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3,592,950 ALKOXYBENZYLIDENE BISPHENOLS AND THEIR ANTIOXIDANT USE

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4 Claims

ABSTRACT OF THE DISCLOSURE

The combustion chamber deposit formation and exhaust hydrocarbon emission of internal combustion engines is reduced by operating the engine on a fuel containing an alkoxybenzylidene bisphenol such as 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol). These same alkoxybenzylidene bisphenols are also antioxidants.

BACKGROUND

Of recent years, much emphasis has been placed on reducing the amount of hydrocarbons released to the atmosphere. A major source of atmospheric hydrocarbons is the exhaust gas of internal combustion engines. Several methods have been employed to reduce the amount of hydrocarbons emitted in engine exhaust. These methods include engine modifications which enable the engine to operate satisfactorily on a lean fuel/air mixture, air injection into the exhaust manifold, direct flame oxidation of the exhaust gas and the use of oxidation catalysts in the exhaust system. All of these methods have brought about a reduction in the amount of hydrocarbons emitted in exhaust gas. However, one troublesome phenomenon that occurs is that, although the exhaust hydrocarbon emission level may initially be brought to an acceptable level, it tends to rise as the engine is used and accumulates deposits. Because of this, the maximum initial exhaust hydrocarbon emissions of the engine must be at a lower level than is actually necessary so that the hydrocarbon emission will not become unacceptable after the engine has been in service for an extended period. The present invention provides an efficient means of reducing the hydrocarbon emission increase normally encountered during engine use, resulting in an overall reduction in the amount of hydrocarbons emitted to the atmosphere.

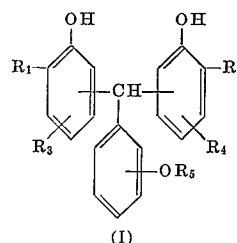
SUMMARY

This invention relates to improved fuel compositions for use in internal combustion engines. It also relates to new antioxidant compounds useful in stabilizing a broad range of organic material. In a preferred embodiment, this invention relates to a liquid hydrocarbon fuel containing an alkoxybenzylidene bisphenol.

One object of this invention is to provide improved liquid hydrocarbon fuel compositions. A further object is to provide liquid hydrocarbon fuel compositions which when used to operate an internal combustion engine reduce the combustion chamber deposit formation and also bring about a reduction in exhaust hydrocarbon emission increase normally encountered during engine use. A still further object is to provide a means of stabilizing organic material normally subject to degradation in the presence

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

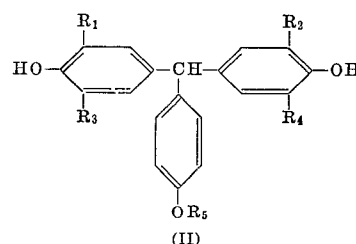


wherein R_1 and R_2 are independently selected from the group consisting of alkyl radicals containing 1–12 carbon atoms and aralkyl radicals containing 7–20 carbon atoms, R_3 and R_4 are selected from hydrogen, alkyl radicals containing 1–12 carbon atoms and aralkyl radicals containing 7–20 carbon atoms, and R_5 is an alkyl radical containing from 1–6 carbon atoms.

Examples of these compounds are:

- 4,4'-(p-methoxybenzylidene) bis(6-tert-butyl-o-cresol)
- 2,2'-(m-methoxybenzylidene) bis(6-tert-butyl-p-cresol)
- 4,4'-(o-hexoxybenzylidene) bis(6-tert-butyl-m-cresol)
- 4,4'-(p-ethoxybenzylidene) bis(2-cyclohexylphenol)
- 4,4'-(p-methoxybenzylidene) bis(6-sec-dodecyl-o-cresol)
- 4,4'-(p-butoxybenzylidene) bis(2-tert-octylphenol)
- 2,2'-(p-pentoxybenzylidene) bis(4,6-di-tert-butylphenol)
- 4,4'-(p-methoxybenzylidene) bis[6-(α -methylbenzyl) o-cresol]

In a preferred embodiment, the alkoxybenzylidene bisphenols have the formula:



wherein R_1 , R_2 , R_3 and R_4 are alkyl radicals containing from 1–12 carbon atoms, and R_5 is an alkyl radical containing from about 1–6 carbon atoms. Examples of these preferred compounds are:

- 4,4'-(p-ethoxybenzylidene) bis(2,6-di-tert-butylphenol)
- 4,4'-(p-butoxybenzylidene) bis(2,6-dicyclohexylphenol)
- 4,4'-(p-hexoxybenzylidene) bis(2,6-di-methylphenol)
- 4,4'-(p-methoxybenzylidene) bis(2,6-di-isopropylphenol)
- 4,4'-(p-methoxybenzylidene) bis(2,6-di-sec-butylphenol)
- 4,4'-(p-methoxybenzylidene) bis(6-tert-octadecyl-o-cresol)

The most preferred additive is 4,4'-(p-methoxybenzylidene) bis(2,6-di-tert-butylphenol).

The additives of this invention are readily prepared by the base catalyzed condensation of 2 moles of the appropriate phenol with an alkoxy-substituted benzaldehyde, as described by Filbey et al. in U.S. 2,807,653.

The following examples serve to illustrate the preparation of typical alkoxybenzylidene bisphenols.

Example 1

In a reaction vessel fitted with a stirrer and thermometer was placed 103 parts of 2,6-di-tert-butylphenol, 34 parts of p-anisaldehyde, 32 parts of 85 percent potassium hydroxide and 240 parts of isopropanol. The mixture was stirred 30 hours at room temperature and then poured into 1000 parts of ice water. A brown product separated which was dissolved in 650 parts of n-hexane. The hexane solution was filtered to remove undissolved solids and the filtrate dried over anhydrous sodium sulfate. The hexane was evaporated at 125° C. under 0.01 mm. Hg. The residue was recrystallized from ethanol, yielding 36.3 parts of which crystals (M.P. 143–145° C.), which analyzed: C, 81.5% and H, 9.48%. Theoretical analysis for 4,4' - (p - methoxybenzylidene)bis(2,6-di-tert-butylphenols) is: C, 81.47% and H, 9.50%.

Example 2

In the reaction vessel of Example 1 place 103 parts of 2,4-di-tert-butylphenol, 34 parts of p-anisaldehyde, 32 parts of 85 percent potassium hydroxide and 240 parts of isopropanol. Heat the mixture to 60° C. and stir for 4 hours. Cool and recover the product, 2,2'-(p-methoxybenzylidene)bis(4,6-di-tert-butylphenol), as in Example 1.

The above procedure may be used to prepare a variety of alkoxybenzylidene bisphenols by changing the starting materials. For example, substituting an equal mole amount of 2,6-di-methylphenol for 2,4-di-tert-butylphenol yields 4,4' - (p-methoxybenzylidene)bis - (2,6-dimethylphenol). Likewise, 6-cyclohexyl-o-cresol yields 4,4'-(p-methoxybenzylidene)bis(6-cyclohexyl-o-cresol). Similarly, 6 - tert-butyl-p-cresol forms 2,2'-(p-methoxybenzylidene)-bis(6-tert-butyl-p-cresol). The use of 6-sec-dodecyl-o-cresol gives 4,4' - (p - methoxybenzylidene)bis(6-sec-dodecyl-o-cresol). Likewise, 6-tert-butyl-m-cresol yields a mixture of 2,2'-(p-methoxybenzylidene)bis(6-tert-butyl-m-cresol) and 4,4' - (p-methoxybenzylidene)bis(6 - tert-butyl-m-cresol).

Similarly, other alkoxy benzaldehydes can be used in the above examples to yield the corresponding substituted benzylidene bisphenol. For example, p-ethoxy benzaldehyde used in Example 1 would form 4,4'-(p-ethoxybenzylidene)bis-2,6-di-tert-butylphenol). In Example 2, the use of 2-methoxy benzaldehyde would result in 2,2'-(o-methoxybenzylidene)bis(4,6-di-tert-butylphenol). Likewise, the use of p-n-butoxy benzaldehyde in the above examples would yield, in Example 1, 4,4'-(p-n-butoxybenzylidene)bis(2,6-di-tert-butylphenyl). In Example 2, 2, would yield 2,2' - (p-n-butoxybenzylidene)bis(4,6-di-tert-butylphenol). Other variations of reactants in the above examples to yield the desired product will be obvious to chemists.

The additives of this invention can be used to reduce emissions and combustion chamber deposits result from the use of a broad range of liquid hydrocarbon fuels including both spark ignition and diesel fuels. It is especially useful in gasoline used in spark ignition engines. These liquid hydrocarbon fuels have a boiling range of from about 95 to about 400° F. and contain aliphatic, aromatic, olefinic and naphthenic hydrocarbons. The hydrocarbon fuels may contain other materials frequently used in such fuels. For example, the fuels may contain antiknock agents such as tetraethyllead, tetramethyllead, triethylmethyllead, diethyldimethyllead, trimethylethyllead, tetravinyllead, triethylvinyllead, diethyldivinyllead, trivinylethyllead, ferrocene, methyl ferrocene, iron carbonyl, methylcyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl nickel nitrosyl, N,N-dimethylaniline, and the like. When metallic antiknock agents are employed, the fuels generally contain a scavenging agent. A particularly useful scavenging agent when lead alkyls

are employed are the halohydrocarbons such as ethylenedichloride, ethylenedibromide, and the like. An especially useful fuel in this invention is a fuel containing from 0.5 to 6 grams of lead per gallon as tetraalkyllead and from 0.5 to 1.5 theories of chlorine as a chlorohydrocarbon and from 0.25 to 0.75 theories of bromine as a bromohydrocarbon. A theory is the amount of halogen required to convert the lead present to lead chloride or lead bromide. Preferred tetraalkyllead anti-knocks are tetraethyllead and tetramethyllead. The most preferred chlorohydrocarbon is ethylenedichloride, and the most preferred bromohydrocarbon is ethylenedibromide.

The fuels can also contain deposit modifying agents such as phosphorus-containing additives, for example, tricresylphosphate, cresyldiphenylphosphate, trimethylphosphate, dimethylcresylphosphate, tris(β -chloropropyl)phosphate, and the like.

The fuels frequently contain antioxidant additives such as 2,6 - di - tert - butylphenol, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4 - methyl-6-tert-butylphenol, phenylenediamines, p-nonylphenol, mixed alkylated phenols, 4,4'-thiobis(3-methyl-6-tert-butylphenol), and the like.

Other materials can be present in the fuel such as deicers, metal deactivators, pour point depressants, boron esters, nickel alkyl phosphates and dyes.

The following examples illustrate the preparation of typical improved fuel compositions of this invention.

Example 3

To a blending vessel is added 1000 gallons of a gasoline having the following properties:

Boiling range, 0° F.	101–375
Research octane number	93
Aromatics (volume percent)	38
Olefins (volume percent)	10
Aliphatics (volume percent)	52

To this gasoline is added a tetraethyllead antiknock agent containing two gram atoms of chlorine as ethylenedichloride per gram atom of lead and one gram atom of bromine as ethylenedibromide per gram atom of lead. The quantity of tetraethyllead antiknock agent added is sufficient to provide 3.17 grams of lead per gallon of fuel. There is then added sufficient 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol) to give a concentration of 0.25 weight percent. The mixture is agitated until thoroughly mixed, resulting in a gasoline having reduced exhaust emission and combustion chamber deposit formation properties.

Example 4

To a blending vessel is added 1000 gallons of a reformat gasoline having the following properties:

Boiling range, ° F.	94–403
Research octane number	97
Aromatics (volume percent)	62
Olefins (volume percent)	5
Aliphatics (volume percent)	33

To this gasoline is added a tetramethyllead antiknock mixture containing one theory of chlorine as ethylenedichloride and 0.5 theory of bromine as ethylenedibromide. A quantity sufficient to provide 2.12 grams of lead per gallon is added. There is also added, as an antioxidant, a mixture of butylated phenols containing about 75 percent 2,6-di-tert-butylphenol, such that the gasoline contains 0.1 weight percent of the antioxidant mixture. Then 0.05 weight percent of 4,4'-(p-hexyloxybenzylidene)bis(2,6-di-sec-butylphenol) is added and the mixture thoroughly stirred, resulting in a gasoline giving reduced emission and combustion chamber deposits weight when used to operate a spark ignition internal combustion engine.

Good results are also obtained in the above example when other alkoxybenzylidene bisphenols such as those

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previously listed are employed as the emission and deposit-reducing agent.

Example 5

To a blending vessel is added 1000 gallons of a gasoline having the following properties:

Boiling range, ° F.	103-399
Research octane number	89
Aromatics (volume percent)	21
Aliphatics (volume percent)	63
Olefins (volume percent)	16

To this gasoline is added an antiknock fluid as shown in Example 8 in quantities sufficient to give a lead concentration of 3.0 grams per gallon as tetraethyllead. This addition concurrently adds 4,4'-(p-ethoxybenzylidene)bis (2,6-di-tert-butylphenol) in an amount equal to 0.05 weight percent.

Example 6

To a blending vessel is added 1000 gallons of gasoline having the following properties:

Boiling range, ° F.	98-410
Research octane	92
Motor octane	85
Aromatics (volume percent)	27
Aliphatics (volume percent)	66
Olefins (volume percent)	7
Sulfur, percent	0.05

To this gasoline is added 2.6 grams of lead per gallon as a mixture of lead alkyls having the approximate composition of 6.25 percent tetramethyllead, 25 percent ethyltrimethyllead, 37.5 percent diethyldimethyllead, 25 percent methyltriethyllead and 6.25 percent tetraethyllead. There is then added 0.3 theories of phosphorous as tricresylphosphate. Following this is added 4,4'-(o-methoxybenzylidene)bis(2-methyl-6-sec-dodecylphenol) in an amount equal to 0.5 weight percent of the mixture. The result is a gasoline having reduced emission-increasing and combustion chamber deposit-forming properties.

Example 7

To a blending vessel is added 1000 gallons of a diesel fuel having a boiling range of from 430-572° F., and a cetane number of 47. To this is added 0.3 weight percent amyl nitrate as a cetane improver. There is then added 0.2 weight percent of 2,2'-(p-methoxybenzylidene)bis (4,6-di-tert-butylphenol), resulting in a diesel fuel having reduced exhaust emission and deposit-forming properties.

In any of the previous examples, the forementioned emission-reducing compounds can be employed, giving fuels having reduced emission properties. Also, the concentrations may be varied from those shown. In general, a concentration of from about 0.01 to 3 weight percent of the emission-reducing additive can be employed. A preferred concentration range is from about 0.05 to about 1 weight percent, and a most useful range is from about 0.1 to 0.5 weight percent.

An especially useful means of adding the alkoxybenzylidene bisphenols to gasoline is to include them in the antiknock fluid concentrate which is normally added to gasoline so that the entire operation can be accomplished in a single blending step. These antiknock fluids contain an antiknock such as, but not limited to, tetra alkyllead plus other materials which beneficially effect the use of the antiknock. Especially useful tetraalkyllead antiknocks are tetraethyllead, tetramethyllead, mixtures thereof, alkyl leads containing both ethyl and methyl groups, and mixtures thereof. These antiknock fluids usually contain a halogen compound as a scavenger. The most frequently employed halogen scavengers are ethylenedichloride and ethylenedibromide. The quantities of these scavengers can be varied within a wide range, but the best results are obtained when the antiknock fluid contains from 0 to 2 theories of chlorine as ethylenedichloride and from 0 to

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1.0 theories of bromine as ethylenedibromide. When less than one theory of chlorine is used there is preferably present about 0.5 theories of bromine. Most preferred antiknock fluids contain tetraethyllead as the antiknock and from 0.5 to 2.0 theories of chlorine as ethylenedichloride and from 0.0 to 1.0 theory of bromine as ethylenedibromide.

An amount of alkoxybenzylidene bisphenol is added to the antiknock fluid such that when the antiknock fluid is added to gasoline in an amount sufficient to raise the octane number of the gasoline to the desired value there will also be included in the gasoline an emission and deposit-reducing amount of the alkoxybenzylidene bisphenol. A preferred range of benzylidene bisphenol concentration in the gasoline is from about 0.1 to 0.5 weight percent. Hence, a useful range of alkoxybenzylidene bisphenol in tetraalkyllead antiknock fluids is from about 0.5 to 30 parts of the alkoxybenzylidene bisphenol per part of lead as tetraalkyllead. This amount will supply from about 0.05 to 3.4 weight percent of the alkoxybenzylidene bisphenol when sufficient antiknock fluid is added to the gasoline to supply 3 grams of lead per gallon as tetraalkyllead. When more or less lead is desired, the concentration range of alkoxybenzylidene bisphenol in the fluid can be varied accordingly to furnish the desired alkoxybenzylidene bisphenol concentration. Following are some representative examples of antiknock fluids containing exhaust and deposit-reducing alkoxybenzylidene bisphenols.

Example 8

An antiknock fluid is prepared by blending the following ingredients:

	Parts
Tetraethyllead	1000
Ethylenedibromide	290
Ethylenedichloride	306
4,4' - (p - methoxybenzylidene) bis(2,6-di-tert-butylphenol)	337
Kerosene	100
Orange dye	5

Example 9

An antiknock fluid is prepared by blending the following ingredients:

	Parts
Tetramethyllead	1000
Ethylenedibromide	295
Trimethyl phosphate	155
4,4' - (p - hexyloxybenzylidene) bis(2,6-di-sec-dodecylphenol)	20,000
Kerosene	200

The above examples are merely illustrative of the typical antiknock fluids which can be prepared. Similar antiknock fluids can be prepared employing other antiknock agents such as triethylmethyllead, diethyldimethyllead, trimethylethyllead, tetravinyllead, triethylvinyllead, diethyldivinyllead, trivinylethyllead, ferrocene, methylferrocene, iron carbonyl, methylcyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl nickel nitrosyl, N,N-dimethylaniline, and mixtures of any of the foregoing. Likewise, any of the previously described alkoxybenzylidene bisphenols can be employed in these antiknock fluids in quantities that will give the desired concentration in the final gasoline blend. These concentrations are easily determined by those experienced in blending additives in gasoline.

Tests have been conducted to demonstrate the useful exhaust emission properties of the present compounds. In these tests, a single cylinder overhead valve engine, having a 10:1 compression ratio and a 36 cubic inch displacement, was operated on a typical commercial gasoline containing 3.17 grams of lead as a commercial tetraethyllead antiknock mixture containing one theory of chlorine as ethylenedichloride and 0.5 theory of bromine as ethylenedibromide. The engine was idled for 45 seconds and

then run at 50 percent wide open throttle for 135 seconds under the following conditions.

Air/fuel ratio ----- 13
R.p.m. ----- 1370
Ignition timing, ° BTC ----- 15

The above cycle was continuously repeated until both deposits and hydrocarbon emissions had stabilized. This usually required from about 100–145 hours of operation. The hydrocarbon content of the exhaust gas was determined using a Beckman 109-A Flame Isomerization Detector, and the deposits were determined by disassembling the engine, removing and weighing the deposits. The procedure was first carried out using a fuel without the emission reducing additive to obtain a baseline exhaust emission increase and then repeated on the same fuel containing an emission reducing additive. This was followed by another test on the fuel, again without the emission additive, to reconfirm the baseline. Using this procedure, the following results in terms of the percent reduction in exhaust hydrocarbon emission increase and combustion chamber deposits were obtained using emission reducing additives of this invention.

Additive—4,4'-(p-methoxybenzylidene)bis-(2,6-di-tert-butylphenol).

Reduction of:

Conc.—0.17.

Emission increase—21%.

Deposit weight—26%.

As these results show, the emission-reducing additives of the present invention effectively reduce both exhaust emission increase and engine deposits.

Another feature of the emission-reducing additives of this invention is that they are readily inducted into an internal combustion engine using a standard Venturi type carburetor. This is unexpected for compounds of such high molecular weight. They would be expected to deposit out in the induction system unless an induction aid or fuel injectors were employed.

The compounds and reaction products of this invention are extremely useful as antioxidants in a wide variety of organic material normally susceptible to deterioration in the presence of oxygen. Thus, liquid hydrocarbon fuels such as gasoline, kerosene and fuel oil are found to possess increased storage stability when blended with a stabilizing quantity of an additive of this invention. Likewise, hydrocarbon fuels containing organometallic additives such as tetraethyllead, tetramethyllead, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl nickel nitrosyl, ferrocene and iron carbonyl have appreciably increased stability when treated with the additives of this invention. Furthermore, lubricating oils and functional fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, have greatly enhanced stability by the practice of this invention. The additives of this invention are extremely useful in stabilizing anti-knock fluids against oxidative degradation. For example, the stabilizing additives of this invention find utility in stabilizing a tetraethyllead antiknock fluid which contains ethylenedichloride and ethylenedibromide.

The additives of this invention are effective in stabilizing rubber against degradation caused by oxygen or ozone. 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. Some examples are acrylic rubber, butadiene-styrene rubber (SBR), polychloroprene, chlorosulfonated polyethylene, fluorocarbon rubbers, isobutylene-isoprene (IIR), polyisoprene, polybutadiene, poly-cis-butadiene, nitrile-butadiene rubber, polyisobutylene rubber, ethylene-propylene rubber, ethylene-propylene-diene terpolymer, polysulfide rubbers, silicone

rubbers, urethanes, india rubber, reclaimed rubber, balata rubber, gutta percha rubber, and the like.

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

The compounds of this invention are superior antioxidants for polymers and copolymers of olefinically unsaturated monomers such as polyethylene (both high pressure and so-called Ziegler type polyethylene), polybutene, polybutadiene (both cis and trans), acrylonitrile-butadiene-styrene terpolymer, and the like.

The additives are especially useful in stabilizing organic material normally subject to oxidative deterioration selected from the group consisting of mineral lubricating oil, synthetic ester lubricants, and polymers and copolymers of ethylenically unsaturated monomers.

The amount of stabilizer used in the organic compositions of this invention is not critical as long as a stabilizing quantity is present, and can vary from as little as 0.001 weight percent to about 5 weight percent. Generally, excellent results are obtained when from 0.1 to about 3 weight percent of the stabilizer is included in the organic compositions.

The following examples serve to illustrate the use of the stabilizers of the present invention in stabilizing some representative organic materials normally subject to deterioration in the presence of oxygen or ozone.

Example 10

A rubber stock is prepared containing the following components:

Component:	Parts
Pale crepe rubber -----	100
Zinc oxide filler -----	50
Titanium dioxide -----	25
Stearic acid -----	2
Ultramarine blue -----	0.12
Sulfur -----	3.00
Mercaptobenzothiazole -----	1.00

To the above base formula is added one part by weight of 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol) and, following this, individual samples are cured for 20, 30, 45 and 60 minutes, respectively, at 274° C. After cure, all of these samples remain white in color and possess excellent tensile strength. Furthermore, they are resistant to degradation caused by oxygen or ozone on aging.

Example 11

A synthetic rubber master batch comprising 100 parts of SBR rubber having an average molecular weight of 60,000, 50 parts 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 prepared. To this is added 1.5 parts of 4,4'-(p-n-butoxybenzylidene)bis(2,6-di-sec-butylphenol). This composition is then cured for 60 minutes employing 45 p.s.i.g. of steam pressure. The resulting synthetic rubber possesses resistance to oxygen and ozone induced degradation.

Example 12

A butadiene acrylonitrile copolymer is prepared from 68 percent 1,3-butadiene and 32 percent acrylonitrile. Two percent, based on the weight of the copolymer, of 4,4'-(p-isopropoxybenzylidene)bis(2,6-di-tert-amylphenol) is added as an aqueous emulsion to the latex obtained from emulsion copolymerization of the butadiene and acrylonitrile monomers. The latex is coagulated with aluminum

sulfate and the coagulum, after washing, is dried for 20 hours at 70° C. The synthetic copolymer so obtained is resistant to oxidative degradation.

Example 13

Three percent of 2,2'-(p-methoxybenzylidene)bis(4-methyl-6-tert-butylphenol) as an emulsion in sodium oleate is added to a rubber-like copolymer of 1,3-butadiene and styrene containing 25 percent styrene. The resulting synthetic elastomer possesses enhanced stability.

Example 14

To a master batch of GR-N synthetic rubber containing 100 parts of GR-N rubber, 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 5 percent, based on weight, of 4,4'-(p-methoxybenzylidene)bis(2-methyl-6-sec-dodecylphenol). After curing, a synthetic rubber is obtained of improved oxidative stability.

Example 15

To a master batch of polyethylene having an average molecular weight of 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 4,4'-(p-methoxybenzylidene)bis(6-tert-butyl-m-cresol). The resulting polyethylene possesses stability against oxidative degradation and shows no tendency to yellow after extensive aging.

Example 16

A linear polyethylene having a high degree of crystallinity (93 percent), and less than one branched chain per 100 carbon atoms, a density of about 0.96 gram per ml. and which has about 1.5 double bonds per 100 carbon atoms, is mixed with 0.005 weight percent of 2,2'-(p-methoxybenzylidene)bis(2,6-di-cyclohexylphenol). The resulting polyethylene is found to possess stability against oxidative degradation.

Example 17

To 100 parts of an ethylene-propylene-dicyclopentadiene terpolymer is added 3 parts of 4,4'-(o-methoxybenzylidene)bis[6-(α -methylbenzyl)-o-cresol], resulting in an ethylenepropylene terpolymer of enhanced stability.

Example 18

To 100 parts of an ethylenepropylene rubber is added 2 parts of 4,4'-(p-hexoxybenzylidene)bis(2,6-di-methylphenol), resulting in an EPR rubber stock of improved stability.

Example 19

After the polymerization of polypropylene in a hexane solvent employing a Ziegler catalyst, the catalyst is neutralized with water and 4,4'-(p-n-propoxybenzylidene)bis(2,6-dicyclohexylphenol) is added to the mixture in quantities such that, after evaporation of the solvent, a Ziegler polypropylene is obtained containing 2 percent of 4,4'-(p-n-propoxybenzylidene)bis(2,6-dicyclohexylphenol). This polypropylene is found to possess excellent stability against degradation caused by oxygen or ozone. Furthermore, this polypropylene is found to resist degradation at elevated temperatures, even in the presence of oxygen. During this high temperature aging the Ziegler polypropylene shows no tendency to discolor.

Example 20

To 1,000 parts of pentaerythritol tetrapelargonate synthetic ester lubricant is added 1 weight percent of 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol). The resulting mixture is melted and stirred, resulting in a molten polypropylene composition possessing excellent resistance to thermal degradation.

Example 21

To 1,000 parts of poly-cis-butadiene dissolved in benzene is added 0.15 weight percent of 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol). The resultant poly-cis-butadiene solution is transferred slowly into boiling water which causes the water and benzene to co-distill, leaving a stabilized poly-cis-butadiene.

Example 22

To 1,000 parts of a crystalline polypropylene made using a Ziegler catalyst is added 1 weight percent of 2,2'-(p-methoxybenzylidene)bis(2,6-di-isopropylphenol). The mixture is melted and immediately stirred, giving a highly stable polypropylene.

Example 23

To 1,000 parts of solvent-refined mid-continent neutral lubricating oil containing 0.05 percent zinc-dilaurylthiophosphate, 4 percent of a poly-laurylmethacrylate VI Improver and 0.05 percent of an over-based calcium sulfonate is added 0.5 percent of 4,4'-(p-methoxybenzylidene)bis(6-tert-m-cresol). The resulting oil is resistant to thermal and oxidant deterioration.

Example 24

To 1,000 parts of an acrylonitrile-styrene-butadiene resin (ABS resin) is added 10 parts of carbon black and 5 parts of 4,4'-(p-butoxybenzylidene)bis(2-tert-butylphenol). The mixture is blended in a Banbury mixer, resulting in a highly stable ABS resin.

Example 25

To 1,000 parts of trimethylol propane tripelargonate synthetic ester-type lubricant is added 5 parts of 4,4'-(p-isopentoxybenzylidene)bis(2-methyl-6-dodecylphenol). The resulting synthetic ester lubricant is stable.

Example 26

To 10,000 parts of di-2-ethylhexyl sebacate is added 200 parts of 4,4'-(p-ethoxybenzylidene)bis(2,6-di-sec-butylphenol). The resulting ester lubricant is stable against oxidative degradation.

Example 27

To 1,000 parts of a solvent-refined neutral oil (95 viscosity index and 200 SUS at 100° F.) containing 6 percent of a commercial methacrylate type VI Improver is added 5 percent of 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol), resulting in a stable lubricating oil.

To 100,000 parts of a commercially available pentaerythritol ester having a viscosity at 100° F. of 22.4 centistokes and known under the tradename of "Hercoflex 600" is added 400 parts of 4,4'-(p-methoxybenzylidene)bis(2,5-di-tert-butylphenol). The resulting synthetic lubricating oil possesses improved resistance against oxidative deterioration.

Example 29

To 100,000 parts of dioctyl sebacate having a viscosity at 210° F. of 36.7 SUS, a viscosity index of 159, and a molecular weight of 427 is added 250 parts of 2,2'-(p-ethoxybenzylidene)bis[2,6-di(α -methylbenzyl)phenol], resulting in a synthetic diester lubricating oil having improved resistance to oxidative degradation.

Example 30

To 1,000 parts of a commercial coconut oil is added 5 parts of 4,4'-(p-methoxybenzylidene)bis(2,6-di-tert-butylphenol), resulting in a vegetable oil with good aging characteristics.

Example 31

To 100,000 parts of lard is added 100 parts of 4,4'-(p-methoxybenzylidene)bis(6-tert-m-cresol), resulting in a lard having resistance to rancidity.

In order to demonstrate the effectiveness of the alkoxybenzylidene bisphenols as antioxidants a, Polyveriform

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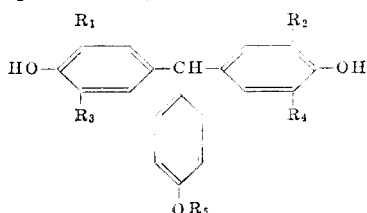
Test was conducted. In this test, 1000 ml. oil samples were prepared from a neutral solvent-refined mid-continent mineral oil containing 0.1 weight percent lead bromide and 0.05 weight percent ferric oxide, as ferric-2-ethylhex-oate. The samples were heated to 300° F. and air passed through them at the rate of 48 l./hr. for 20 hours. After this, the acid number and viscosity of the oil was measured to determine the acid number increase and percent viscosity increase. These are both measures of the degree of deterioration of the oil. The results obtained comparing the unstabilized oil with the oil stabilized with one weight percent of an alkoxybenzylidene bisphenol are shown in the following table.

Additive	Acid No. increase	Viscosity increase percent
None.....	9.1	135
4,4'-(p-methoxybenzylidene) bis (2,6-di-tert-butylphenol).....	7.0	112

The results confirm that the alkoxybenzylidene bisphenols of this invention are not only emission and deposit reducing agents for internal combustion engines, but are also effective antioxidants.

I claim:

1. A compound having the formula:



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wherein R₁ and R₂ are independently selected from the group consisting of alkyl radicals containing 1-12 carbon atoms and aralkyl radicals containing 7-20 carbon atoms, R₃ and R₄ are selected from hydrogen, alkyl radicals containing 1-12 carbon atoms and aralkyl radicals containing 7-20 carbon atoms, and R₅ is an alkyl radical containing from 1-6 carbon atoms.

2. The compound of claim 1 wherein R₁, R₂, R₃ and R₄ are tert-butyl radicals and R₅ is the methyl radical; namely, 4,4' - (p - methoxybenzylidene) bis(2,6-di-tert-butylphenol).

3. The compound of claim 1 wherein R₁, R₂, R₃ and R₄ are tert-butyl radicals and R₅ is the ethyl radical; namely, 4,4' - (p-ethoxybenzylidene) bis(2,6-di-tert-butylphenol).

4. The compound of claim 1 wherein R₁, R₂, R₃ and R₄ are tert-butyl radicals and R₅ is the n-propyl radical; namely, 4,4' - (p - n - propoxybenzylidene) bis(2,6-di-tert-butylphenol).

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