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ORGANIC MATERIALS CONTAINING 3,5-DIALKYL-4-HYDROXYBENZYL ETHERS AS ANTIOXIDANTS

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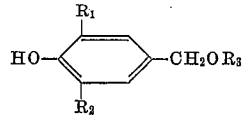
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10 Claims. (Cl. 252—52)

This invention relates to and has as its principal object the stabilization of organic material. In particular, this invention relates to certain asymmetric ethers as antioxidants, particularly in unsaturated polymeric material such as rubber.

This application is a continuation-in-part of application Serial No. 536,318, filed September 23, 1955, now U.S. Patent No. 2,838,571, entitled "3,5 - Dialkyl - 4-Hydroxybenzene Ethers."

This invention is accomplished by providing, as a new composition of matter, organic material normally tending to undergo oxidative deterioration in the presence of air, oxygen or ozone, containing a small antioxidant quantity, up to 5 percent, of a 3,5-dialkyl-4-hydroxybenzyl ether having the general formula:



wherein R_1 is an alkyl group containing from 3 to 8 carbon atoms and is branched on the alpha carbon atom, R_2 is an alkyl group containing from 1 to 8 carbon atoms, and R_3 is selected from the group consisting of alkyl, cycloalkyl, aralkyl and alkenyl. In the above compounds, it is preferable that the groups designated by R_3 contain up to about 12 carbon atoms.

A preferred embodiment of this invention relates to the use as antioxidants of 3,5-dialkyl-4-hydroxybenyl ethers as above defined, in which R_1 and R_2 are both alkyl groups containing from 3 to 8 carbon atoms, both of said alkyl groups being branched on their respective alpha carbon atoms, and R_3 is a lower alkyl group—i.e., an alkyl group containing from 1 to 6 carbon atoms. The compounds of this preferred embodiment are particularly useful antioxidants in various applications and are prepared in good yield and high purity from readily available, inexpensive starting materials.

The compounds of this invention are very useful as antioxidants for oxygen-sensitive organic materials normally tending to deteriorate when in contact with oxygen, air, or ozone. Thus, the compounds of this invention may be added to, or blended with, such materials as gasoline; leaded gasoline, i.e. gasoline which contains a lead alkyl antiknock compound such as tetraethyllead; tetraalkyllead compounds such as tetramethyllead, tetraethyllead, etc.; lubricating oils; turbine oils, transformer oils; industrial oils such as gear oil, cutting oil, transmission lubricants, glass annealing oils, brake fluids, etc.; greases, high molecular weight polymers such as natural and synthetic rubber, polyethylene, polystyrene, polyisobutylene, etc.; diesel fuels; domestic heating oils; asphalt; edible material such as fats, oils, vitamins; alfalfa and the like.

The following examples, in which all parts are by weight, are illustrative specific examples of the use of the novel compounds of this invention in organic material normally tending to undergo oxidative deterioration in the presence of air, oxygen or ozone.

Example I

To 1000 parts of a liquid hydrocarbon fuel having 38.1 percent paraffins, 21.0 percent olefins, 17.1 percent aromatics and 22.8 percent naphthenes, an initial evaporation temperature of 88° F. and a final evaporation temperature of 426° F. is added 1 part of (3,5-di-tert-butyl-4-hydroxybenzyl)-(methyl) ether. The mixture is agitated to dissolve the (3,5-di-tert-butyl-4-hydroxy-benzyl) - (methyl) ether in the fuel, and the resulting composition is extremely resistant to oxidative deterioration.

Example II

To 1000 parts of a gasoline having 44.0 percent paraffins, 17.9 percent olefins and 38.1 percent aromatics, an initial evaporation temperature of 94° F. and a final evaporation temperature of 119° F. is added 10 parts of (3-isopropyl-5-methyl-4-hydroxy - benzyl) - (methyl) ether. The mixture is agitated to dissolve the (3-isopropyl-5-methly - 4 - hydroxybenzyl) - (methyl) ether. The resulting fuel has an excellent stability to oxidative deterioration.

Example III

To 5000 parts of a liquid hydrocarbon fuel having 49.7 percent paraffins, 22.3 percent olefins and 28.0 percent aromatics, an initial evaporation temperature of 81° F and a final evaporation temperature of 410° F. is added 25 parts [3,5 - di(1',3',3' - tetramethylbutyl)4 - hydroxybenzyl]-(dodecyl) ether. The fuel is agitated to dissolve the mixture. The resulting fuel is stable to oxidative deterioration.

Example IV

To 1000 gallons of the fuel described in Example III is added 3000 milliliters of tetraethyllead, 0.5 theory bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride and 9 grams of (3-methyl-5-tert-butyl-4-hydroxybenzyl)-(n-hexyl) ether. The mixture is agitated until a homogeneous oxygen stable solution of all the ingredients is achieved.

Example V

To 1000 parts of a commercially available diesel fuel having an octane number of 51.7 and a 50 percent evaporation temperature of 509° F. is added 3 parts of (3,5-di-tert-butyl-4-hydroxybenzyl)-(isopropyl) ether. The resulting fuel is stable to oxidative deterioration.

Example VI

To 1000 parts of a kerosene-type liquid hydrocarbon fuel having an initial evaporation temperature of 325° F. and a final evaporation temperature of 585° F. is added 6 parts of (3 - tert - butyl-5-isopropyl-4-hydroxybenzyl)-(sec-amyl) ether. The mixture is agitated until a homogeneous oxygen stable solution of the ingredients is achieved.

Example VII

To an antiknock fluid composition which is to be used as an additive to gasoline and which contains 61.5 parts of tetraethyllead, 17.9 parts of ethylene dibromide and 18.8 parts of ethylene dichloride, is added, with agitation, 1.3 parts of (3,5-di-tert-butyl-4-hydroxybenzyl)-(methyl) ether. The resulting composition is stable for long periods when exposed to air.

Example VIII

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 5 parts of [3(1',1',2'-trimethylpropyl) 5 - hexyl - 4 - hydroxybenzyl]-(ethyl) ether as an antioxidant.

The above examples illustrate compositions of this invention which possess greatly enhanced resistance to oxidative deterioration by virtue of the presence therein of an antioxidant of this invention.

The 3,5-dialkyl-4-hydroxybenzyl ethers find important utility as antioxidants in a wide variety of other oxygen sensitive materials. Thus, the addition of small quantities of these compounds to such materials as turbine, hydraulic, transformer and other highly refined industrial oils; waxes; soaps and greases; plastics; organometallic compositions such as tetraethyllead and tetraethyllead antiknock fluids; crankcase lubricating oils; and the like, greatly increases their resistance to deterioration in the presence of oxygen, air or ozone.

The 3,5-dialkyl-4-hydroxybenzyl ethers of this invention are also useful in protecting petroleum wax—paraffin wax and micro-crystalline wax—against oxidative deterioration. The compounds of this invention also find use in the stabilization of edible fats and oils of animal or vegetable origin which tend to become rancid especially during long periods of storage because of oxidative deterioration. Typical representatives of these edible fats and oils are linseed oil, cod liver oil, castor oil, soybean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter, fat, lard, beef tallow, and the like.

The following examples illustrate typical edible compositions protected by an antioxidant of this invention.

Example IX

Two parts of (3-methyl-5-tert-butyl-4-hydroxybenzyl)-(methyl) ether are blended with 10,000 parts of lard. The resulting protected lard is stable over long storage periods in contradistinction to the unprotected product.

Example X

To 5,000 parts of olive oil is added 1 part (3,5-di-tert-butyl-4-hydroxybenzyl)-(n-octyl) ether and the mixture is agitated to produce a homogeneous blend which is stable to oxidative deterioration for a long period.

The amount of 3,5-dialkyl-4-hydroxybenzyl ether stabilizer employed is dependent upon the nature of the material to be protected and the conditions to be encountered. Generally speaking, amounts in the order of about 0.001 to about 5 percent by weight of the material to be protected can be used. However, in most instances where the material to be protected does not have an unusual oxidative instability, amounts from about 0.01 to about 2 percent are satisfactory.

A preferred embodiment of this invention is rubber containing as an antioxidant therefor, a 3,5-dialkyl-4-hydroxybenzyl ether. Another part of this invention is the method of preserving rubber which comprises incorporating therein a 3,5-dialkyl-4-hydroxybenzyl ether. The stabilizer is incorporated into the rubber by milling, Banbury mixing, or similar process, or is emulsified and the emulsions added to the rubber latex before coagulation. In the various embodiments of this invention the 3,5-dialkyl-4-hydroxybenzyl ether stabilizer is used in small amounts, generally ranging from about 0.01 to about 5.0 percent, based on the rubber.

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

Among the definite advantages provided by this invention is that the present rubber compositions possess unusually great resistance against oxidative deterioration. Moreover, these compositions exhibit excellent non-staining and non-discoloration characteristics. Furthermore, the stabilizer—3,5-dialkyl-4-hydroxybenzyl ether—is relatively inexpensive and easily prepared, and possesses the highly beneficial property of low volatility. As is well known, a highly desirable feature of a rubber antioxidant is that it has a low volatility so that it remains admixed with the rubber during vulcanization and related process steps.

The preferred invention will be still further apparent from the following specific examples wherein all parts and percentages are by weight.

Example XI

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

Example XII

One percent of [3(1',1',3',3' - tetramethylbutyl)5-methyl-4-hydroxybenzyl]-(benzyl) ether is added to a synthetic rubber master batch comprising 100 parts of GR–S rubber having an average molecular weight of 100,000, 5 parts of zinc stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 1.5 parts of mercaptobenzothiazole. This batch is then cured as described in Example XI.

Example XIII

Two parts of (3,5 - diisopropyl - 4 - hydroxybenzyl)-(methyl) ether is incorporated in 100 parts of raw butyl rubber prepared by the copolymerization of 90 percent of isobutylene and 10 percent of isoprene.

Example XIV

To 200 parts of raw butyl rubber prepared by copolymerization of 95 percent of isobutylene and 5 percent of butadiene is added 1.5 parts of (3,5-di-tert-butyl-4-hydroxybenzyl)-(methyl) ether.

Example XV

To a master batch of GR–N synthetic rubber comprising 100 parts of GR–N rubber, 5 percent of zinc stearate, 50 parts of carbon black, 5 parts of road tar, 2 parts of sulfur and 2 parts of mercaptobenzothiazole is added 5 percent based on the weight of the batch of (3-tert-amyl-5-ethyl-4-hydroxybenzyl)-(isobutyl) ether.

Example XVI

To natural rubber (Hevea) is added 0.1 percent of (3,5-diisopropyl-4-hydroxybenzyl)-(cyclohexyl) ether.

Example XVII

Natural rubber stock is compounded according to the following formula:

	Parts
Thick gristly crepe natural rubber	100
Wax	2
Ultramarine dye	0.1
Zinc oxide	70
Titanium dioxide	20
Sulfur	3
Stearic acid	1.2
(3-isopropyl-5-ethyl-4-hydroxybenzyl)-(ethyl) ether	1
Benzothiazyl disulfide	0.4
Amine activator	0.5

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

Example XVIII

A butadiene-acrylonitrile co-polymer is produced from butadiene-1,3 and 32 percent of acrylonitrile. Two percent (based on the dry weight of the co-polymer) of (3-tert-butyl-5-n-propyl-4-hydroxybenzyl)-(methyl) ether is added as an emulsion in sodium oleate solution to the latex obtained from emulsion copolymerization of the monomers. The latex is coagulated with a pure grade of aluminum sulfate and the coagulum, after washing, it dried for 20 hours at 70° C.

Example XIX

Three percent of (3,5-di-tert-butyl-4-hydroxybenzyl)-(methyl) ether emulsified in sodium oleate is added to a rubber-like, co-polymer of butadiene-1,3 and styrene containing 25 percent of combined styrene.

Example XX

A rubber stock is compounded from 100 parts of smoked sheet rubber, 60 parts of zinc oxide, 20 parts of lithopone, 2 parts of sulfur, 0.7 parts of diphenyl guanidine phthalate, 0.8 parts of benzoyl thiobenzothiazole, 0.2 parts of paraffin and 2 parts of (3,5-di-tert-butyl-4-hydroxybenzyl)-(n-decyl) ether. The stock so compounded is cured by heating for 45 minutes at 126° C. in a press.

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

To illustrate the enhanced oxygen resistance of the rubber compositions of this invention and the excellent non-staining and non-discoloration characteristics of a 3,5-dialkyl-4-hydroxybenzyl ether, a light-colored stock is selected for test. This stock has the following composition:

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

To the above base formula is added one part by weight of 2,6-di-tert-butyl - α-methoxy-p-cresol and individual samples are cured for 20, 30, 45 and 60 minutes at 274° C. using perfectly clean molds with no mold lubricant. Another set of samples of the same base formula which did not contain an antioxidant was cured under the same conditions.

To demonstrate the protection afforded to the rubber by 2,6-di-tert-butyl-α-methoxy-p-cresol and to contrast the same with the unprotected rubber, the tensile strength and the ultimate elongation of the inhibited stocks are determined before and after aging. These properties are also determined on the inhibitor-free stocks. The aging is accomplished by conducting the procedure of ASTM Designation: D–572–52, described in the ASTM Standards for 1952, Part 6, for a period of 168 hours at a temperature of 70° C. with an initial oxygen pressure in the test bomb of 300 p.s.i.g.

The tensile strength and the ultimate elongation of the test specimens before and after aging are measured by ASTM Test Procedure, D–412–51T (ASTM Standards for 1952, Part 6). The tensile strength is the tension load per unit cross-sectional area required to break a test specimen, while the ultimate elongation is the elongation at the moment of rupture of a test specimen. A decrease in the values for either of these properties upon aging represents a decrease in the usefulness of the article fabricated therefrom, so that the degree to which these properties are retained is a direct measure of the utility of the protective substance.

Measurements are also made of the increase in weight of the test specimens which occur during the accelerated aging. This is a direct measure of the oxygen up-take of the samples and provides another criterion of the effectiveness of an inhibitor in suppressing oxidative deterioration of the rubber. Thus, the larger the weight increase, the greater is the deterioration and the less effective is the inhibitor.

On exposure to ultraviolet light in a weatherometer, it is noted that the typical composition of this invention produces only a slight discoloration, whereas a sample containing a conventional inhibitor exhibits a marked change to a light-brown color.

The amount of antioxidant employed in the rubber compositions of this invention varies from about 0.01 to about 5 percent by weight based on the weight of the rubber. The amount used depends somewhat upon the nature of the rubber being protected and the conditions of service to be encountered. Thus, in the stabilization of natural and synthetic rubber to be used in the manufacture of tires which are normally subjected to exposure to the elements, as well as to the action of sunlight, frictional heat, stress, and the like, the use of relatively high concentrations of this inhibitor is advantageous. On the other hand, when the article of manufacture is not to be subjected to such severe conditions, relatively low concentrations can be successfully utilized. Generally speaking, amounts ranging from about 0.1 to about 3 percent by weight give uniformly satisfactory results.

Other rubbers and elastomers which can be prepared according to this invention are the rubbery polymerizates of isoprene, butadiene-1,3, piperylene; also the rubbery co-polymer of conjugated dienes with one or more polymerizable monoolefinic compounds which have the capability of forming rubbery co-polymers with butadiene-1,3, outstanding examples of such monoolefinic compounds being those having the group $CH_2=<$, exemplified by styrene. Examples of such monoolefins are styrene, vinyl naphthalene, alpha methyl styrene, para-chlorostyrene, dichlorostyrene, acrylic acid, methyl acrylate, methyl methacrylate, methacrylonitrile, methacrylamide, methyl vinyl ether, methyl vinyl ketone, vinylidine chloride, vinyl carbazole, vinyl pyridines, alkyl-substituted vinyl pyridines, etc. In fact, excellent stabilization is achieved by incorporating a 3,5-dialkyl-4-hydroxybenzyl ether in any of the well-known elastomers which are normally susceptible to deterioration in the presence of air, such as elastoprenes, elastolenes, elastothiomers, and elastoplastics.

The antioxidant compounds of this invention for the most part are white or pale yellow crystalline solids and are soluble in various organic solvents and in gasolines, diesel fuels, hydrocarbon oils, and the like. These compounds are further characterized by being relatively stable, and for the most part easily crystallizable materials.

The antioxidant compounds of this invention are prepared by reacting (1) a 2,6-dialkyl phenol in which one of the alkyl groups contains from 3 to 8 carbon atoms and is branched on its alpha carbon atom and the other alkyl group contains from 1 to 8 carbon atoms, (2) formaldehyde, and (3) a monohydric alcohol in which the organic portion conforms with the group designated hereinabove as R_3, in the presence of a catalytic quantity

of a metallic hydroxide condensation catalyst, the metallic hydroxide being of a metal selected from the group consisting of alkali and alkaline earth metals. The reaction temperature of this process is in the range of about 20 to about 100° C. It is preferred to conduct the process of this invention within the range of about 30 to about 80° C.

In conducting the above process, the relative proportions of the three reactants can be varied. The actual condensation reaction involves reaction among equimolar amounts of the three reactants. However, it is frequently advantageous to employ excess monohydric alcohol, which excess constitutes the efficacious reaction solvent. Likewise, it is frequently advantageous to employ an excess of formaldehyde in relation to the amount of phenol used because such excess results in higher yield of the desired ether. Thus, the process of this invention can be conducted using from 1 to about 20 moles of monohydric alcohol and from 1 to about 2 moles of formaldehyde per mole of appropriate 2,6-dialkyl phenol used.

The mole ratios of formaldehyde discussed above are based upon the use of formaldehyde monomer. If a polymer of formaldehyde is employed, the amount of this polymer used is based upon the moles of the monomer appearing in the polymer. A particularly convenient form of formaldehyde is an aqueous solution thereof, known in the art as a formalin solution. By using such a solution in the process of this invention, the necessity of using gaseous formaldehyde is avoided.

The metallic hydroxide condensation catalyst is employed in catalytic quantity. This quantity ranges from about 1 to about 50 percent by weight based on the weight of the phenol used in conducting the process. Deviations from these ranges of proportions are permissible, particularly when an excess of alcohol is employed. The alkali metal hydroxide catalysts include lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide and cesium hydroxide. The alkaline earth metallic hydroxides used as catalysts in the process of this invention include magnesium hydroxide, calcium hydroxide, strontium hydroxide and barium hydroxide. Mixtures of these catalysts can be used, especially mixtures of a plurality of alkali metal hydroxides or alkaline earth metal hydroxides. Of the foregoing hydroxides, sodium hydroxide, potassium hydroxide and calcium hydroxide are readily available at low cost and are preferably used.

The preparation of the antioxidant compounds of this invention is illustrated by the following specific examples, wherein all parts and percentages are by weight.

Example XXI

In a reaction vessel equipped with stirring means, reflux condenser, and reagent-adding device were placed 100 parts of 95 percent ethanol, 9 parts of 37 percent aqueous formalin solution, 18 parts of 2,6-diisopropyl phenol, and 7 parts of potassium hydroxide. This mixture was stirred at 75° C. for 3.5 hours. After adding 100 parts of water and 10 parts of concentrated hydrochloric acid, the organic phase was decanted and dried. Vacuum distillation at 1 millimeter of mercury pressure gave 12 parts of (3,5-diisopropyl-4-hydroxybenzyl)-(ethyl) ether melting at 50–51° C. Analysis—Calculated for $C_{15}H_{24}O_2$: Carbon, 76.2 percent; hydrogen, 10.2 percent. Found: Carbon, 76.1 percent; hydrogen, 10.2 percent.

Example XXII

In the reaction vessel of Example XXI were placed 40 parts of absolute ethanol, 9 parts of a 37 percent aqueous formalin solution, 20 parts of 2,6-di-tert-butylphenol, and 7 parts of potassium hydroxide. This mixture was stirred at 45° C. for 1 hour. The product which was isolated from the neutralized organic phase melted at 38–38.5° C. Analysis—Calculated for (3,5-di-tert-butyl-4-hydroxybenzyl)-(ethyl) ether: Carbon, 77.4 percent; hydrogen, 10.7 percent. Found: Carbon, 77.8 percent; hydrogen, 10.8 percent.

Example XXIII

(3,5-di-tert-butyl-4-hydroxybenzyl)-(methyl) ether was prepared as follows: In the reaction vessel described in Example XXI were placed 40 parts of methanol, 9 parts of a 37 percent aqueous formalin solution, 21 parts of 2,6-di-tert-butylphenol, and 4 parts of sodium hydroxide. The mixture was heated at 50° C. for 6 hours. The product was recovered by neutralization followed by distillation as described in Example XXI. The purified (3,5-di-tert-butyl-4-hydroxybenzyl)-(methyl) ether was a pale yellow crystalline material melting at 96° C.

Example XXIV

In the reaction equipment described in Example XXI are placed 60 parts of isobutanol, 9 parts of a 37 percent aqueous formalin solution, 19 parts of 2-isopropyl-6-tert-butylphenol, and 4 parts of sodium hydroxide. After heating the mixture at 60° C. for 4 hours the reaction mixture is distilled at 5 millimeters of mercury pressure to give (3-isopropyl-5-tert-butyl-4-hydroxybenzyl)-(isobutyl) ether.

Example XXV

One hundred parts of cyclohexanol, 12 parts of a 37 percent aqueous solution of formalin, and 16 parts of 2-methyl-6-tert-butylphenol are reacted in the presence of 1 part of sodium hydroxide at a temperature of 80° C. The reaction time is 4 hours. After this time the reaction mixture is poured into cold water, neutralized with 10 percent hydrochloric acid solution, and the organic phase separated. The organic phase is distilled at 10 millimeters of mercury pressure to yield (3-methyl-5-tert-butyl-4-hydroxybenzyl)-(cyclohexyl) ether.

It can be seen from the above illustrative examples that the monohydric alcohols employed in the process of this invention comprise alkanols, cycloalkanols, aralkanols, and alkenols which preferably contain up to about 12 carbon atoms.

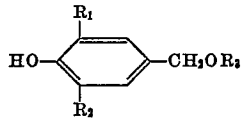
Typical antioxidant compounds of this invention include (3-methyl-5-isopropyl-4-hydroxybenzyl)-(methyl) ether, (3-methyl-5-tert-butyl-4-hydroxybenzyl)-(ethyl) ether, (3-ethyl-5-tert-amyl-4-hydroxybenzyl)-(isopropyl) ether, (3-methyl-5-(2-heptyl)-4-hydroxybenzyl)-(butyl) ether, (3-ethyl-5-(1,1,3,3-tetramethylbutyl)-4-hydroxybenzyl)-dodecyl) ether, (3,5-diisopropyl-4-hydroxybenzyl)-(cyclohexyl) ether, (3,5-di-tert-butyl-4-hydroxybenzyl)-(p-ethylcyclohexyl) ether, (3-isopropyl-5-tert-butyl-4-hydroxybenzyl)-(benzyl) ether, (3-methyl-5-tert-amyl-4-hydroxybenzyl)-(p-methylbenzyl) ether, (3,5-di-tert-amyl-4-hydroxybenzyl)-(allyl) ether, (3,5-diisopropyl-4-hydroxybenzyl)-(7-octenyl) ether, (3,5-di-sec-butyl-4-hydroxybenzyl)-(4-hexenyl) ether, (3,5-diisopropyl-4-hydroxybenzyl)-(heptyl) ether, (3,5-di-tert-butyl-4-hydroxybenzyl)-(2-dodecyl) ether, and the like.

The preferred antioxidant compounds of this invention are illustrated by (3,5-diisopropyl-4-hydroxybenzyl)-(methyl) ether, (3,5-diisopropyl-4-hydroxybenzyl)-(isopropyl) ether, (3,5-diisopropyl-4-hydroxybenzyl)-(hexyl) ether, (3,5-di-tert-butyl-4-hydroxybenzyl)-(ethyl) ether, (3,5-di-tert-butyl-4-hydroxybenzyl)-(tert-butyl) ether, (3,5-di-tert-butyl-4-hydroxybenzyl)-(amyl) ether, (3-isopropyl-5-tert-butyl-4-hydroxybenzyl)(methyl) ether, (3,5-di-tert-amyl-4-hydroxybenzyl)-(tert-amyl) ether, (3-isopropyl-5-(1,1,2,2-tetramethylpropyl-4-hydroxybenzyl)-(ethyl) ether, (3,5-di-(1,1,3,3-tetramethylbutyl)-4-hydroxybenzyl)-(1,1-dimethylbutyl) ether, and the like.

I claim:

1. As a new composition of matter, organic material normally tending to undergo oxidative deterioration in the presence of air, oxygen or ozone, containing a small anti-

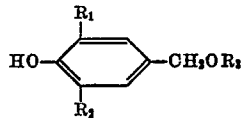
oxidant quantity, up to 5 percent, of a 3,5-dialkyl-4-hydroxybenzyl ether having the general formula:



wherein R_1 is an alkyl group containing from 3 to 8 carbon atoms and is branched on the alpha carbon atom, R_2 is an alkyl group containing from 1 to 8 carbon atoms, and R_3 is selected from the group consisting of alkyl, cycloalkyl, aralkyl and alkenyl.

2. The composition of claim 1 wherein said 3,5-dialkyl-4-hydroxybenzyl ether is 3,5-di-tert-butyl-4-hydroxybenzyl-(methyl) ether.

3. Rubbery conjugated diolefin polymer containing, as an antioxidant therefor, a 3,5-dialkyl-4-hydroxybenzyl ether having the general formula:



wherein R_1 is an alkyl group containing from 3 to 8 carbon atoms and is branched on the alpha carbon atom,

R_2 is an alkyl group containing from 1 to 8 carbon atoms, and R_3 is selected from the group consisting of alkyl, cycloalkyl, aralkyl and alkenyl.

4. The composition of claim 3 wherein said 3,5-dialkyl-4-hydroxybenzyl ether is 2,6-di-tert-butyl-α-methoxy-p-cresol.

5. The composition of claim 1 where said organic material is polyethylene.

6. The composition of claim 7 wherein said 3,5-dialkyl-4-hydroxybenzyl ether is 3,5-di-tert-butyl-4-hydroxybenzyl-(methyl) ether.

7. The composition of claim 1 wherein said organic material is lubricating oil.

8. The composition of claim 2 wherein said organic material is lubricating oil.

9. The composition of claim 1 wherein said organic material is gasoline.

10. The composition of claim 4 wherein said rubbery conjugated diolefin polymer is a butadiene-styrene copolymer.

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