their resistance to deterioration in the presence of air, oxygen or ozone. Furthermore, the organic soaps used in the preparation of lubricating greases are themselves stabilized by the practice of this invention.

Organometallic compositions such as tetraethyllead and tetraethyllead antiknock fluids containing halohydrocarbon scavengers, dyes and which may contain various phosphorus compounds and other organometallic additives are stabilized against deterioration during storage by the addition thereto of an antioxidant quantity of the compounds of this invention.

The compounds of this invention are also extremely effective antioxidants for elastomers including high molecular weight unsaturated hydrocarbon polymers both derived from naturally occurring sources and those synthetically prepared. Thus, natural rubbers and synthetic rubbers, including oil extended rubbers and sulfur vulcanized rubbers are greatly benefited by the practice of this invention. Examples of the synthetic rubbers protected by the practice of this invention include such synthetics as polybutadiene, methyl rubber, polybutadiene rubber, butyl rubber, GR–S rubber, GR–N rubber, piperylene rubber and dimethylbutadiene rubber.

The practice of this invention is also useful in protecting paraffin and micro-crystalline petroleum waxes against the oxidative deterioration which leads to rancidity. Furthermore, the compounds of this invention are extremely useful in the stabilization of fats and oils of animal or vegetable origin which become rancid during periods of storage due to oxidative deterioration. Typical animal fats benefited by the practice of this invention include butter fat, lard, beef tallow, fish oils—such as cod liver oil—as well as various foods containing or prepared in animal fats which tend to deteriorate. These include, for example, potato chips, fried fish, donuts, crackers, and various types of pastry such as cakes and cookies. Furthermore, fat fortified animal feeds and fish meals used as animal feeds are greatly benefited by the practice of this invention. Not only are these compositions protected against oxidative deterioration but the inclusion of a compound of this invention in such materials inhibits the degradation of vitamins A, D and E and certain of the B complex vitamins. Examples of compositions containing oils derived from vegetable sources which are benefited by the practice of this invention include castor oil, soy bean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, citrus oils, cotton seed oil and various compositions containing these including peanut butter, peanuts and other whole nuts, salad dressings, margarine and other vegetable shortenings.

The compounds of this invention are also outstanding antioxidants for various organic compounds and polymeric materials including polystyrene, polyvinylchloride, polyvinyl acetate, various epoxide resins and polyester resins and polymers including the alkyds. However, in particular the compounds of this invention are outstanding antioxidants for saturated hydrocarbon synthetic polymers derived from polymerization of an aliphatic monoolefin hydrocarbon compound having preferably up to 5 carbon atoms and only a single unit of unsaturation per monomeric molecule. Examples of such monomers include ethylene, propylene, butylene, isobutylene, 2-methyl-4-butene, 2-methyl-3-butene and the like. Thus the polymers are homopolymers and copolymers of ethylene, propylene, butylene, isobutylene and the pentenes and are usually solid. Polyethylene and polypropylene are preferred polymers in the practice of this invention and they are derived from the polymerization of ethylene and propylene respectively.

A preferred embodiment of this invention involves providing a lubricating oil normally susceptible to oxidative deterioration containing, in amount sufficient to inhibit such deterioration, a small quantity of a novel compound of this invention. It has been found in actual practice that small amounts of these compounds very effectively stabilize lubricant compositions—e.g., petroleum hydrocarbon oils and synthetic oils—against oxidative deterioration.

To prepare the preferred lubricants of this invention, appropriate quantities of the compound are blended with the base oil to be protected. Suitable base oils include minerals oils and also synthetic oils, such as the diester sebacates, adipates, etc., which find particular use as aircraft instrument oils, hydraulic and damping fluids, and precision bearing lubricants. All of these base oils are normally susceptible to oxidative deterioration, especially at elevated temperatures.

The finished lubricants of this invention have much greater oxidation stability and many other improved performance characteristics as compared with the corresponding base oils. In the case of lubricating oils of this invention, spectacular improvements are afforded, including markedly reduced engine wear characteristics, greatly improved oxidation stability and greatly reduced bearing corrosion properties.

The following examples illustrate various specific embodiments of this invention. The physical characteristics of the illustrative oils used in Examples 15–20 are as shown in Table I.

Table I

PROPERTIES OF REPRESENTATIVE PETROLEUM HYDROCARBON OILS

Oil	A	B	C	D	E	F
Gravity at 60° API	30.3	30.5	28.8	31.1	20.5	31.0
Viscosity, Saybolt:						
Seconds at 100° F	178.8	373.8	309.8	169.0	249.4	335.4
Seconds at 210° F	52.0	58.4	63.8	51.5	45.7	68.4
Viscosity Index	154.2	107.4	141.9	157.8	35.8	144.4
Pour Point	−30	+10	−20	−15	-------	0
Flash Point	410	465	-------	-------	365	385
Sulfur, Percent	0.2	0.3	0.3	0.3	0.3	0.1

EXAMPLE 15

To 100,000 parts of Oil A is added with stirring 120 parts (0.12 percent) of 4,4′-dithiobis(2,6-diethylaniline). The resulting oil is found to possess greatly improved resistance to oxidative deterioration.

EXAMPLE 16

To 100,000 parts of Oil B is added 1000 parts (1 percent) of 4,4′-thiobis(2-methyl-6-tert-butylaniline). On agitating this mixture, a homogeneous solution results and the resulting oil composition possesses enhanced oxidation resistance.

EXAMPLE 17

With 100,000 parts of Oil C is blended 500 parts (0.5 percent) of 4,4′-trithiobis(2-ethyl - 6 - isopropylaniline). The resulting oil possesses enhanced resistance against oxidative deterioration.

EXAMPLE 18

To 100,000 parts of Oil D is added 1000 parts (1.0 percent) of 4,4′-dithiobis(2-methyl-6-ethylaniline). The resulting oil is found to possess enhanced resistance against oxidative deterioration.

EXAMPLE 19

With 100,000 parts of Oil E is blended 5000 parts (5 percent) of 4,4'-dithiobis(2,6-diethylaniline). After mixing the resulting oil possesses enhanced resistance to oxidation.

EXAMPLE 20

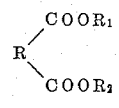
To 100,000 parts of Oil F is added 250 parts (0.25 percent) of 4,4'-tetrathiobis(2-ethyl-6-sec-butylaniline). The resulting oil possesses greatly enhanced resistance against oxidative deterioration.

The additives of this invention effectively stabilize such lubricating and industrial oils as crankcase lubricating oils, transformer oils, turbine oils, transmission fluids, cutting oils, gear oils, industrial oils, mineral white oils, glass annealing oils, and, in general, engine and industrial oils which are derived from crude petroleum and are normally susceptible to deterioration in the presence of air, particularly at elevated temperatures and most particularly in the presence of iron oxide.

In the lubricating oil compositions of this invention effective use can be made of other additives which are known to the art, such as detergent-dispersants, pour point depressants, viscosity index improvers, anti-foam agents, rust inhibitors, oiliness or film strength agents, dyes, and the like. Typical of the detergent additives that can be used in the compositions of this invention are metallic soaps of high molecular weight acids, such as aluminum naphthenates, calcium phenyl stearates, calcium alkyl salicylates, alkaline earth metal petroleum sulfonates, alkaline earth metal alkyl phenol sulfides (barium amyl phenol sulfide, calcium octyl phenol disulfide, etc.), metal salts of wax-substituted phenol derivatives, and the like. Of the viscosity index improvers and pour point depressants, effective use can be made of polymers of the esters of methacrylic acids and higher fatty alcohols and the corresponding polymers of esters of acrylic acid and higher fatty alcohols. These and other additives which can be employed in the compositions of this invention will now be well known to those skilled in the art.

The synthetic lubricants which are enhanced by the practice of this invention are, in general, non-hydrocarbon organic compositions which contain elements other than carbon and hydrogen. Examples of general classes of material which are protected against oxidative deterioration by the practice of this invention include diester lubricants, silicones, halogen containing organic compounds including the fluorocarbons; polyalkylene glycol lubricants, and organic phosphates which are suitable as hydraulic fluids and lubricants. The synthetic diester oils stabilized by the practice of this invention include sebacates, adipates, etc., which find particular use as aircraft instrument oils, hydraulic and damping fluids, and precision bearing lubricants. These diester oils are exceedingly difficult to stabilize under high temperature conditions. In this invention, use can be made of a wide variety of diester oils of the type described in Industrial and Engineering Chemistry, 39, 484–91 (1947). Thus, use can be made of the diesters formed by the esterification of straight chain dibasic acids containing from 4 to about 16 carbon atoms with saturated aliphatic monohydric alcohols containing from 1 to about 10 carbon atoms. Of these diester oils, it is preferable that the alcohol used in their preparation be a branched chain alcohol because the resultant diesters have very valuable lubricating properties and the inhibitor of this invention very effectively stabilizes these materials against oxidative deterioration. Thus, use can be made of oxalates, malonates, succinates, glutarates, adipates, pimelates, suberates, azelates, sebacates, etc.

The diester lubricants used in the lubricant compositions of this invention have the formula:



where R is an aliphatic hydrocarbon radical which may be saturated or unsaturated and has from 2 to 14 carbon atoms and R_1 and R_2 are straight or branched chain alkyl groups. The diesters utilized in the preferred lubricant compositions, include esters of succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid. Typical examples of such esters are diisooctyl azelate, di(2-ethylhexyl) sebacate, di-sec-amyl sebacate, diisooctyl adipate, di(2-ethylhexyl)adipate, di(2-ethylhexyl)azelate, di(1-methyl-4-ethyloctyl)glutarate, diisoamyl adipate, di(2-ethylhexyl) glutarate, di(2-ethylbutyl)adipate, ditetradecyl sebacate and di(2-ethylhexyl)pinate.

The preferred diesters are generally prepared by esterifying one mole of a dicarboxylic acid having the general formula:

$$HOOC(CH_2)_xCOOH$$

where x is an integer of from 2 to 8, with 2 moles of a branched chain alcohol containing at least 4 carbon atoms. Typical are the reactions of succinic, glutaric, adipic, pimelic, suberic or azelaic acid with sec-amyl alcohol, 3-ethyl butanol, 2-ethyl hexanol or the branched chain secondary alcohols undecanol or tetradecanol.

The preferred diester lubricant fluids have molecular weights ranging from about 300 to about 600 and freezing and pouring points from about −40° to less than about −100° F. Their flash and fire points range from about 300° F. to about 500° F. and their spontaneous ignition temperatures range from about 100° to about 800° F. The diesters made by reacting a dicarboxylic acid with a branched chain alcohol have been found to have superior viscometric properties as compared with diesters made by reacting dihydric alcohols with mono-carboxylic acids and thus, diesters prepared by the former method are preferred in formulating the lubricant compositions of this invention.

Another class of synthetic lubricants which achieve enhanced oxidative stability by the practice of this invention includes the "silicone" lubricants. The term "silicone" as used in the specification and claims of this application is defined as a synthetic compound containing silicon and organic groups. In naming specific compounds, the nomenclature system recommended by the American Chemical Society Committee on Nomenclature, Spelling, and Pronunciation (Chem. Eng. News, 24, 1233 (1946)) will be used. Thus, the compounds which have the —Si—O—Si— linkages are the siloxanes. Derivatives of silane, SiH_4, in which one or more of the hydrogens in silane are replaced with organic groups are termed the silanes, silicates and silicate ester compounds are named as oxy derivatives of silane and are called alkoxy or aryloxy silanes.

The silicone oils and greases serving as the base medium for the lubricant compositions of the invention include the polysiloxane oils and greases of the type, polyalkyl-, polyaryl-, polyalkoxy-, and polyaryloxy-, such as polydimethyl siloxane, polymethylphenyl siloxane, and polymethoxyphenoxy siloxane. Further included are silicate ester oils, such as tetraalkyloxy and tetraaryloxy silanes of the tetra-2-ethylhexyl and tetra-p-tert-butylphenyl types, and the silanes. Also included are the halogen substituted siloxanes, such as the chlorophenyl polysiloxanes.

The polyalkyl, polyaryl, and polyalkyl polyaryl siloxanes are the preferred types of base medium for the silicon-containing lubricant compositions of the invention because of their high oxidative stability over a wide temperature range. The polyalkyl siloxanes, such as the dimethyl polysiloxane, are slightly preferred over the polyaryl, and polyalkyl polyaryl siloxanes because they show the least change in viscosity over a wide temperature range.

Certain halogen containing organic compounds have physical properties which render them particularly well suited as lubricants. Ordinarily, the halogen is either chlorine or fluorine. Typical of the chlorinated organic compounds suitable as lubricants are the chlorodiphenyls,

chloronaphthalenes, chlorodiphenyl oxides and chlorinated paraffin waxes.

The fluorocarbon lubricants which are enhanced by this invention are linear polymers built up of a recurring unit which is



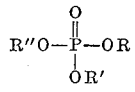
The fluorocarbon oils and greases are very stable chemically and have high thermal stability. These desirable physical properties appear to be closely related to the bond distances occurring in the fluorocarbon polymeric molecule, which may also contain chlorine bonded to carbon.

Polyalkylene glycol lubricants which are benefited by the practice of this invention are ordinarily the reaction product of an aliphatic alcohol with an alklene oxide. The preferred alkylene oxides are ethylene oxide and propylene oxide. Depending upon the alcohol employed and the molecular weight of the compound, the polyalkylene glycol lubricants may be either water insoluble or water soluble. The molecular weights of these polymers may vary from about 400 to over 3,000. In general, the polyalkylene glycol lubricants are characterized by high viscosity indices, low API gravities, low pour points and they have the general formula:

$$R—(—O—C_nH_{2n})_xOH$$

where n is a small integer and depends upon the alkylene oxide employed and x is a large integer from about 10 to about 100 depending upon the molecular weight of the finished lubricant and R represents the hydrocarbon group derived from the particular aliphatic alcohol employed.

Another important class of synthetic materials which are enhanced by the practice of this invention are phosphate esters which are, in general, prepared by the reaction of an organic alcohol with phosphoric acid and have the general formula:



where R, R′ and R″ represent either hydrogen or an organic radical and where at least one of the groups represented by R, R′ and R″ is an organic radical. Typical of these materials is tricresylphosphate. The phosphate esters are in general characterized by excellent fire resistant properties and high lubricity. However, their thermal stability is such that they are ordinarily unsuited for high temperature applications above about 300° F. Other examples of phosphate esters include: tris(2-chloro-1-methylethyl)phosphate; tri-n-butyl-phosphate; tris(2-ethylhexyl)phosphate; triphenyl phosphate; tris(p-chlorophenyl)phosphate; diethyl-m-tolyl phospate; p-chlorophenyl dimethyl phosphate; tris(2-n-butoxyethyl)phosphate; dimethyl-m-tolyl phosphate; di-n-propyl-m-tolyl phosphate; di-n-butyl phenyl phosphate; 1,3-butylene β-chloroisopropyl phosphate; methyl-di-m-tolyl phosphate; bis(2-chloro-1-methylethyl)-m-tolyl phosphate; dimethyl 3,5-xylyl phosphate; 4-chloro-m-tolyl dimethyl phosphate; 2-ethyl-1-n-propyltrimethylene methyl phosphate; 4-chloro-m-tolyl 1-methyltrimethylene phosphate; dimethyl-n-octyl phosphate, and the like.

The synthetic base greases used in formulating lubricant compositions of the invention are formed by admixing a soap with an oil of any of the types described above. Such soaps are derived from animal or vegetable fats or fatty acids, wool grease; rosin, or petroleum acids. Typical examples are lead oleate, lithium stearate, aluminum tristearate, calcium glycerides, sodium oleate and the like. In addition, the polyester greases may contain unreacted fat, fatty acids, and alkali; unsaponifiable matter including glycerol and fatty alcohols; rosin or wool grease; water; and certain additives which may function as modifiers or peptizers.

In formulating the grease compositions of this invention, greases prepared by admixing a lithium soap with the polyester oils are preferred as they have superior oxidative stability as compared with greases formulated with other soaps, such as the sodium calcium or lead soaps.

In preparing the improved lubricant compositions of this invention, an appropriate quantity of compound is blended with the oil to be stabilized. If desired, preformed concentrated solutions of the stabilizer in the base lubricant can be prepared and then subsequently diluted with additional lubricant to the desired concentration. An advantage of this invention is the fact that the additives are easily and rapidly blended with the base oil. An additional advantage of this invention is that the additives are compatible with the usual additives that are frequently used to fortify lubricant compositions, such as detergent-dispersants, viscosity index improvers, dyes, anti-rush additives, anti-foaming agents and the like.

The following examples further illustrate various specific embodiments of this invention.

EXAMPLE 21

With 100,000 parts of di-(sec-amyl) sebacate having a viscosity of 210° F. of 33.8 Saybolt Universal seconds (SUS), a viscosity index of 133 and a molecular weight of 342.5 is blended 100 parts (0.1 percent) of 4,4′-thiobis(N,N,2-trimethyl-6-ethyl-aniline). The resulting diester lubricant possesses greatly enhanced resistance against oxidative deterioration.

EXAMPLE 22

To 100,000 parts of di-(2-ethylhexyl) sebacate having a viscosity at 210° F. of 37.3 SUS, a viscosity index of 152 and a molecular weight of 426.7 is added 1000 parts (1 percent) of 4,4′-dithiobis(N,N,2-trimethyl-6-ethylaniline). After mixing, the resultant diester lubricant possesses greatly enhanced oxidation resistance.

EXAMPLE 23

To 100,000 parts of di-(2-ethylhexyl) adipate having a viscosity at 210° F. of 34.2 SUS, a viscosity index of 121 and a molecular weight of 370.6 is added 2000 parts (2 percent) of 4,4′-tetrathiobis(N-octyl-2,6-diethylaniline). After mixing, the resultant diester lubricant possesses outstanding resistance against oxidative deterioration.

EXAMPLE 24

Three parts of 4,4′-trithiobis(N-amyl-2-methyl-6-isopropylaniline) is blended and mixed with 197 parts of a grease comprising 12.5 percent of lithium stearate, 1 part of polybutene (12,000 molecular weight), 2 percent of calcium xylyl stearate and 84.5 percent of di(2-ethylhexyl) sebacate, to prepare an improved grease of this invention.

EXAMPLE 25

Blended with 750 parts of diisooctyl adipate having a viscosity of 35.4 SUS at 210° F., a viscosity of 57.3 SUS at 100° F., a viscosity of 3,980 SUS at −40° F., a viscosity of 22,500 at −65° F.; its viscosity index is 143, its ASTM pour point is below −80° F. and its specific gravity (60° F./60° F.) is 0.926, is one part of 4,4′-dithiobis(2-methyl-6-ethylaniline).

EXAMPLE 26

One part of 4,4′-dithiobis(N,N-dimethyl-2,6-diethylaniline) is blended with 100 parts of a polymethylpolyphenyl siloxane grease of medium weight consistency having a penetration of 240–280 (ASTM-217–48), a minimum melting point of 400° F. and a serviceable temperature range of from −30 to 400° F. (This siloxane grease is sold under the trade name "Dow-Corning 44."

EXAMPLE 27

To a poly(trifluorochloroethylene) having the formula $(CF_2CHCl)_x$ and an average molecular weight of 880, pour point of 5° C. and a viscosity of 45 centistokes at 160° F. is added 1.25 percent of 4,4'-thiobis(N-butyl-2,6-diethylaniline) to prepare an improved lubricant of this invention.

EXAMPLE 28

To a polyalkylene glycol oil lubricant having a viscosity index of 148, ASTM pour point of −55° F., a flash point of 300° F., a specific gravity of 0.979 and a Saybolt viscosity of 135 at 100° F. is added one percent of 4,4'-dithiobis(N-methyl-2,6-diethylaniline) to prepare an extremely oxidation resistant polyalkylene glycol lubricant.

EXAMPLE 29

An improved lubricant of this invention comprising a chlorinated organic compound is prepared by admixing 0.5 percent of 4,4'-dithiobis(2-methyl-6-ethylaniline) with a chlorodiphenyl oil having a distillation range of from 554 to 617° F., a Saybolt viscosity at 100° F. of about 49, a pour point of −30° F. and a specific gravity of about 1.267.

EXAMPLE 30

An improved hydraulic fluid and lubricant according to this invention is prepared by adding 5 percent of 4,4'-trithiobis(2,6-di-sec-butylaniline) to tricresylphosphate.

The compounds of this invention very effectively enhance the oxidation resistance of such diester oils as diethyl oxalate, di-sec-butyl malonate; di-(2-hexyl) succinate; di-(isoheptyl)pimelate; di-(3-decyl)seberate; di-sec-amyl gluterate; di-(isobutyl)glutarate; di-(2-ethylbutyl) glutarate; di-(2-ethylhexyl)glutarate; di-sec-amyladipate; di-methyl-butyl)adipate; diethyl adipate, di-2-ethylhexyl adipate; di-sec-amyl azelate, di-(isobutyl)azelate; di-(2-ethylbutyl)azelate; di-(2-ethylhexyl)azelate; di-sec-amyl sebacate; di-sec-dutyl sebacate; di-(2-ethylexyl)sebacate; the glutarates; adipates, acelates and sebacates of branched chain secondary alcohols, such as undecanol, tetradecanol; etc., and, in general, diesters of the type described above and in the literature as useful for synthetic lubricant purposes.

In the lubricant compositions of this invention effective use can be made of other additives which are known to the art, such as other inhibitors, detergent-dispersants, pour point depressants, viscosity index improvers, antifoam agents, rust inhibitors, oiliness of film strength agents, dyes, and the like. Of the inhibitors which can be effectively used with synthetic lubricants in combination with the additives of this invention are sulfurized sperm oil, sulfurized terpenses, sulfurized paraffin wax olefins, alkyl phenols, lecithin, neutralized dithiophosphates, phosphorus pentasulfideterpene reaction products, diphenylamine, phenylnaphthyl amine, β-naphthol, pyrogallol, and the like. Typical of the detergent additives that can be used in the compositions of this invention are metallic soaps of high molecular weight acids, such as aluminum naphthenates, calcium phenyl stearates, calcium alkyl salicylate, alkaline earth metal petroleum sulfonates, metal salts of wax-substituted phenol derivatives and the like. Of the viscosity index improvers and pour point depressants, effective use can be made of polymers of the esters of methacrylic acids and higher fattly alcohols and the corresponding polymers of esters of acrylic acid and higher fatty alcohols. These and other additives which can be employed in the compositions of this invention will now be well known to those skilled in the art.

The antioxidant mixtures 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 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 of 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 salts of aluminium 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 phenol sulfide and an alkaline-earth metal oxide or hydroxide at an elevated temperature. The overbased phenate formed from the reaction contains up to two or three times as much metal as the normal phenate.

In addition, functional fluids may contain additional components which improve the properties of the fluid including anti-squawk additives such as sulfurized oil; a pour point depressent such as a wax-substituted naphthalene, an ester of a wax-substituted phenol, a polymerized unsaturated ester or an acrylic polymer; a foam inhibitor such as a fatty acid or fatty acid ester, pine oil, an alkyl lactate or a higher ether [such as 2-(di-tert-amyl phenoxy) ethanol]; a rust preventive such as carboxylic acid derivative, an amine derivative, a long chain alkyl ketone, an organic phosphate or phosphite, a morpholine derivative or a phosphatide; an extreme pressure agent such as a chlorinated wax, a P_2S_5-terpene reaction product, or an organic phosphate or phosphite; a metal deactivator which may be a complex organic nitrogen and sulfur-containing compound, an organic dihydroxyphosphine, a trialkyl or triaryl phosphite, a diamine or a soap containing a metal; and a viscosity index improver such as a polymerized olefin or isoolefin, a butylene polymer or an alkylated styrene polymer.

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 31

An automatic transmission fluid is made by mixing 97 percent of an oil blend comprising 59.0 parts of a solvent-extracted, Coastal oil, 40 SUS at 210° F.; 2.0 parts of 4,4'-dithiobis(2,6-diethylaniline), 1.0 part of a barium phenol sulfide containing 2.4 percent barium, 2 percent calcium and 3.5 percent sulfur, having a viscosity of 126 SUS at 210° F., a flash point of 430° F., a pour point of 10° F. and a specific gravity 60/60° F. of 0.97; 1.0 part of sulfurized sperm oil.

EXAMPLE 32

96 parts of a conventionally-refined Pennsylvania mineral oil (99 SUS at 100° F.); 1.5 parts of 4,4'-dithiobis(2-methyl-6-ethylaniline); 2 parts of a mixed barium phenol sulfide-calcium sulfonate containing 5.7 percent barium, 0.68 percent calcium and 2.9 percent sulfur, having a vis-

cosity of 92 SUS at 210° F., a flash point of 410° F., a pour point of 10° F. and a specific gravity 60/60° F. of 0.988 are blended into an effective fluid of this invention.

As noted above, the compounds of this invention are also excellent antioxidants for saturated hydrocarbon polymers.

Polyethylene and polypropylene are, for example, hydrocarbon polymers derived from the polymerization of ethylene and propylene. This polymerization can be accomplished by a great variety of methods which lead to products of diverse properties. Polymers of any nature may advantageously be utilized for prepared compositions according to the present invention. The polymers which are employed may, for example, be similar to those which may be obtained by polymerizing ethylene in a basic aqueous medium and in the presence of polymerization favoring quantities of oxygen under relatively high pressures in excess of 500 or 1,000 atmospheres at temperatures between 150 and 275° C. Or, if desired, they may be similar to the essentially linear and unbranched polymers ordinarily having greater molecular weights which may be obtained under relatively low pressures of 1 to 100 atmospheres using such catalysts to polymerize the ethylene as mixtures of strong reducing agents and compounds of Groups IVB, VB and VIB metals of the Periodic System; chromium oxide on silicated alumina; hexavalent molybdenum compounds; charcoal supported nickel-cobalt. The polymer which results from these various polymerization processes may have a molecular weight in the range from 1300 to over 1,000,000 depending on the particular conditions of polymerization employed.

There are several methods available for preparing the inhibited hydrocarbon polymer compositions of this invention. Thus the blending of the additives of this invention, with a polymer such as, for example, polyethylene, may be carried out on open rolls, on internal mixers or may be accomplished by mixing with extrusion. It is also possible to prepare concentrated batches of the polymer containing excessive amounts of the additive and then mix the concentrate with additional polymer to prepare a composition of this invention. The preferred method of compounding the polymers is by milling on heated open rolls at slightly elevated temperatures by methods well-known to the art. The temperature range employed is sometimes critical as certain polyethylenes will not melt at low temperatures and tend to stick to the rolls at high temperatures. The additive may be initially mixed with the polymer in the dried state or may be first dissolved in a suitable solvent, then sprayed on the polymer and milled in.

Examples of the hydrocarbon polymer compositions of this invention prepared as described above follow. All parts and percentages are by weight in these examples.

EXAMPLE 33

To 1,000 parts of polyethylene produced by oxygen catalyzed reaction under a pressure of 20,000 atmospheres and having an average molecular weight of 40,000 is added and mixed 2 parts of 4,4′-trithiobis(N-hexyl-2-methyl-6-isopropylaniline). The resulting composition has a greatly increased oxidative stability.

EXAMPLE 34

To 100 parts of polyisobutylene having an average molecular weight of 100,000 is added 0.5 part of 4,4′-dithiobis(2,6-diethylaniline). The oxidative stability of the polymer is greatly increased by the addition of this compound.

EXAMPLE 35

A linear polyethylene having a high degree of crystallinity (up to 93 percent) and below one ethyl branched chain per 100 carbon atoms, a density of about 0.96 gram per milliliter and which has about 1.5 double bonds per 100 carbon atoms is treated with 50×10^{-6} roentgens of β-radiation. To the thus irradiated polymer is added 0.3 percent of 4,4′-dithiobis(2,6-diethylaniline). The resulting product has improved stability characteristics.

EXAMPLE 36

To 1,000 parts of a solid polypropylene polymer having a density of 0.905 and a Rockwell hardness greater than 85, in which isotactic is added and blended to 5 parts of 4,4′-thiobis(N,N-dioctyl-2,6-diisopropylaniline).

EXAMPLE 37

To an isotactic polypropylene having a tensile strength greater than 4300 p.s.i. and a compressive strength of about 9,000 p.s.i. is added sufficient 4,4′-tetrathiobis(2-methyl-6-sec-butylaniline) to give a composition containing 1.5 percent of the compound.

EXAMPLE 38

To a wax-like polypropylene having a melting point above 130° C. and a molecular weight of about 4,000, a density of 0.913 is added 0.2 percent of 4,4′-dithiobis(2-methyl-6-ethylaniline). The antioxidant is added to the polypropylene in the molten state and the mixture is allowed to solidify into the desired shape. A polypropylene product of outstanding oxidative stability results.

In addition to the additives of this invention saturated hydrocarbon polymers may contain other compounding and coloring additives including minor proportions of carbon black, elastomers, polyvinyl compounds, carboxylic acid esters, urea-aldehyde condensation products, flame retarding agents such as antimony trioxide and chlorinated hydrocarbons and various pigment compositions designed to impart color to the finished product.

Other hydrocarbon polymers which are stabilized against oxidative deterioration according to this invention include natural rubber, GR–S and GR–N rubbers, butyl rubber, methyl rubber, polybutene rubber, butadiene rubbers, piperylene rubbers, dimethylbutadiene rubbers, polystyrene, polybutadiene, polyisobutylene, polyethylene, isobutylene-styrene copolymer and, in general, elastomeric hydrocarbon polymers which are normally susceptible to oxidative deterioration. Such polymers are well-known in the art and besides being susceptible of oxidative deterioration are characterized by having molecular weights above 10,000. The problem resulting from heat, light and catalyst promoted oxidative deterioration in such hydrocarbon polymers is intensified because of free radical formation within the polymers. This leads to various forms of physical and chemical degradation such as chain scission, autocatalytic oxidation, reduction in molecular weight and loss of original physical properties. The net result is that the desirable useful and necessary properties of the polymers which are associated with their original chemical structure and molecular weights are lost to a greater or lesser extent unless the polymers are stabilized against such deterioration.

Typical stabilized hydrocarbon polymers of this invention are illustrated by the following specific examples wherein all parts and percentages are by weight.

EXAMPLE 39

To a synthetic rubber master batch comprising 100 parts of GR–S rubber having an average molecular weight of 60,000, 5 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 4,4′-thiobis(2-ethyl-6-isopropylaniline). This batch is then cured for 60 minutes at 45 pounds per square inch of steam pressure.

EXAMPLE 40

Two parts of 4,4′-dithiobis(2-methyl-6-ethylaniline) is incorporated in 100 parts of raw butyl rubber prepared by the copolymerization of 90 percent of isobutylene and 10 percent of isoprene and having an average molecular weight of 100,000.

EXAMPLE 41

To a master batch of GR–N synthetic rubber comprising 100 parts of GR–N rubber having an average molecular weight of 75,000, 5 parts of zinc stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 2 parts of mercaptobenzothiazole is added 2 percent based on the weight of the batch of 4,4'-dithiobis(N,N,2,6-tetraethylaniline).

EXAMPLE 42

0.25 percent by weight of 4,4'-trithiobis(N,2-dimethyl-6-ethylaniline) is incorporated in polybutadiene having an average molecular weight of 50,000.

EXAMPLE 43

To natural rubber (Hevea) is added 0.1 percent of 4,4'-dithiobis(2,6-diethylaniline).

The above examples illustrate the improved compositions of this invention. Other such compositions and the methods of preparing the same will now be apparent to one skilled in the art.

The stabilizers of this invention are also excellent additives to tetraalkyllead antiknock compositions. The tetraalkyllead antiknock agents which are stabilized according to this invention are represented by such compounds as tetramethyllead, tetraethyllead, tetrapropyllead, dimethyldiethyllead, trimethylethyllead, and the like, or mixtures thereof. Such compounds containing from 4 to about 12 carbon atoms, one atom of lead and a plurality of lead-to-carbon bonds, are capable of increasing the octane quality of gasoline when employed therein in antiknock quantities—0.5 to 6.5 grams of lead per gallon. Halogen-containing compounds such as triethyllead bromide may also be stabilized according to this invention.

The scavengers which are preferably, but not necessarily, present in the antiknock compositions of this invention are organic halide compounds which react with the lead during combustion in the engine to form volatile lead halide. The halogen of these scavengers has an atomic weight between 35 and 80; that is, the active scavenging ingredient is chlorine and/or bromine. Such scavengers include carbon tetrachloride, propylene dibromide, 2-chloro-2,3-dibromobutane, 1,2,3-tribromopropane, hexachloropropylene, mixed bromoxylenes, 1,4-dibromobutane, 1,4 - dichloropentane, β,β' - dibromodiisopropyl ether, β,β'-dichlorodiethyl ether, trichlorobenzene, dibromotoluenes, and in general those disclosed in U.S. Patents 1,592,954; 1,668,022; 2,364,921; 2,479,900; 2,479,-901; 2,479,902; 2,479,903; and 2,496,983. In short, the preferred scavengers contain only elements selected from the group consisting of carbon, hydrogen, bromine, chlorine and oxygen. The amount of scavengers used is from about 0.5 to about 2.0 theories, a theory being defined as the quantity required to react with the lead to form lead halide—i.e., 2 atoms of halogen per atom of lead. When we use mixtures of bromine-containing and chlorine-containing scavengers, particularly bromo and chlorohydrocarbons, we can employ concentrations and proportions as described in U.S. Patent 2,398,281. Such concentrations are sufficient to control the amount of deposits formed in the engine.

The tetraalkyllead antiknock compositions of this invention may contain other ingredients such as dyes for identification purposes, metal deactivators, diluents and the like.

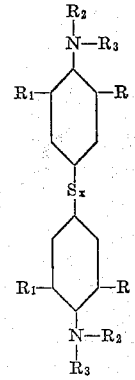
Antiknock compositions containing tetraalkyllead antiknock agents are employed by adding them to gasoline to improve the antiknock quality thereof. Such gasolines both before and after addition of the antiknock fluid are benefited by the practice of this invention. Thus gasolines to which have been added a compound of this invention are found to be more stable upon prolonged periods of storage.

The additive combinations of this invention are also extremely useful in inhibiting and stabilizing non-petroleum fats and oils normally subject to the deteriorating effect of oxidative rancidity. In particular, compounds of this invention are excellent stabilizers for animal fats and oils, especially lard, against the effects of rancidity.

In formulating the stabilized non-petroleum fats and oil of this invention, the additive or combination of additives is incorporated by appropriate means into the substrate to be stabilized. Thus, in the case of animal, vegetable and fish oils, the additive or combination of additives is added in appropriate quantity and the resulting mixture agitated to insure homogeneity. Where the substrate is a solid at room temperature—e.g., fats, butters, etc.—the mixing is preferably carried out at temperatures above the melting point of the substrate. When a combination of additives is used, they can be mixed with the substrate as a preformed mixture or can be separately blended therewith in either order. Generally speaking, it is desirable to first dissolve the additive combination in high concentration in a small portion of the material to be stabilized. The resulting concentrated solution then blended with the remaining bulk. Another way of facilitating the formulation of the composition of this invention is to pre-dissolve the additive or combination of additives in a suitable solvent, such as ethanol, glycerol, propylene glycol, etc., and then mix the resultant solution with the material to be stabilized. However, the preferred way of formulating the compositions of this invention is to pre-dissolve the additive mixture in a fatty acid partial ester of a polyhydroxy compound, notably a monoglyceride, and then blend this mixture with the material to be stabilized. The nature of these monoglyceride compositions is well known in the art and may be made from either animal or vegetable fats, with or without previous hydrogenation. These compositions generally contain about 40 percent of the monostearyl, monooleayl, and/or monopalmityl glycerides or mixtures thereof with the balance comprising a mixture of di- and triglycerides. Molecularly distilled monoglycerides may also be used for this purpose.

We claim:

1. A 4,4'-thiobis[2,6-di(lower alkyl)aniline] compound having the formula

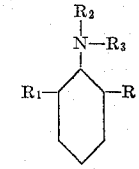


wherein R is an alkyl group having from 2 to 4 carbon atoms, R_1 is an alkyl group having from 1 to 4 carbon atoms, R_2 and R_3 are each hydrogen, and x ranges from 1 to 4 inclusive.

2. The compound of claim 1 in which x is 2.

3. 4,4'-dithiobis(2,6-diethylaniline).

4. Process for the preparation of the compound of claim 2 which comprises reacting, with a sulfur halide, a compound having the formula

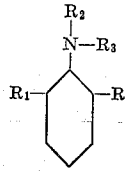


where R is a lower alkyl group having from 2 to 4 car-

bon atoms, R_1 is a lower alkyl group of 1 to 4 carbon atoms and R_2 and R_3 are each hydrogen, said compound being reacted as a strong acid salt.

5. Process for the preparation of 4,4'-dithiobis(2,6-diethylaniline) which comprises reacting the hydrochloride salt of 2,6-diethylaniline with sulfur dichloride.

6. Process for the preparation of the compound of claim 2 which comprises reacting a compound having the formula:



where R is a lower alkyl group having from 2 to 4 carbon atoms, R_1 is a lower alkyl group of 1 to 4 carbon atoms and R_2 and R_3 are each hydrogen, with a strong acid to form an acid salt of said compound and subjecting said salt to reaction with a sulfur halide.

7. Process for the preparation of 4,4'-dithiobis(2,6-diethylaniline) which comprises reacting 2,6-diethylaniline with hydrochloric acid to form an acid salt of said 2,6-diethylaniline and reacting said salt with sulfur dichloride.

8. A process for the preparation of 4,4'-dithiobis(2,6-diethylaniline) which comprises reacting 2,6-diethylaniline with hydrochloric acid to form the hydrochloride of said 2,6-diethylaniline, reacting said hydrochloride with sulfur monochloride, whereby the hydrochloride salt of 4,4'-dithiobis(2,6-diethylaniline) precipitates, separating said hydrochloride of 4,4'-dithiobis(2,6-diethylaniline) from the reaction mixture and regenerating 4,4'-dithiobis (2,6-diethylaniline) from said hydrochloride of 4,4'-dithiobis(2,6-diethylaniline).

9. A process for the preparation of 4,4'-dithiobis(2,6-diethylaniline) which comprises reacting 2,6-diethylaniline with hydrochloric acid to form the hydrochloride of said 2,6-diethylaniline, reacting said hydrochloride with sulfur dichloride, whereby the hydrochloride salt of 4,4'-dithiobis(2,6-diethylaniline) precipitates, separating said hydrochloride of 4,4'-dithiobis(2,6-diethylaniline) from the reaction mixture and regenerating 4,4'-dithiobis(2,6-diethylaniline) from said hydrochloride of 4,4'-dithiobis (2,6-diethylaniline).

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