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ORGANIC MATERIAL STABILIZED WITH 3,5-DI-TERT-BUTYL-4-HYDROXYBENZOIC ACID

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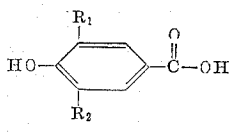
This invention relates to the stabilization of lubricating oil and polyethylene.

Additives which function effectively as antioxidants in lubricating oil have often been found to not function effectively as antioxidants in polyethylene, and vice versa. Lubricants, especially petroleum hydrocarbon oils and diester synthetic oils, undergo oxidative deterioration in service, particularly at elevated temperatures short of the cracking temperature of the particular oil. This deterioration results in the formation of gums and insoluble sludges, the corrosion of metal parts of the equipment with which the oils are used, the loss of useful properties of the oil, and the like. While some antioxidants have been developed which are somewhat effective in inhibiting this deterioration, they had to be used at relatively high concentrations in order to provide effective prolongation of the useful life of the lubricant. Still others are quite effective at low temperatures but are essentially ineffective when the oil is subjected to drastic oxidizing conditions, such as elevated temperatures and the presence in the oil of metallic substances tending to catalyze its deterioration.

Polyethylene also undergoes oxidative deterioration. It not only needs an antioxidant during use as a finished product, but also needs protection from oxidative deterioration during its critical processing stages. During these stages it is subjected to high temperatures which, in the absense of an effective inhibitor, deteriorate the polyethylene. Here too, prior art antioxidants had to be used at relatively high concentrations.

An object of this invention is to provide an additive which can stabilize both lubricating oil and polyethylene. Another object of this invention is to provide lubricant compositions and polyethylene having enhanced resistance to oxidative deterioration. A further object is to provide petroleum hydrocarbon oils normally subject to oxidative deterioration containing an effective amount of an inhibitor. A still further object is to provide synthetic lubricants containing a small amount of a potent additive which very effectively inhibits oxidative deterioration. Still another object is to provide polyethylene compositions normally subject to oxidative deterioration containing an additive which inhibits such deterioration. Other important objects will be apparent from the ensuing description.

The above and other objects of this invention are accomplished by providing a composition selected from the group consisting of lubricating oil and polyethylene normally susceptible to oxidative deterioration containing a small antioxidant quantity of a 3,5-dialkyl-4-hydroxybenzoic acid having the formula:



wherein R_1 is an alkyl group of from 1–12 carbon atoms and R_2 is an alpha-branched alkyl group of from 3–12 carbon atoms.

These compounds are, in general, white or yellow-white crystalline solids 3,5-diisopropyl-4-hydroxybenzoic acid, for example, has a melting point of 146° C., while

3,5-di-tert-butyl-4-hydroxybenzoic acid has a melting point of 218–219° C. They can be prepared by carboxylation of the sodium salt of the corresponding phenol. For example, 2,6-diisopropyl phenol can be added to a dispersion of sodium in toluene, refluxed (e.g. for 2 hours) and cooled. Carboxylation can then be effected by heating the mixture in a pressure vessel under carbon dioxide pressure (e.g. for 15 hours at 260° C. under 28–30 atmospheres of carbon dioxide pressure). The contents of the pressure vessel can be treated with water, the aqueous phase separated and acidified with 12-N hydrochloric acid, and the resultant 3,5-diisopropyl-4-hydroxy-benzoic acid removed and vacuum dried. Modifications can be made in this procedure. For example 3,5-di-tert-butyl-4-hydroxybenzoic acid can be prepared by first reacting 2,6-di-tert-butylphenol with sodium methiodide in toluene at reflux. Methanol is continuously removed as the azeotrope and carboxylation carried out as described above. Separation of the aqueous phase can be accomplished with dilute aqueous sodium bicarbonate, followed by acidification and separation of the 3,5-di-tert-butyl-4-hydroxybenzoic acid. Using another procedure, and as further illustration of the preparation of the additives of this invention, the sodium salt of 2,6-di-tert-butyl phenol in the dimethyl ether of diethylene glycol, as solvent, was heated in a pressure vessel to 155–160° C. under 825–850 pounds Co_2 pressure. After reaching this temperature the mixture was cooled and discharged from the reaction vessel using benzene. The liquid was decanted, stripped to remove solvent and the solids treated with aqueous base and extracted with benzene. Acidification of the aqueous portion gave a precipitate which was filtered, dried and, by infrared analysis, was found to be 3,5-di-tert-butyl-4-hydroxybenzoic acid. By following the above procedures other 3,5-dialkyl-4-hydroxybenzoic acids can be prepared.

Examples of 3,5-dialkyl-4-hydroxybenzoic acids useful in this invention are: 3-tert-amyl-5-(2-decyl)-4-hydroxybenzoic acid, prepared by adding 2-tert-amyl-6-(2-decyl) phenol to a dispersion of sodium in toluene, followed by carboxylation of the resultant sodium salt; 3-methyl-5-tert-butyl-4-hydroxybenzoic acid, obtained by carboxylation of the sodium salt of 2-methyl-6-tert-butylphenol; 3-(3-hexyl)-4-hydroxy-5-n-nonylbenzoic acid, prepared by reacting 2-(3-hexyl)-6-n-nonylphenol with sodium methiodide and carboxylating the resultant salt; 3-isopropyl-4-hydroxy-5-(4-undecyl)benzoic acid, obtained by carboxylation of the sodium salt of 2-isopropyl-6-(4-undecyl) phenol; 3-sec-butyl-5-ethyl-4-hydroxybenzoic acid, prepared by adding 2-sec-butyl-6-ethylphenol to a dispersion of sodium in toluene, followed by carboxylation of the resultant sodium salt; 3-tert-butyl-4-hydroxy-5-isopropylbenzoic acid, prepared by carboxylating the sodium salt of 2 - tert-butyl-6-isopropylphenol. 3-(2-dodecyl)-4-hydroxy-5-n-propylbenzoic acid, obtained from the carboxylation of the sodium salt of 2-(2-dodecyl)-6-n-propylphenol; and 3-n-heptyl-4-hydroxy-5-tert-octylbenzoic acid, prepared by carboxylating the sodium salt of 2-n-heptyl-6-tert-octylphenol.

Preferred compounds are those of the above formula in which R_1 and R_2 are the same and are alpha-branched alkyl groups of from 3 to 4 carbon atoms, for example, 3,5 - di-tert-butyl-4-hydroxybenzoic acid and 3,5-diisopropyl - 4 - hydroxybenzoic acid. These compounds are preferred because they are generally more effective antioxidants than those of the broader class.

In general, effective concentrations of the 3,5-dialkyl-4-hydroxybenzoic acid are from about 0.001 to about 5 percent by weight, and preferably from about 0.01 to about 2 percent by weight of the material to be protected, i.e. lubricating oil or polyethylene.

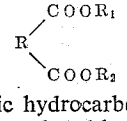
The compounds described above are effective antioxidants for lubricating oils. In preparing the improved lubricant compositions of this invention, an appropriate quantity of the additive compound is blended with the oil to be stabilized. If desired, preformed concentrated solutions of the stabilizer 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 3,5-dialkyl-4-hydroxybenzoic acids are easily and rapidly blended with the base oil. An additional advantage of this invention is that such compounds are highly compatible with the usual additives that are frequently used to fortify lubricant compositions, such as detergent-dispersants, viscosity index improvers, dyes, anti-rust additives, anti-foaming agents, and the like.

An embodiment of this invention is petroleum hydrocarbon derived mineral lubricating oil normally susceptible to oxidative deterioration at elevated temperatures containing a small antioxidant quantity, from about 0.001 to about 5 percent by weight of a 3,5-dialkyl-4-hydroxybenzoic acid as described above. Preferred concentrations are from 0.01 to about 2 percent by weight of the oil. Another embodiment of this invention is a synthetic lubricating oil stabilized against oxidative deterioration at elevated temperatures by such a 3,5-dialkyl-4-hydroxybenzoic acid.

The synthetic lubricating oils which are enhanced by the practice of this invention are, in general, non-hydrocarbon organic compositions; i.e., organic compositions which contain elements other than carbon and hydrogen. Examples of general classes of material which are protected against oxidative deterioration by the inclusion therein of a 3,5-dialkyl-4-hydroxybenzoic acid include diester oils, silicone oils, oils of halogen-containing organic compounds including the fluorocarbons; polyalkylene glycol lubricating oils, and organic phosphates which are suitable as hydraulic fluids and lubricating oils. Excellent results are obtained when a 3,5-dialkyl-4-hydroxybenzoic acid, such as 3,5-di-tert-butyl-4-hydroxybenzoic acid, is added to any of these classes of materials.

As noted, diester lubricating oils are enhanced by the practice of this invention. Thus a synthetic diester lubricant containing a small antioxidant quantity, up to about 5 percent by weight of a 3,5-dialkyl-4-hydroxybenzoic acid, as described above, constitutes an embodiment of this invention. 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 oils used in the 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 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.

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 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.

The diester oils may be formed by the reaction of a polycarboxylic acid with a mono-hydric alcohol, the reaction of a polyhydric alcohol with a mono-carboxylic acid, reaction between a polyhydric alcohol and a polycarboxylic acid, or combinations of the above reactions; for example, reaction of a polycarboxylic acid with a glycol and a mono-hydric alcohol, reaction of a glycol with a polycarboxylic acid and a mono-carboxylic acid, or the reaction of a glycol, a mono-hydric alcohol, a polycarboxylic acid and a mono-carboxylic acid. The acids may be mono-carboxylic aliphatic acids such as, propionic acid, valeric acid, 2-ethyl enanthic acid, 2,2-di-propyl butyric acid or 3-(2-methylhexyl) valeric acid. They may contain unsaturated linkages, such as, in senecioic acid, sorbic acid, or angelic acid; they may be polycarboxylic aliphatic acids suc has succinic acid, glutaric aid, azelaic acid, 5-octene-1,8-dicarboxylic acid, or 3-hexene-2,3,4-tricarboxylic acid, and they may be aromatic or cycloaliphatic acids, such as cyclohexane-acetic acid, 1,4-cyclopentylenebis acetic acid, phthalic acid, hemimellitic acid, and terephthalic acid.

The alcohols used in preparing the polyester lubricant base materials may be aliphatic mono-hydric alcohols such as propanol, 2-ethyl-3-hexanol, 2-ethyl-4-propyl heptanol, 2-butenol, or 2-methyl propanol. They may be polyhydric aliphatic alcohols, such as 1,6-hexamethylene glycol, 1,10-decamethylene glycol, 2-hexene-1,6-diol, and 1,6-heptylene glycol, and they may be mono or polyhydric alicyclic or aromatic alcohols, such as 4-[m-(2-hydroxyethyl) phenyl] butanol, 3 - (2 - hydroxyethyl) cyclohexanebutanol, p-(hydroxymethyl) phenethyl alcohol, α-methyl-p-xylene-α,α′-diol, 1,4-cyclohexane-β,β′-diethyl-dimethanol, 2,3-bis(4-hydroxybutyl) benzyl alcohol, 4,4′ - [3-(3 - hydroxyhexyl)-o-phenylene]dibutanol, and 5-[3-(3-hydroxypropyl) cyclopenta-2,4-dienylene] 3-ethyl amyl alcohol.

Another class of synthetic oils which achieve enhanced oxidative stability by the practive 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 serving as the base medium for the lubricating oils of the invention include the polysiloxane oils 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-butyl-phenyl types, and the silanes. Also included are the halogen substituted siloxanes, such as the chlorophenylpolysiloxanes.

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, chloronaphthalene, chlorodiphenyl oxides and chloronated paraffin waxes.

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



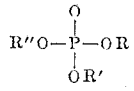
The fluorocarbon oils and greases are very stable chemically and have high thermal stability. These desirable physical properties appear to be closely related to the bond distances occuring in the fluorocarbon polymeric molecule, which may also contain chlorine bonded to carbon.

Polyalkylene glycol lubricants which are benefited by the practice of this invention are ordinarily the reaction products of an aliphatic alcohol with an alkylene 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 3000. 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 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 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 phosphate; p-chlorophenyl dimethyl phosphate; tris(2-n-butoxyethyl) phosphate; dimethyl m-tolyl phosphate; di-n-propyl m-toyly 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 following examples illustrate various specific embodiments of this invention. The physical characteristics of the illustrative oils used in Examples 1–6 are 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 1

To 100,000 parts of Oil A is added with stirring 12 parts (0.012 percent) of 3,5-di-tert-butyl-4-hydroxybenzoic acid. The resulting oil is found to possess improved resistance to oxidative deterioration.

Example 2

To 100,000 parts of Oil B is added 2000 parts (2 percent) of 3,5-diisopropyl-4-hydroxybenzoic acid. On agitating this mixture, a homogeneous solution results and the resulting oil composition possesses enhanced oxidation resistance.

Example 3

With 100,000 parts of Oil C is blended 50 parts (0.05 percent) 3-tert-amyl-5-(2-nonyl)-4-hydroxybenzoic acid. The resulting oil possesses enhanced resistance against oxidative deterioration.

Example 4

To 100,000 parts of Oil D is added 100 parts (0.1 percent) of 3-methyl-5-tert-octyl-4-hydroxybenzoic acid. The resulting oil is found to possess enhanced resistance against oxidative deterioration.

Example 5

With 100,000 parts of Oil E is blended 5 parts (0.005 percent) of 3-(2-hexyl)-4-hydroxy-5-n - undecylbenzoic acid. After mixing, the resulting oil possesses enhanced resistance to oxidation.

Example 6

To 100,000 parts of Oil F is added 150 parts (0.15 percent) of 3-isopropyl-4-hydroxy-5-(4 - nonyl)benzoic acid. The resulting oil possesses enhanced resistance against oxidative deterioration.

Example 7

With 100,000 parts of di-(sec-amyl) sebacate having a viscosity at 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 3-sec-butyl-5-ethyl-4-hydroxybenzoic acid. The resulting diester lubricant possesses greatly enhanced resistance against oxidative deterioration.

Example 8

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 3-tert-butyl-4-hydroxy-5-isopropylbenzoic acid. After mixing, the resultant diester lubricant possesses greatly enhanced oxidation resistance.

Example 9

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 5,000 parts (5 percent) of 3-(5-dodecyl)-4-hydroxy-5-propylbenzoic acid. After mixing, the resultant diester lubricant possesses outstanding resistance against oxidative deterioration.

Example 10

Five parts of 3-n-heptyl-4-hydroxy-5-tert-amylbenzoic acid are blended with 2495 parts of diisooctyl azelate having a kinematic viscosity of 3.34 centistokes at −65° F. (ASTM 445–52T), an ASTM slope from −40° F. to 210° F. of 0.693 (ASTM D341–43) and a pour point of −85° F. (ASTM D97–47). Its flash point is 425° F. (ASTM D92–52), and its specific gravity is 0.9123 at 25° C. The resulting lubricant is extremely stable to oxidation.

Example 11

One part of 3,5-di-(2-heptyl)-4-hydroxybenzoic acid is blended with 75 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. and a viscosity of 22,500 at −65° F. Its viscosity index is 143, is ASTM pour point is below −80° F. and its specific gravity (60° F./60° F.) is 0.926.

Example 12

To a siloxane fluid having viscosity of 71 centistokes at 25° C. and 24 centistokes at 75° C., a specific gravity of 1.03 at 25° C., a freezing point of −70° C. and a flash point of 540° F., which is composed of a halogen substituted polyphenylpolymethyl siloxane is added sufficient 3,5-di-sec-butyl-4-hydroxybenzoic acid to give a composition containing 1.5 percent of the additive. This oil has an extremely high degree of resistance against oxidative deterioration due to the presence of the 3,5-di-sec-butyl-4-hydroxy-benzoic acid.

Example 13

To a phenylmethyl polysiloxane fluid having a viscosity of 100–150 centistrokes at 25° C., and open cup flash point of 575° F. (ASTM–D–92–33). A freezing point of −60° F., and a specific gravity of 1.07 at 77° F. is added sufficient 3,5-di-(3-dodecyl)-4-hydroxybenzoic acid, to give a composition containing 0.1 percent of the additive.

Example 14

Ten parts of 3-tert-butyl-4-hydroxy-5-methylbenzoic acid are blended with about 1,000 parts of monoethyl diethoxy monoacetoxy silane (boiling point 191.5° C.) to prepare an enhanced oil of this invention.

Example 15

A 1 percent solution of 4-hydroxy-3-isopropyl-5-methylbenzoic acid in tribenzyl-n-hexadecyl silane (boiling point 245–248° C.) constitutes an improved lubricant within the scope of this invention.

Example 16

To a poly(trifluorochloroethylene) having the formula $(CF_2CFCl)x$ 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, 3,5-di-tert-octyl-4-hydroxybenzoic acid to prepare an improved lubricant of this invention.

Example 17

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 1 percent 3-n-heptyl-5-(2-hexyl)-4-hydroxybenzoic acid to prepare an extremely oxidation resistant polyalkylene glycol lubricant.

Example 18

A composition containing 0.2 percent of 3-ethyl-4-hydroxy-5-isopropylbenzoic acid is prepared by adding an appropriate quantity of the compound to a polyalkylene glycol lubricant which is insoluble in water and which has a Saybolt viscosity of 62.7 at 200° F., a viscosity index of 146, ASTM pour point of −40° F., a fire point of 490° F. and a specific gravity of 0.991.

Example 19

An improved lubricant of this invention comprising a chloronated organic compound is prepared by admixing 0.5 percent of 3,5-diisopropyl-4-hydroxybenzoic acid 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 20

An improved hydraulic fluid and lubricant according to this invention is prepared by adding 2 percent 3,5-di-sec-butyl-4-hydroxybenzoic acid to tricresyl phosphate.

The compositions of this invention and the methods by which they are formulated will now be apparent to those skilled in the art.

To illustrate the effectiveness of the 3,5-dialkyl-4-hydroxybenzoic acids of this invention, recourse is had to the Polyveriform Oxidation Stability Test as described in the pages entitled, "Factors Causing Lubricating Oil Deterioration in Engines" (Ind. and Eng. Chem. Anal. Ed., 17, 302 (1945)). See also "A Bearing Corrosion Test for Lubricating Oils and Its Correlation With Engine Performance" (Anal. Chem., 21, 737 (1949)). This test effectively evaluates the performance of lubricating oil antioxidants. The test equipment, procedure employed and correlations of the results with engine performance are discussed in the first paper above cited. By employing various compounds of this invention in oxygen-sensitive lubricating oil, effective inhibition of oxidation deterioration is achieved.

To demonstrate the effectiveness of the preferred additive of this invention—3,5-di-tert-butyl-4-hydroxybenzoic acid—as an antioxidant for industrial lubricants, comparative tests were conducted using the method and apparatus essentially as described in the publication first above mentioned. One minor modification was that the steel sleeve and copper test piece described in this publication were omitted from the apparatus. In these tests an initially additive-free, 95 V.I. solvent-refined SAE–10 crankcase oil was used. The principal test conditions consisted of passing 50 liters of air per hour through the test oil for a total period of 20 hours while maintaining the oil at a temperature of 280° F. Oxidation deterioration of the oil was further promoted by employing as oxidation cata-

lysts 0.05 percent by weight of ferric oxide (as ferric 2-ethyl hexoate) and 0.10 percent by weight of lead bromide, both of these amount being based upon the weight of oil employed. A lubricating oil of this invention was then prepared by blending 1 percent by weight of 3,5-di-tert-butyl-4-hydroxybenzoic acid with another portion of the above lubricating oil. This composition was then subjected to the above stringent oxidation test. As an indication of oxidation, the viscosity of the oil is measured before and after the test. Since increases in viscosity are found with almost all additives, the increase of the test sample as compared to the blank is a measure of oxidative protection. In addition the oil is rated visually for sludge, a rating of "A" being very clean. The results of these tests are shown in the followling table.

EFFECT OF ANTIOXIDANTS ON OXIDATION OF LUBRICATING OIL

Test No.	Additive	Percent Viscosity Increase SUS at 100° F.	Visual Sludge Rating
1	None	98	B
2	3,5-di-tert-butyl-4-hydroxybenzoic acid.	32	A

By referring to the data presented in the table it is apparent that 3,5-di-tert-butyl-4-hydroxybenzoic acid effectively inhibits oxidative deterioration of lubricating oil.

3,5-di-tert-butyl-4-hydroxybenzoic acids 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, oils thickened with soaps and inorganic thickening agents (grease), 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 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, anti-foam agents, rust inhibitors, oiliness or film strength agents, dyes, and the like. Of the inhibitors which can be effectively used in combination with a 3,5-dialkyl-4-hydroxybenzoic acid are sulfurized sperm oil, sulfurized terpenes, sulfurized paraffin wax olefins, aromatic sulfides, alkyl phenol sulfides, lecithin, neutralized dithiophosphates, phosphorus pentasulfide-terpene 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 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.

The compounds described above are also effective antioxidants for polyethylene and an embodiment of this invention is polyethylene, normally susceptible to oxidative deterioration at elevated temperatures, containing a small antioxidant quantity from about 0.001 to about 5 percent by weight of a 3,5-dialkyl-4-hydroxybenzoic acid as described above. Preferred concentrations are from 0.01 to about 2 percent by weight of the polyethylene.

Polyethylene is a hydrocarbon polymer derived from the polymerization of ethylene. This polymerization can be accomplished by a great variety of methods which lead to products of diverse properties. Polyethylene of any nature may advantageously be utilized for preparing compositions according to the present invention. The polymers of ethylene 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 to 1,000 atmospheres at temperatures between 150 and 275° C. Or, if desired, they may be similar or identical 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 Group IV–B, V–B and VI–B metals of the Periodic System; chromium oxide on silicated alumina; hexavalent molybdenum compounds; and charcoal supported nickel-cobalt. The polyethylene 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.

The benefits derived from the practice of this invention are demonstrated by comparative oxidation tests of uninhibited polyethylene and polyethylene containing an antioxidant of this invention. These tests are conducted as follows: The selected amount of antioxidant is blended with the polyethylene by milling a weighed quantity of plastic pellets on a warm roll-mill. The weighed quantity of antioxidant is added to the mill after the polyethylene has been premilled for a short period of time. The plastic containing the antioxidant is then added in weighed quantity to a standard size vessel and melted to give a surface of reproducible size. The vessel is then inserted into a chamber which may be sealed and which is connected to a capillary tube leading to a gas burst and leveling bulb. The apparatus is flushed with oxygen at room temperature, sealed, and the temperature is raised to 150° C. The oxygen pressure is maintained at 1 atmosphere by means of a leveling bulb. The oxygen uptake at the elevated temperature is recorded until sharp increase in the oxygen uptake occurs. This procedure has been adopted since it has been found that many compounds may inhibit the oxidation for a certain induction period after which time a very sharp increase in the rate of oxygen uptake occurs indicating that the antioxidant has been exhausted. In tests of this nature compositions of this invention have effectively increased "induction periods."

There are several methods available for preparing the inhibited hydrocarbon polyethylene compositions of this invention. Thus, the blending of a 3,5-dialkyl-4-hydroxybenzoic acid with 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 polyethylene containing excessive amounts of the additive and then mix the concentrate with additional polyethylene to prepare a composition of this invention. The preferred method of compounding the polyethylene 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 3,5-dialkyl-4-hydroxybenzoic acid may be initially mixed with the polyethylene in the dried state or it may be first dissolved in a suitable solvent, then sprayed on the polyethylene and milled in.

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

Example 21

To 1000 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 3,5-di-tert-butyl-4-hydroxybenzoic acid. The resulting composition has greatly increased oxidative stability.

Example 22

With 200 parts of polyethylene having an average molecular weight of 100,000 is blended 1.0 part 3,5-di-sec-butyl-4-hydroxybenzoic acid.

Example 23

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 3,5-diisopropyl-4-hydroxybenzoic acid.

Example 24

A linear polyethylene having a high degree of crytallinity (about 93 percent) and below 1 ethyl branched chain per hundred 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 0.005 percent 3-tert-amyl-5-(2-decyl)-4-hydroxybenzoic acid, and the resulting product has better stability characteristics.

Example 25

To a polyethylene having an average molecular weight of 1500, a melting point of 88–90° C. and a specific gravity of 0.92 is added 1 percent of 3-methyl-5-tert-butyl-4-hydroxybenzoic acid. After milling in the antioxidant an extremely oxidation resistant product results.

Example 26

Two parts of 3-(3-hexyl)-4-hydroxy-5-n-nonylbenzoic acid are added with milling to 100 parts of a low density polyethylene prepared by high pressure polymerization and which has an average molecular weight of about 20,000. The resulting product is vastly improved in its oxidative stability.

Example 27

To 10,000 parts of a polyethylene having an average molecular weight of about 100,000 and which has a tensile strength of 5400 p.s.i., a Shore D hardness of 70 and a softening temperature of 130° C. under low load is added ten parts 3 - isopropyl - 4-hydroxy-5-(4-undecyl)benzoic acide to prepare a composition of outstanding oxidative stability.

Example 28

To the polyethylene in Example 23 is added 0.05 percent 3-sec-butyl-5-ethyl-4-hydroxybenzonic acid. The resulting composition has improved antioxidant characteristics.

Example 29

To a polyethylene having an average molecular weight of 35,000 is added sufficient 3-(2-dodecyl)-4-hydroxy-5-n-propylbenzoic acid to give a composition containing 0.03 percent of the antioxidant. The composition has improved antioxidant properties due to the presence of the 3-(2-dodecyl)-4-hydroxy-5-n-propylbenzoic acid.

In addition to a 3,5-dialkyl-4-hydroxybenzoic acid, the polyethylene compositions of this invention 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 chloronated hydrocarbons and various pigment compositions designed to impart color to the finished product.

I claim:

1. Lubricating oil containing an antioxidant quantity of 3,5-di-tert-butyl-4-hydroxybenzoic acid.

2. Polyethlene containing an antioxidant quantity of 3,5-di-tert-butyl-4-hydroxybenzoic acid.

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