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ANTIOXIDANTS FOR OILS AND OIL COMPOSITIONS CONTAINING THE SAME

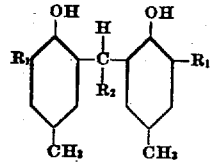
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4 Claims. (Cl. 252—52)

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This invention relates to antioxidants for oils and oil compositions containing the same, and more particularly, it relates to oil compositions containing a compound having the following structural formula:



wherein R_1 is a substituent selected from the class consisting of secondary butyl and tertiary butyl groups, and R_2 is a substituent selected from the class consisting of alkyl, cycloalkyl, aryl, aralkyl, and alkaryl groups and hydrogen. Compounds of this type are insoluble in water and in dilute aqueous alkali solutions, while soluble in hydrocarbon oils and serve as antioxidants and as bearing corrosion inhibitors when incorporated therein.

Gasolines made by the thermal cracking of heavier petroleum oils, and gasolines made by the polymerization of normally gaseous hydrocarbons, contain certain undesirable constituents which are subject to oxidational changes with resultant formation of gums and color-imparting bodies. Catalytic cracking processes have, in general, given gasolines having better oxygen and gum stability than gasolines produced by thermal cracking processes; however, considerable quantities of undesirable constituents, for example, diolefins and cyclic olefins, are still produced. Unless these undesirable constituents are removed or unless their oxidation is inhibited, gasolines are obtained which tend to deposit gums and to discolor in storage and in handling.

Various methods have been employed for removing the undesirable constituents from gasolines such as washing with sulfuric acid or contacting with a solid adsorbent. These methods, however, have not been entirely satisfactory in that high treating losses are encountered and in many instances, gasolines are obtained which are not sufficiently free from the undesirable gum-forming constituents.

A large number of oxidation inhibitors have been developed for obviating the effects of the undesirable constituents, but many of these inhibitors are subject to the disadvantage that they are water soluble and soluble in dilute aqueous alkali solutions so that gasolines to which they have been added tend to be deprived of the anti-

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oxidant material upon contact with water or dilute aqueous alkali solutions.

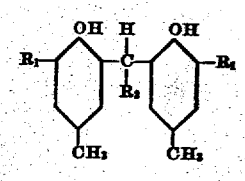
In addition to gasolines, other petroleum oils such as lubricating oils, turbine oils, transformer oils, and the like, as well as animal and vegetable oils are also subject to undesirable oxidational changes in storage and in use, which result in definite deterioration of quality and character of these oils. For example, oxidation of petroleum lubricating oils results not only in the formation of compounds which are corrosive to metals, but also in the deposition of sludge in the crankcase and the formation of varnish and gum on the pistons and cylinder walls of an internal combustion engine. Oxidation of animal and vegetable oils results in the development of rancidity of the oils.

It is an object achieved by this invention, therefore, to provide an oil composition having improved resistance to oxidational changes in storage and in use.

It is a further object achieved by this invention to provide an oil composition containing a compound which will inhibit or substantially retard deterioration of the oil.

It is a still further object achieved by this invention to provide an oil composition containing an antioxidant which is substantially insoluble in water and in dilute aqueous alkali solutions.

We have discovered that animal oils, vegetable oils and mineral oils, particularly petroleum lubricating oils and hydrocarbon oils boiling within a gasoline boiling-point range, susceptible to deterioration, can be effectively inhibited against such deterioration without substantial modification of the other desirable properties of such oils by incorporating into the oils a small amount of a compound having the following structural formula:



wherein R_1 is a substituent selected from the class consisting of secondary butyl and tertiary butyl groups and R_2 is a substituent selected from the class consisting of alkyl, cycloalkyl, aryl, aralkyl, and alkaryl groups and hydrogen. As examples of compounds falling within this class may be included bis(2-hydroxy-3-t(butyl-5-methylphenyl)methane; 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)ethane; 1,1-bis(2-hydroxy-

3-t-butyl-5-methylphenyl) propane; 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl) butane; 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl) isobutane; bis(2-hydroxy-3-t-butyl-5-methylphenyl)-phenylmethane; bis(2-hydroxy-3-t-butyl-5-methylphenyl)-4-methylphenylmethane; 1,1-bis-(2-hydroxy-3-t-butyl-5-methylphenyl)-2-phenylethane; bis(2-hydroxy-3-sec-butyl-5-methylphenyl) methane; 1,1-bis(2-hydroxy-3-sec-butyl-5-methylphenyl) ethane; 1,1-bis(2-hydroxy-3-sec-butyl-5-methylphenyl) propane; 1,1-bis(2-hydroxy-3-sec-butyl-5-methylphenyl) butane; 1,1-bis(2-hydroxy-3-sec-butyl-5-methylphenyl)-isobutane; bis(2-hydroxy-3-sec-butyl-5-methylphenyl) phenylmethane; bis(2-hydroxy-3-sec-butyl-5-methylphenyl)-4-methylphenylmethane; 1,1-bis(2-hydroxy-3-sec-butyl-5-methylphenyl)-2-phenylethane; and the like.

The compounds of the type herein disclosed in addition to stabilizing gasolines are also useful in retarding the oxidation of other petroleum oils, such as lubricating oils, turbine oils, transformer oils, and the like, as well as animal and vegetable oils. We have found that the addition of from about 0.005 to about 2 per cent by weight of the compounds of the type herein disclosed to an oil normally tending to undergo oxidational changes will substantially inhibit or greatly retard the formation of compounds which are corrosive to metals in lubricating oils, will increase the oxygen and gum stability of gasolines and other motor fuels, and inhibit the development of rancidity in animal and vegetable oils. The exact amount of antioxidant used in any particular case will depend upon the nature of the base oil as well as the severity of the conditions to which it is subjected, in any case the amount being sufficient to inhibit the oxidation of said base oils.

The finished lubricating oil may also contain other "additive" agents including oiliness and extreme pressure agents, such as aromatic chlorine compounds, stabilized chlorinated paraffins, sulfurized fatty oils and high molecular weight ketones and esters; viscosity index improvers, such as high molecular weight polymers of isobutylene and the polymers of methacrylic esters; pour point depressants, such as a condensation product of chlorinated wax and naphthalene and a condensation product of chlorinated wax and phenol followed by further condensation of this reaction product with organic acids; detergents, such as nickel naphthenate, metal salts of ethylhexyl salicylate, and metal salts of alkyl substituted phenol sulfides; foam inhibitors, such as organo-silicon oxide condensation products, organo-silicol condensation products, and organo-germanium oxide condensation products; and other oxidation inhibitors, such as alkylated phenols, if desired.

The oxidation inhibitors for use in accordance with our invention may be prepared by various methods. They may for example be prepared by condensing either o-tertiary-butyl-paracresol or o-secondary-butyl-paracresol and an aliphatic or an aromatic aldehyde in the presence of a condensation catalyst. The following are examples of a few of the aldehydes which may be used in accordance with our invention: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, isovaleraldehyde, pivalic aldehyde, caproaldehyde, benzaldehyde, o-, m-, and p-toluic aldehyde, phenylacetaldehyde, α-ethyl caproaldehyde, and the like.

In carrying out the condensation reaction, the molecular ratio of the butyl paracresol to the aldehyde is advantageously maintained at about 2:1. This ratio is based on an aldehyde monomer such as formaldehyde or acetaldehyde. If an aldehyde polymer, such as in the case of formaldehyde, trioxymethylene, or polyoxymethylene is employed, the amount of the polymer used is based upon the equivalent number of moles of the monomer appearing in the polymer. For instance, if trioxymethylene and o-tertiary-butyl-paracresol are condensed, the molecular ratio of the o-tertiary-butyl-paracresol to the trioxymethylene would be about 3:1. In carrying out the reaction, it may further be desirable to dissolve the reactants in a common solvent such as glacial acetic acid. Water is formed in the course of the reaction and the reaction product separates out as a liquid or as a solid. Where the reaction product is a liquid, the product may be found in the upper layer, with the acetic acid on the bottom, or just the reverse may occur. It is therefore essential before discarding either layer to determine which layer contains the product and which layer contains the acetic acid. The product is then separated from the acid layer and washed with water and/or aqueous sodium hydroxide. This washing removes any remaining acid condensation catalyst and also any remaining acetic acid. The washed product may then be purified by recrystallization from a suitable solvent or by fractional distillation.

As condensation catalysts, we may employ sulfuric acid, phosphoric acid, anhydrous aluminum chloride, boron trifluoride, boron fluoride complexes, ferric chloride, anhydrous zinc chloride, hydrogen chloride, activated clays such as acid treated fuller's earth, bentonite, floridin, and the like. The amount of the condensing agent required may be as little as 1 per cent based on the total weight of the reactants. However, larger amounts, as high as 20 per cent by weight, may also be employed. More than about 10 per cent of the condensation catalyst is not ordinarily necessary.

The condensation reaction is carried out at a temperature below about 100° C. and advantageously at a temperature within the range of from about 0° to about 50° to 55° C. If the temperature is allowed to exceed 100° C. for an extended period of time, undesirable side reactions may take place.

The following examples will illustrate the general method employed in preparing the antioxidants for use in accordance with our invention. These examples will also show the oxidation stability of a gasoline containing the compounds prepared in the various examples as compared to an uninhibited sample of the same gasoline. The oxidation stability test employed is known as the A. tS.Ts.Mdrdan.Rzzff–hz,b as the A. S. T. M. standard test, D525-46 (committee D-2).

EXAMPLE I

Bis(2-hydroxy-3-t-butyl-55-methylphenyl)-methane

Into a flask were placed 64.1 grams (0.39 mole) of o-tertiary-butyl-paracresol, 5.9 grams (0.65 mole) of trioxane and 50 ml. of glacial acetic acid. To this was added a solution consisting of 5 grams of anhydrous zinc chloride in 15 ml. of glacial acetic acid. Anhydrous hydrogen chloride was then introduced slowly below the surface of the solution in the flask. The temperature of the solution rose immediately, and was held at a maximum of about 45° C. by regulating

the flow of the hydrogen chloride. After the initial reaction took place, as evidenced by the separation of about 20 ml. of clear liquid, the reaction mixture was cooled to between about 0° and about 10° C. in an ice bath. The addition of hydrogen chloride was continued at this reduced temperature for a period of two hours. During this period white crystals formed. These crystals were separated from the reaction mixture, washed with water and recrystallized from an 80 per cent aqueous alcohol solution. The resulting white crystals melted at 130° to 130.5° C. and were determined to be bis(2-hydroxy-3-t-butyl-5-methylphenyl) methane.

The ultimate analysis of the bis(2-hydroxy-3-t-butyl-5-methylphenyl) methane as above obtained compared with the theoretical composition was as follows:

Ultimate Analysis	Found for Product	Calculated for bis(2-hydroxy-3-t-butyl-5-methylphenyl)-methane
Carbon	81.29	81.13
Hydrogen	9.52	9.47
Oxygen	[1] 9.19	9.40

[1] By difference.

When bis(2-hydroxy-3-t-butyl-5-methylphenyl) methane, prepared as above described, was added to a reference gasoline, having an induction period of 1.6 hours, in the proportion of 0.0002 mole per 100 ml. of gasoline (0.0681 gram per 1 ml.), the induction period increased to 13.6 hours.

EXAMPLE II

1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl) ethane

Into a flask were placed 65.8 grams (0.4 mole) of o-tertiary-butyl-paracresol, 3 grams of anhydrous zinc chloride and 25 ml. of glacial acetic acid. To this was added 8.9 grams (0.202 mole) of acetaldehyde. The mixture thus formed was cooled to between about 0° C. and about 10° C. in an ice bath after which anyhdrous hydrogen chloride was introduced slowly below the surface of the solution. The addition of hydrogen chloride was continued for four hours while maintaining the temperature of the reactants between about 0° and about 10° C. The reaction mixture was then allowed to stand over night during which time white crystals were formed. These crystals were separated from the reaction mixture, washed with water, and recrystallized from a 78 per cent aqueous alcohol solution. The resulting white crystals melted at 105° C. and were determined to be 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)-ethane.

Ultimate Analysis	Found for Product	Calculated for 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)ethane
Carbon	81.37	81.31
Hydrogen	9.80	9.67
Oxygen	[1] 8.83	9.02

[1] By difference.

When 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl) ethane, prepared as above described, was added to a reference gasoline, having an induction period of 1.6 hours, in the proportion of 0.0002 mole per 100 ml. of gasoline (0.0709 gram per 100 ml.) the induction period increased to 10.5 hours.

EXAMPLE III

1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)-isobutane

Into a flask were placed 49.3 grams (0.3 mole) of o-tertiary-butyl-paracresol, 10.8 grams (0.15 mole) of isobutyraldehyde and 25 ml. of glacial acetic acid. The mixture thus formed was cooled to between about 0° and about 10° C. in an ice bath after which anhydrous hydrogen chloride was introduced slowly below the surface of the solution. The addition of hydrogen chloride was continued for three hours while maintaining the temperature of the reactants between about 0° C. and about 10° C. A white crystalline product which formed was washed with 5 per cent aqueous sodium hydroxide, then with water, and recrystallized from an alcohol solution. The white crystals thus obtained melted at 188°–189° C. and were determined to be 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl) isobutane.

Ultimate Analysis	Found for Product	Calculated for 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl)-isobutane
Carbon	81.71	81.62
Hydrogen	9.99	10.01
Oxygen	[1] 8.30	8.37

[1] By difference.

When 1,1-bis(2-hydroxy-3-t-butyl-5-methylphenyl) isobutane, prepared as above described was added to a reference gasoline, having an induction period of 1.0 hours, in the proportion of 0.0002 mole per 100 ml. of gasoline (0.0765 gram per 100 ml.), the induction period increased to 6.4 hours.

EXAMPLE IV

Bis(2-hydroxy-3-t-butyl-5-methylphenyl)phenylmethane

Into a flask were placed 49.3 grams (0.3 mole) of o-tertiary-butyl-paracresol, 15.9 grams (0.15 mole) of benzaldehyde, 3 grams of anhydrous zinc chloride, and 15 ml. of glacial acetic acid. The solution thus formed was cooled to between about 0° and about 10° C. in an ice bath after which anhydrous hydrogen chloride was introduced slowly below the surface of the solution. The addition of hydrogen chloride was continued for one hour while maintaining the temperature of the reactants between about 0° and about 10° C. The reaction mixture was then allowed to stand until the next day, during which time a solid material precipitated out of solution. The solid was separated from the liquid reaction mixture and recrystallized from an alcohol solution. A white crystalline product having a melting point of 171°–172° C. was obtained. This product was determined to be bis(2-hydroxy-3-t-butyl-5-methylphenyl) phenylmethane.

Ultimate Analysis	Found for Product	Calculated for bis(2-hydroxy-3-t-butyl-5-methylphenyl)-phenylmethane
Carbon	83.70	83.61
Hydrogen	8.94	8.71
Oxygen	[1] 7.36	7.68

[1] By difference.

When bis(2-hydroxy-3-t-butyl-5-methylphenyl) phenylmethane, prepared as above described,

was added to a reference gasoline, having an induction period of 1.6 hours, in the proportion of 0.0002 mole per 100 ml. of gasoline (0.0833 gram per 100 ml.), the induction period increased to 8.6 hours.

EXAMPLE V

Bis(2-hydroxy-3-sec-butyl-5-methylphenyl)methane

Into a flask were placed 41.1 grams (0.25 mole) of o-sec-butyl-paracresol, 3.8 grams (0.042 mole) of trioxane, 3 grams of anhydrous zinc chloride and 50 ml. of glacial acetic acid. The solution thus formed was cooled to about 10° to 15° C. in an ice bath after which anhydrous hydrogen chloride was introduced slowly below the surface of the solution. The addition of hydrogen chloride was continued for about 15 minutes during which time the reaction temperature was not allowed to rise above about 50° C. A product consisting essentially of bis(2-hydroxy - 3 - sec - butyl - 5 - methylphenyl)-methane was obtained.

When the product consisting essentially of bis(2 - hydroxy - 3 - sec - butyl - 5 - methylphenyl)methane, was prepared as above described, was added to a reference gasoline, having an induction period of 3.5 hours, in the proportion of 0.002 mole per 100 ml. of gasoline (0.0681 gram per 100 ml.), the induction period increased to 7.0 hours.

The fact that the other desirable properties of a lubricating oil are not deleteriously effected by the addition of the antioxidants in accordance with our invention is illustrated in the following table wherein oil compositions containing from 0.1 to 1.0 per cent by weight of bis(2-hydroxy - 3 - t - butyl - 5 - methylphenyl)-methane are compared with an uninhibited base oil. As will be noted from the Lauson Engine Test, the addition of bis(2-hydroxy-3-t- butyl-5-methylphenyl)methane greatly reduced the corrosion of a copper-lead bearing.

Composition per cent by weight:					
Base oil	100	99.9	99.7	99.5	99.0
(bis (2-hydroxy-3-t-butyle-5-methylphenyl) methane	---	0.1	0.3	0.5	1.0
Oil inspection characteristics:					
Gravity,° A. P. I	29.1	29.7	29.1	29.0	28.9
Viscosity, SUS at—					
100° F	522	510	520	525	530
210° F	67.2	67.5	67.2	67.0	67.0
Viscosity index	107	109	106	105	104
Color, N. P. A	2—	2—	2—	2½—	2—
Neutralization No	0.01	0.01	0.01	0.01	0.01
Ash, per cent	0.01	0.01	0.01	0.01	0.01
40 hour results of Lauson Engine Test (L-4-prototype):					
C/L bearing corrosion, Chevrolet equivalent, grams	—0.176	—0.121	—0.05	—0.05	—0.019

Compounds of the class herein described were also found to be extremely satisfactory as antioxidants for turbine oils. For example, we determined the tendency of a turbine oil to oxidize in use and compared this with the tendency toward oxidation of the same oil having incorporated therein a small amount of bis(2-hydroxy - 3 - t - butyl - 5 - methylphenyl)-methane. The test was then repeated using 1,1 - bis(2 - hydroxy - 3 - t - butyl - 5 - methylphenyl)isobutane as the inhibitor. The tendency toward oxidation was determined in both cases by a standardized method of testing steam turbine oils, being that of Rogers and Miller (Ind. Eng. Chem., 19, 308, (1927)), modified in that we controlled the supply of oxygen by metering to provide 4 liters per hour; we used a 300 ml. sample instead of a 500 gram sample, and

ran the test in the presence of 60 mls. of distilled water and in the presence of metallic iron and copper. The presence of water necessitated the provision of a reflux condenser to prevent loss from volatilization. About 3 feet each of fine iron wire and fine copper wire were submerged in the oil during the test.

In this test the deterioration of the oil due to oxidation in the presence of water, iron and copper, is measured in terms of neutralization numbers over a long period of time while the oil undergoing test is subjected to conditions of accelerated oxidation.

In accordance with this test, an uninhibited turbine oil having an initial neutralization number of 0.01 had a neutralization number of 0.2 after only 48 hours under accelerated oxidation. A sample of the same turbine oil having incorporated therein 0.2 per cent by weight of bis(2-hydroxy - 3 - t - butyl - 5 - methylphenyl)-methane had a neutralization number of only 0.16 even after 4128 hours. When 0.2 per cent of 1,1 - bis(2 - hydroxy - 3 - t - butyl - 5 - methylphenyl)isobutane was added to the same turbine oil, the neutralization number even after 2000 hours was only 0.16.

In order to illustrate the advantageous results obtained when a compound of the class herein described is added to a vegetable oil, separate samples of linseed oil and linseed oil containing 0.5 per cent of bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane were subjected to an oxidation stability test in a bomb at 100° C. under 125 p. s. i. of oxygen. After twenty-three hours in the test bomb the oxygen pressure on the uninhibited sample had decreased eighty pounds while the oxygen pressure on the inhibited sample had decreased only nineteen pounds, indicating much less absorption of oxygen by the inhibited sample. From these results, it can be seen that the compounds herein described are effective in suppressing the oxidation of vegetable oils.

The compounds of the class herein described are also useful in inhibiting the oxidation of animal oils. For example, 125 gram samples of lard oil and lard oil containing 0.5 per cent of bis(2 - hydroxy-3-t-butyl-5-methylphenyl)methane were separately agitated and blown with air for six hours at 160°–170° C., the rate of air introduction being ten liters per hour.

The following results were obtained:

Time, Hours at 160°–170° C.	Viscosity, 110° F., SUS	
	Uninhibited	Inhibited
0	199	209
6	2,003	1,665

The fact that the compounds of the class herein described inhibit the oxidation of animal oils is evidenced from the above difference in viscosity increase.

While our invention has been described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such illustrated examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A lubricant comprising a major amount of a lubricating oil normally tending to undergo

oxidational changes and a small amount, sufficient to substantially retard such oxidational changes, of bis(2-hydroxy-3-t-butyl-5-methylphenyl) methane.

2. A composition of matter comprising a major amount of an oil selected from the group consisting of animal, vegetable, and mineral oils normally tending to undergo oxidational changes and a small amount, sufficient to substantially retard such oxidational changes, of bis(2-hydroxy-3-t-butyl-5-methylphenyl) methane.

3. A composition of matter comprising a major amount of a hydrocarbon oil normally tending to undergo oxidational changes and a small amount, sufficient to substantially retard such oxidational changes, of a bis(2-hydroxy-3-butyl-5-methylphenyl) methane, wherein the butyl group is selected from the class consisting of secondary butyl and tertiary butyl groups.

4. A composition of matter comprising a major amount of an oil selected from the group consisting of animal, vegetable, and mineral oils normally tending to undergo oxidational changes

and a small amount, sufficient to substantially retard such oxidational changes, of a bis(2-hydroxy-3-butyl-5-methylphenyl) methane, wherein the butyl group is selected from the class consisting of secondary butyl and tertiary butyl groups.

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