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3,361,672

STABILIZED ORGANIC COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

The presence of aromatic cyclic dioxaboron compounds prepared by the reaction of an orthodihydroxy or 2,2'-dihydroxy diaromatic compound with boric acid or boron trihalide and water provides lubricating compositions with improved antioxidant properties. Of particular value are those dioxaboron compounds which contain one or more alkyl substituents having from 10 to 30 carbon atoms on the aromatic nucleus.

This invention relates to the stabilization of organic compositions and particularly it relates to lubricant and fuel compositions containing novel compounds which provide stabilizing properties thereto.

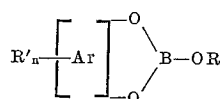
The failure of performance of certain organic compositions, such as lubricants and fuels, including mineral oils, synthetic ester lubricants, fuel oils and the like, is often attributable to the deterioration caused by oxidation. For example in modern internal combustion engines and in turbojet aircraft engines, lubricants may be attacked by oxygen or air at high temperatures to form heavy viscous sludges and resins which become deposited on the engine surfaces and acids corrosive enough to destroy metal. Quite often, the oxidation attack is catalyzed by the very metals used in engine construction. As a result, the lubricant cannot perform its required task effectively and the engine does not operate efficiently. In the long run therefore parts of the engine become worn or damaged in unduly short periods of service.

To overcome such undesirable results, lubricants and fuels and other such working organic compositions are originally blend with a variety of additives to disperse the sludge and gummy resins, to neutralize acid by-product, to aid the lubricant in withstanding the pressure found in engines, or simply to prevent oxidation. Increasing demands on the lubricant, however, such as brought about by the use of newer and larger engines operating at higher temperatures and pressures, urge the search for newer additives which can provide increased oxidation resistance.

A major object of this invention is to provide novel additives for organic composition. Another object is to provide novel additives for lubricant and fuel compositions which help resist the attack of oxidation on such compositions. A further object is to provide mineral oil and synthetic ester lubricant compositions containing novel antioxidants. Other objects of this invention will become apparent from the following disclosure.

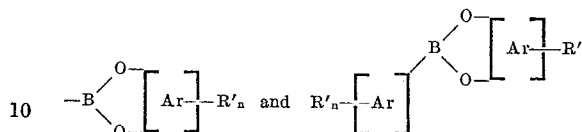
It has now been discovered that organic compositions may be provided with improved oxidation by incorporating therewith a minor amount of a novel boron compound of the class designated as aromatic dioxaboron compounds prepared by the reaction of an orthodihydroxy or 2,2'-dihydroxy aromatic compound and boric acid or boron trihalide and water.

The product is believed to have the general structure



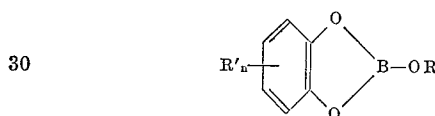
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wherein Ar may be o-phenylene, o-naphthalene, 2,2'-diphenylene, 2,2'-dinaphthalene, or 5,6-benzo-2,2'-diphenylene, R may be hydrogen, and hydrocarbyl, including alkyl, aryl, aralkyl and alkaryl, the alkyl groups for R having from 1 to about 20 carbon atoms,

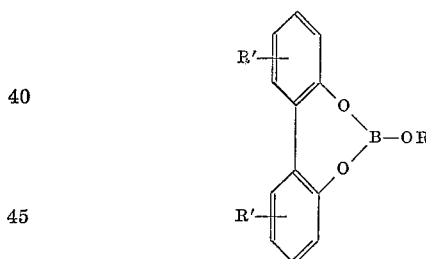


R' may be hydrogen, hydroxy, hydrocarbyl, including alkyl, alkenyl, aryl, aralkyl, alkaryl, oxyhydrocarbyl and halohydrocarbyl wherein the alkyl groups in R' may have from 1 to about 40 carbon atoms; and n is from 0 to any number of available substituent positions for R' on the nucleus. For convenience in referring to these boron compounds, they are herein also designated as aromatic 1,3,2-dioxaboroles and 1,3,2-dioxaborepins. The mole ratios of the reactants used in preparing the novel compounds of this invention may be varied in a manner to be described to obtain the said compounds. These compounds evidence effective antioxidant stability for fuels and for hydrocarbon and synthetic ester lubricants.

The simplest boron compound, benzo-1,3,2-dioxaborole, in this invention is believed to have the following structure



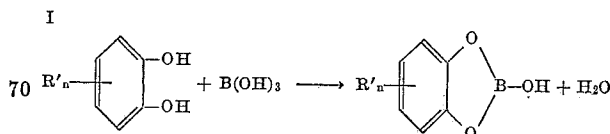
wherein R and R' have the above definitions and n is from 0 to 4. When Ar is a diarylene such as 2,2'-diphenylene, the simplest structure is theorized to be as follows:



wherein R and R' have the above definitions. This compound may be termed benzo-1,3,2-dioxaborepin. Since R' may occupy all of the available positions on the aromatic ring, the four positions on the phenylene radical may be substituted. For naphthalene up to six R' groups may be present. When Ar is diphenyl a maximum of 8 positions are available, and 12 for dinaphthyl.

These novel compounds are prepared by reacting boric acid or a boron trihalide with a polyhydroxy aromatic compound. In the case of phenylene and naphthalene, the hydroxy radicals are in the ortho position. In the case of diphenylene and dinaphthalene, the hydroxy radicals are in the 2,2'-position. The structures given for the resulting boron compounds of this invention are not necessarily conclusive. It is theorized from the expected course of the reaction that the structures as disclosed above most probably result.

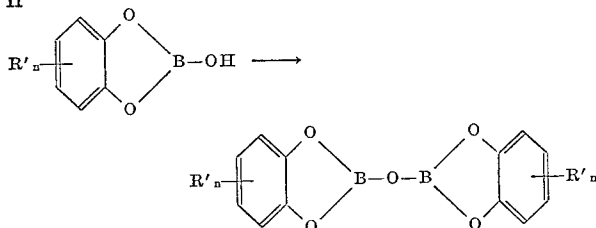
For example, boric acid may be reacted with an alkylated catechol as follows:



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By heating two moles of the above product in reaction I to drive off water, the anhydride form may result as follows:

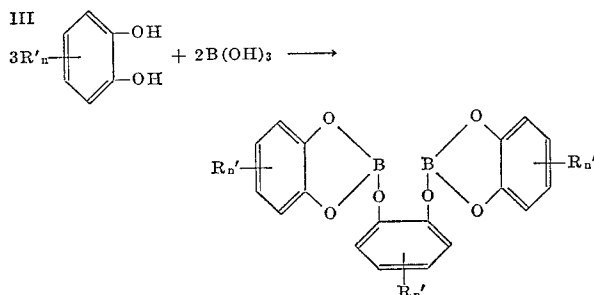
II



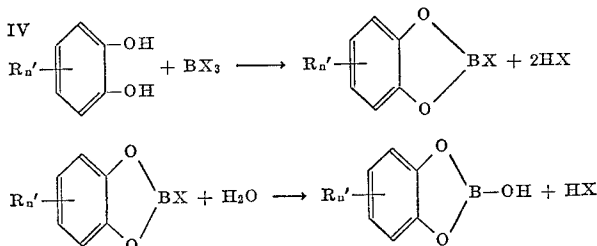
It may be seen that by performing reaction II with two different 1,3,2 - dioxaboron compounds, unsymmetrical products may be produced. In this series of reactions I and II, the catechol and boric acid were reacted on an equimolar basis; the products of the reactions may be mixtures of products as well.

In reaction sequence III the ratio of catechol to boric acid is 3 to 2 as follows:

III

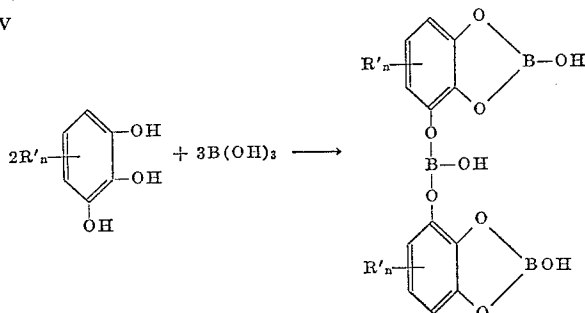


If the product of reaction I is prepared with a boron trihalide, an additional step of hydrolyzing the halogen indicated in reaction IV.



A further variation of the dioxaboroles in this invention utilizes a trihydroxy compound, such as a substituted pyrogallol. To illustrate this reaction, the mole ratio of pyrogallol to boric acid is 2 to 3 although this is not a critical limitation. It is theorized that the sequence occurs as follows:

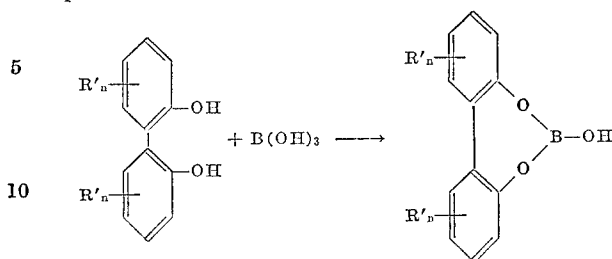
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By employing a 1:1 ratio, instead however, the reaction product of I may be obtained wherein one of the R' radicals is hydroxy.

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When Ar is a diaryl, the reaction sequence may be depicted as follows:



15 Again the boron trihalide may be used in place of boric acid, followed by the water treatment to hydrolyze the halogen atom.

The reaction is preferably performed in the presence of an inert organic solvent for the two reactants. The common solvents are benzene, toluene, xylene, and the lower aliphatic alcohols such as ethyl, propyl, and butyl alcohol. When the reactant is boron trihalide, the reaction mixture is maintained at a low temperature, usually in the range of from -50°C. to about 25°C. , and preferably an inert atmosphere is maintained in the reaction vessel. The hydrolysis step is performed with no external temperature controls needed. When boric acid is used, the reaction need not be cooled in the initial phase as with the halide. To insure complete reaction in either case, the reaction mass is heated to remove the water of condensation. Thereafter the solvent may be stripped off and the remaining product filtered, or otherwise refined, as may be necessary.

If it is desired to convert R from hydrogen to an alkyl or other substituent, the products formed above may be further reacted with an alcohol, or phenol or alkyl halide using known esterification methods, whereby the hydrogen atom is replaced by the desired group.

Specific substituents for R and R' aside from hydrogen include straight chain and branched chain alkyl groups such as methyl, ethyl, propyl, isopropyl, tert-butyl, octyl, dodecyl, hexadecyl, octadecyl, tetradecyl; aryl groups such as phenyl, naphthyl and substituted aryl or aralkyl groups, such as tolyl, nonylphenyl, phenyloctyl and the like; and cycloaliphatic groups, such as cyclohexyl. R' may also include oxygen-containing hydrocarbyl groups, such as those hydrocarbyl radicals listed above attached to an oxygen atom, including methoxy, ethoxy, hydroxybutyl and the like; halogen such as chlorine, bromine and iodine; halogenated hydrocarbyl and halogenated oxhydrocarbyl groups, and nitrogen-containing groups such as amino, alkylamino and nitro.

The most desirable R' groups, according to this invention, are obtained from hydrocarbons, and especially polyolefins containing from 10 to 30 carbon atoms, which may be substituted onto the nucleus of the aromatic hydroxy compound. Such olefins as a C_{15} to C_{20} 1-olefin mixture, a C_{18} to C_{20} 1-olefin mixture, hexadecene, propylene tetramer, and other similar ethylenic olefins may be used in providing substituents for the aromatic structure.

The method of alkylating the aromatic rings with these preferred olefins and other hydrocarbyl groups may be performed by known reaction techniques, wherein the reaction is catalyzed by the use of the typical alkylation catalysts, such as AlCl_3 and boron trifluoride. A particularly preferred catalyst is boron trifluoride etherate. The reaction may be performed at a temperature in the range of about 80°C. to about 125°C. for a period of from about 30 minutes to about 20 hours.

We have found that the aromatic dioxaboron compounds of this invention provide a variety of functions for organic compositions in which they are present. They reduce the formation of acids and sludge in the presence of an oxidizing medium. The large viscosity change usual

ly attendant upon the oxidation of said organic materials is effectively decreased and the loss of metals normally used in engine construction is greatly reduced.

The additives of this invention may be employed in mineral oil lubricants and in synthetic lubricants, and industrial fluids, including diesters prepared from monohydric alcohols or glycols and mono- and dicarboxylic acids, such as di-(2-ethylhexyl)sebacate; trimethylolpropane and pentaerythritol esters of monocarboxylic acids, including acetic, propionic, butyric, valeric, caprylic, pelargonic and capric, and such esters prepared from a mixture of acids to produce mixed esters; olefin polymer fluids, such as decene-1 polymer. Other organic compositions in which these compounds may find utility are in light distillate fuels, diesel fuels, and fuel oils, which may undergo oxidation during storage at relatively lower temperatures than encountered in engines. Solid organic compositions include polymers which may become embrittled by oxidation. The preferred utility, however, lies in the lubricant compositions, particularly hydrocarbon and synthetic ester oil formulations.

The following specific examples illustrate the invention more clearly although the invention is not limited thereto. Any mention of parts or percentage is deemed to be on a weight basis unless otherwise specified.

Example 1

Into a reactor equipped with a thermometer, stirrer, condenser and condensate trap, were added 60 grams (0.375 mole) of 2,3-naphthalenediol, 363 grams (1.5 moles) of a C_{15} to C_{20} 1-olefin mixture (average molecular weight of 242) and 35 grams of boron trifluoride etherate. The mixture was stirred at a temperature of from 90° to 95° C. for 12 hours. The product was washed with water until the washings were neutral to litmus paper and the resulting solution was topped to 230° C.

To 81.2 grams (0.07 mole) of the tetra-(C_{15} - C_{20})-substituted-2,3-naphthalenediol prepared above was added 4.3 grams (0.07 mole) of boric acid in 300 ml. of benzene. The reaction mixture was refluxed and water of reaction was collected in the condensate trap. Approximately 1.1 ml. of water had been collected after about 2.5 hours of reaction (1.26 ml. theory). The product was stripped to 150° C. and the remainder was filtered through a funnel coated with a diatomaceous earth filter aid. The yield of tetra-(C_{16} - C_{20})-2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole) product was 83 grams (98% of theory).

Analysis.—Calc'd: Percent B, 0.92. Found: Percent B, 0.80.

Example 2

In 200 ml. of toluene in a nitrogen-blanketed vessel was dissolved 8.2 grams of boron trichloride (0.07 mole) at -35° C. To the solution was added 81.8 grams (0.07 mole) of the tetra-(C_{16} - C_{20})-2,3-naphthalenediol prepared in Example 1 in 100 ml. of toluene dropwise at a temperature of from -30° to -40° C. After this addition was completed the contents of the reactor were stirred and allowed to warm to room temperature during which time hydrogen chloride evolution took place. The reaction mass was stirred for another two hours at room temperature and then heated to 50° C. until no further hydrogen chloride was detected. To the reaction mixture was added 1.26 grams (0.07 mole) of water at room temperature and the reaction contents were stirred for an additional 30 minutes. The mixture was stripped to 150° C. under the vacuum and filtered through the diatomaceous earth filter aid. The yield of resulting tetra-(C_{16} - C_{20})-2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole) product was 84.7 grams (100% of theory).

Analysis.—Calc'd: Percent B, 0.92. Found: Percent B, 0.85.

Example 3

The procedure of Example 1 was followed in the preparation of tri(tetrapropyl)-2,3-naphthalenediol by reacting

three molar equivalents of propylene tetramer with one molar equivalent of the 2,3-naphthalenediol, using boron trifluoride etherate as a catalyst. A mixture of 40 grams (0.06 mole) of tritetrapropyl-2,3-naphthalenediol and 3.72 grams (0.06 mole) of boric acid was reacted in benzene using the method of Example 1 to produce tri(tetrapropyl)-2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole).

Analysis.—Calc'd: Percent B, 1.6. Found: Percent B, 1.51.

Example 4

The product of Example 3 was prepared by the reaction of the diol with an equivalent number of moles of boron trichloride in toluene. By the method of Example 2 the resulting chloride intermediate was hydrolyzed with an equivalent amount of water.

Analysis.—Calc'd: Percent B, 1.6. Found: Percent B, 1.9.

Example 5

In this example tetra(tetrapropyl)-2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole) was prepared according to the method of Example 2. The reaction was performed in the presence of benzene at a temperature ranging from -35° to 30° C. over a 2.5-hour period. The resulting chloride intermediate was hydrolyzed with an equivalent amount of water.

Analysis.—Calc'd: Percent B, 0.98. Found: Percent B, 0.85.

Example 6

Into a reaction vessel as described in Example 1, one molar equivalent of catechol was reacted with two molar equivalents of a decene trimer using boron trifluoride etherate as a catalyst. The alkylation procedure was the same as followed in Example 1. A reaction mixture of 95 grams (0.1 mole) of the resulting ditriacontylcatechol, 6.2 grams (0.1 mole) of boric acid and 200 ml. of toluene was prepared and the reaction conducted according to the procedure of Example 1 to form ditriacontylbenzo-(2-hydroxy-1,3,2-dioxaborole).

Analysis.—Calc'd: Percent B, 1.1. Found: Percent B, 1.0.

Example 7

Following the procedure of Example 1 an amount of 66 grams (0.6 mole) of catechol was reacted with 478 grams (1.8 moles) of a C_{18} - C_{20} 1-olefin mixture using boron trifluoride etherate as the catalyst. The resulting product was reacted with 37.2 grams (0.6 mole) of boric acid in the manner of Example 1, to form a tri-(C_{18} - C_{20}) benzo-(2-hydroxy-1,3,2-dioxaborole).

Analysis.—Calc'd: Percent B, 0.94. Found: Percent B, 0.78.

Example 8

A mixture of 391 grams (0.5 mole) of trihexadecylcatechol prepared according to the methods of the above examples and 30.9 grams (0.5 mole) of boric acid was reacted in the presence of benzene according to the procedure of Example 1 to produce tri-2-hexadecylbenzo-(2-hydroxy-1,3,2-dioxaborole).

Example 9

A mixture of 162 grams (1 mole) of pyrogallol, 672 grams (3 moles) of hexadecene-1 and 50 grams of boron trifluoride etherate was prepared in a reaction vessel similar to that of Example 1 and stirred at 90° to 95° C. for 16 hours. The reaction mass was washed with water until the washings were neutral to litmus paper. The organic layer was topped to 230° C.

A mixture of 300 grams (0.36 mole) of the resulting trihexadecylpyrogallol and 33.5 grams (0.54 mole) of boric acid was refluxed in the presence of 100 ml. of benzene until 12 ml. of water had been collected in the trap. The reaction mass was topped to 260° C. under vacuum to yield tri-2-hexadecylpyrogallol borate.

Example 10

In the reaction vessel similar to that described in Example 1, 18.3 grams (0.1 mole) of 2,3-naphthalenediol was dissolved in 400 ml. of toluene. The vessel was blanketed in a nitrogen atmosphere and 11.7 grams (0.1 mole) of boron trichloride was added at a temperature of from -35° to -45° C. At the end of this addition step, the reaction mass was allowed to warm to room temperature, i.e. about 27° C., and was stirred until the hydrogen chloride evolution subsided. The mixture was heated at 50° C. for an additional 20 minutes without further hydrogen chloride evolution. The mixture was cooled to room temperature and 1.8 grams (0.1 mole) of water was added. A further quantity of hydrogen chloride evolved upon this addition and the reaction mass was stirred at room temperature until no further hydrogen chloride evolution was noticed. A solid 2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole) was obtained, having a melting point of 142° – 145° C.

Analysis.—Calc'd: Percent B, 5.9. Found: Percent B, 5.2.

Example 11

In the reaction vessel as described in Example 1, a mixture of 66 grams (0.6 mole) of catechol, 300 grams (1.8 moles) of dodecene-1 and 25 grams of boron trichloride etherate was heated at 85° to 90° C. for 10 hours. The product was washed with water until the washings were neutral to litmus paper. The organic layer was stripped to 125° C. under vacuum.

The resulting product was dissolved in 200 ml. of benzene and 37.2 grams (0.6 mole) of boric acid was added. Upon refluxing, water was removed in an azeotropic mixture with benzene and collected in a condensate trap. The product was topped to 150° C. under vacuum and

filtered through a diatomaceous earth filter aid. The yield of tridodecylbenzo(2-hydroxy-1,3,2-dioxaborole) product was 357.5 grams (93.5% theory).

Analysis.—Calc'd: Percent B, 1.65. Found: Percent B,

5 1.2.

Example 12

A mixture of 120 grams (0.65 mole) of 2,2'-biphenol and 600 grams (2.6 moles) of hexadecene and 35 grams of boron trifluoride etherate was stirred at about 90° C. for 10 hours. The reaction mass was washed with water until the washings were neutral to litmus paper. The organic layer was topped to 245° C. under vacuum.

A mixture of 200 grams of the above product, 11.1 grams (0.18 mole) of boric acid, 50 ml. of isopropyl alcohol and 50 ml. of benzene was heated at 90° C. for several hours. The mixture was thereafter heated slowly to 245° C. until the clear liquid product of tetrahexyldecyl-2,2'-biphenyl-1,3,2-dioxaborepin was obtained.

20 EVALUATION OF PRODUCTS—CATALYTIC OXIDATION TEST

The test procedure involves passing a stream of air at a rate of five liters per hour through the test composition for 40 hours, at 325° F. The air treatment is conducted in the presence of iron, copper, lead, and aluminum. The neutralization, or acid, number and kinematic viscosity at 210° F. of the samples are taken before and after the test. Weight loss of the lead specimen and the quantity of visual sludge are also observed. The difference in neutralization number and viscosity increase, the lead loss and sludge formation are tabulated below in Table 1. For comparison purposes the products prepared in accordance with this invention are compared with a known borate, i.e., trioctyl borate. The oil medium used for the test samples is a solvent-refined mineral oil.

TABLE 1

Additive	Conc., Wt. Percent	ANN	Viscosity Increase, Percent	Lead Loss, mg.	Sludge ¹
None.....	-----	19.3	460	220	Medium.
Example 1.....	4.0 2.0 1.0 0.5	0.4 0.5 2.4 16.2	9.0 7.5 10.1 102	0.2 0 3.9 124	Trace. Do. Do. Medium.
Example 2.....	4.0 2.0 1.0	0.3 0 0.5	6.7 1.1 -1.3	0.2 0.4 0	Light. Nil. Nil.
Example 3.....	4.0 2.0 1.0 0.5	-0.05 0 0 0	7.0 0 0.37 0.19 -2.0	0.3 0.3 0.3 0.2	Light. Nil. Nil. Nil.
Example 4.....	2.0 1.0 0.5	0 -0.1 0.25	1.5 0 0.5	Nil Nil Nil	Nil. Trace. Do.
Example 5.....	4.0 2.0 1.0	-0.3 0 4.3	7.0 5.7 18.4	0 0 15.5	Nil. Nil. Light.
Example 6.....	4.0 2.0 1.0	0.25 0.12 16.0	3.0 -3.0 105	0 0 50.9	Nil. Nil. Medium.
Example 7.....	4.0 2.0 1.0 0.5	0.20 0.15 0.33 17.6	7.0 0 0 149	0.6 0.7 6.9 127	Nil. Nil. Nil. Trace.
Example 8.....	4.0 2.0 1.0 0.5	0 0 0.4 14.6	9.1 8.0 3.0 95.0	0 0.3 0.5 56.0	Nil. Nil. Nil. Light.
Example 9.....	4.0 2.0 1.0 0.5	-0.6 -0.7 0.15 15.0	13.5 11.0 10.0 166	1.0 1.0 0.3 67.0	Nil. Nil. Nil. Medium.
Example 10.....	0.1	0	7.5	0.6	Trace.
Example 11.....	4.0 2.0 1.0 0.5	0.2 -0.1 -0.2 11.4	7.5 6.5 4.5 67.0	2.7 2.6 1.9 54	Nil. Nil. Nil. Trace.

TABLE 1—Continued

Additive	Conc., Wt. Percent	ΔNN	Viscosity Increase, Percent	Lead Loss, mg.	Sludge ¹
Example 12-----	4.0 2.0 1.0 0.5	0 0.25 9.0 11.1	9.5 6.5 35.0 53.5	0.4 0.6 0 52.2	Nil. Nil. Medium. Heavy.
Trioleyl borate-----	4.0 2.0 1.0 0.5	19.4 14.2 17.7 20.3	1,230 126 625 796	341 75 44 183	Medium. Heavy. Do. Do.

¹ Estimated visually.

It will be seen from the above results that the mineral oil containing no additives is highly susceptible to the deteriorating attack of oxidation. Moreover, the presence of a normal borate provided no protection whatsoever, even at a concentration of 4%. In fact, an increase in lead loss resulted. However, the products of the examples of this invention, even at concentrations of as low as 0.1%, provide extremely effective antioxidant protection as well as protection against metal corrosion.

In Table II below the mineral oil is tested using the same catalytic oxidation test described above in the presence of a number of known detergents. Detergent A is a polyalkylene succinimide, detergent B is the boronated product of the alkylene succinimide detergent. To the base fluid-detergent compositions was added the product of Example 3, tri(tetrapropyl)-2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole). The product of Example 3 is taken as representative of the compounds of this invention. While no antioxidant protection can be obtained from the detergents, even that containing boron, which in some respects can lower the oil's resistance yet the novel dioxaboron compounds in combination with detergents provide satisfactory working lubricants. The results are tabulated below in Table 2.

TABLE 2

Composition	Additive	Conc., Wt. percent	ΔNN	Viscosity Increase, percent	Lead Loss, mg.	Sludge ¹
1-----	None-----	4.5	19.3	460	220	Medium.
2-----	Detergent B ² -----	4.5 2.25 1.13 3.8 1.9 0.95	16.5 8.2 12.5 12.6 16.9 24.7	283 74 73 170 353 4,880	210 22.8 28.1 202 380 417	Heavy. Do. Do. Light. Trace. Light.
3-----	Detergent A ³ -----	4.5 2.0 4.5 1.0 2.25 2.0 3.7 2.0 3.7 1.0	0.6 7.0 -0.15 0.5 10.5	6.0 49.5 5.5 7.5 90	1.0 7.4 1.0 2.9 45.5	Nil. Trace. Nil. Trace. Do.

¹ Estimated visually.² A boron- and nitrogen-containing ashless detergent.³ A nitrogen-containing ashless detergent.

As seen from the above data in Table 2, the detergents are inadequate in themselves for stabilizing the lubricating oil against the effects of oxidation. However, with the addition of the novel compounds of this invention, a complete lubricant formulation may be obtained. Compositions 4 to 8 have excellent oxidation stability when compared with compositions 2 and 3.

The product of Example II was tested in a CRC L-38 engine test. This test measures copper-lead bearing corrosion. The test engine is operated for 40 hours during which the engine is lubricated by the sample composition. The composition is evaluated on the basis of bearing weight loss and appearance of the bearing surface. A passing grade is one in which the bearing weight loss does not exceed 50 mg. and the bearing surface does not have undue pitting or discoloration. The test blend using the product

of Example 11, tridodecylbenzo-1,3,2-dioxaborole, was compared against one containing a commercial corrosion inhibitor, a zinc dialkylphosphorodithioate. The mineral oil used as the base stock was an SAE 30 grade. The results of the two engine runs are tabulated below in Table 3.

TABLE 3

Additive	Additive, Wt. Percent	Conc., Percent Boron	Bearing Wt. Loss, mg.	Bearing ¹ Surface
Tridodecylbenzo-1,3,2-dioxaborole-----	2.0	0.017	42	A-B
Zinc dialkylphosphorodithioate-----	1.0	-----	48	B

¹ A = smooth bearing surface, copper to brassy color; B = smooth surface, uniform brassy color. A pitted bearing would be rated D.

The above table shows that a representative product prepared in accordance with our invention unexpectedly discloses that these novel compounds possess metal protection properties, which is not an expected property for antioxidants.

As is well known, the oxidation stability of hydrocarbon lubricants is not an analogous mechanism to the stabilization of synthetic ester lubricants. Different chemical reactions may occur in the oxidation attack of each type of lubricant. Surprisingly, however, the compounds of this invention protect synthetic esters as effectively as they do hydrocarbons. In another form of oxidation test similar to the catalytic oxidation test described above, a base stock prepared from technical-grade pentaerythritol and a mixture of C₅- and C₉-monocarboxylic acids was used. In this case the test is performed for a duration of 24 hours at 425°. The kinematic viscosity readings are taken at 100° F. The equipment used, the air-flow rate and catalytic metals are the same as in the previous oxidation test. The products of Example 8, tri-2-hexadecylbenzo-(2-hydroxy-1,3,2-dioxaborole), and Example 4, tritetrapropyl-

2,3 - naphthylene - (2-hydroxy - 1,3,2 - dioxaborole) were tested in this base fluid at various concentrations. The results of the tests are tabulated in Table 4.

TABLE 4

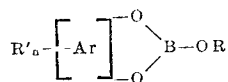
Additive	Conc., Wt. Percent	Δ NN	Viscosity Increase, Percent
None		8.5	265
Example 8	4.0	0.7	38.5
	2.0	1.2	31.0
	1.0	1.9	19.5
	4.0	1.1	26.5
Example 4	2.0	1.5	38.1
	1.9	1.5	65.0

As indicated in the above test results, the uninhibited base fluid undergoes a significant increase in viscosity, and the formation of acids is evident. However, the presence of the additives of this invention provides an effective reduction in both of these characteristics.

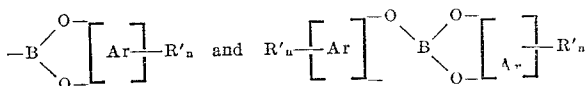
It is clear that the compounds prepared and used in accordance with the teachings of this invention are excellent antioxidant stabilizers and metal corrosion inhibitors. Their activity is not reliant on the presence of other additives although, as has been shown, they may be blended suitably with other known lubricant additives which are typically employed in the preparation of oil blends. The compounds of this invention may be used in concentrations of from about 0.05% to about 10% by weight of lubricant or other organic media. Although this invention has been described with the use of specific illustrations and examples, the invention is not limited in the above except as appearing in the following claims.

We claim:

1. A lubricating oil composition comprising a lubricating oil and a minor amount sufficient to provide antioxidant and anti-metal corrosion properties thereto of a dioxaboron compound of the formula



wherein Ar is selected from the group consisting of o-phenylene, o-naphthylene, 2,2'-diphenylene, 2,2'-dinaphthylene, and 5,6-benzo-2,2'-diphenylene; R is selected from the group consisting of hydrogen, alkyl, and aralkyl having 1 to about 20 alkyl carbon atoms, aryl, alkaryl having 1 to about 20 alkyl carbon atoms,



R' is alkyl having from 10 to 30 carbon atoms; and n is 1 to the number of available substitutive positions of Ar.

2. The composition of claim 1 wherein R is hydrogen.

3. The composition of claim 2 wherein Ar is o-phenylene.

4. The composition of claim 3 wherein the dioxaboron compound is ditriacontylbenzo - (2 - hydroxy - 1,3,2-dioxaborole).

5. The composition of claim 3 wherein the dioxaboron

compound is tri-(C₁₈-C₂₀)-benzo(2-hydroxy-1,3,2-dioxaborole).

6. The composition of claim 3 wherein the dioxaboron compound is tri-2-hexadecylbenzo-(2-hydroxy-1,3,2-dioxaborole).

7. The composition of claim 3 wherein the dioxaboron compound is tridodecylbenzo - (2 - hydroxy - 1,3,2 - dioxaborole).

8. The composition of claim 2 wherein Ar is o-naphthalene.

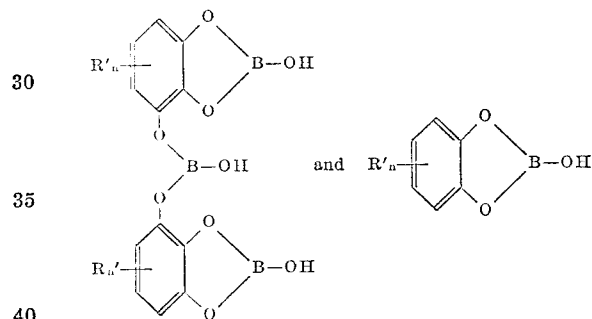
9. The composition of claim 8 wherein the dioxaboron compound is tetra-(C₁₅-C₂₀)-2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole).

10. The composition of claim 8 wherein the dioxaboron compound is tri(tetrapropyl) - 2,3 - naphthalene - (2-hydroxy-1,3,2-dioxaborole).

11. The composition of claim 8 wherein the dioxaboron compound is tetra(tetrapropyl) - 2,3-naphthalene-(2-hydroxy-1,3,2-dioxaborole).

12. The composition of claim 1 wherein the dioxaboron compound is tetrahexadecyl-2,2'diphenyl-1,3,2-dioxaboron.

13. A lubricating oil composition comprising a lubricating oil and a minor amount sufficient to provide antioxidant properties thereof of a dioxaboron compound selected from the group consisting of



wherein R' is alkyl having 10 to 30 carbon atoms and n is 1 to 3.

14. The composition of claim 13 wherein the dioxaboron compound is tri-2-hexydecylpyrogallol.

15. The composition of claim 1 wherein the oil is a mineral oil.

16. The composition of claim 1, wherein the oil is a synthetic oil.

17. The composition of claim 1 wherein the oil is a pentaerythritol ester.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

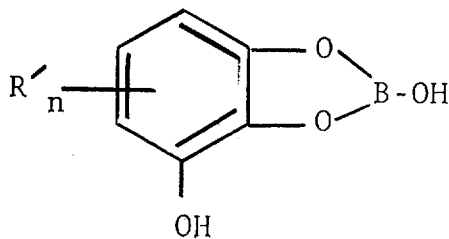
Patent No. 3,361,672

January 2, 1968

Harry J. Andress, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, lines 46, 55 and 69, for "C₁₆", each occurrence read -- C₁₅ --; column 12, lines 32 to 35, the structure should appear as shown below instead of as in the patent:



Signed and sealed this 25th day of February 1969.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents