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PHENOLIC BORATE ESTERS AND PRODUCTION THEREOF

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14 Claims. (Cl. 260—462)

The present invention is a continuation-in-part of our now abandoned application Ser. No. 648,502 dated Mar. 26, 1957.

This invention relates as indicated to phenyl esters of boron acids and has particular reference to hindered phenyl esters of boron acids having exceptional stability to water and heat.

It is known that phenyl esters of boron acids would be useful as fuel additives if they could be made to resist hydrolysis. Until the present invention, the previously known phenyl esters of boron acids were subject to rapid hydrolysis even at normal temperatures.

We have discovered that it is possible to form between a boron acid and a substituted phenol an ester linkage that is substantially stable in the presence of water. Such hydrolytically stable materials are particularly useful as additives for lubricating oils, greases, gasolines, diesel oils and jet engine fuels. We have found our compositions to be particularly useful when added to fuels and lubricants in amounts of from about 0.005 to about 5%.

It is therefore an object of this invention to provide new phenyl esters of boron acids which are substantially stable in the presence of water.

It is a further object of the present invention to provide new phenyl esters of boron acids which are effectively thermally stable.

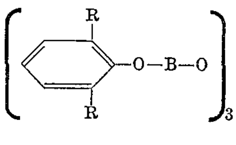
Other objects will appear as the description proceeds.

To the accomplishment of the foregoing and related ends the invention then comprises the features hereinafter fully described and pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the ways in which the principle of the invention may be employed.

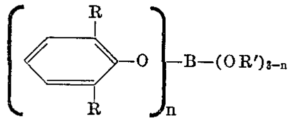
The present invention is predicated upon the discovery that the hydrolytic stability of the phenyl metaborates, diphenyl alkyl borates, and the phenyl dialkyl borates is obtained when each phenoxy group of the ester is substituted at both the 2-position and at the 6-position by tertiary alkyl radicals. Secondary alkyl radicals in those positions do not effectively stabilize the ester bond. A single tertiary alkyl radical at the 2-position of the phenoxy group does not lead to hydrolytic stability and, moreover, little or no stability is provided by even a plurality of tertiary alkyl radicals which are located at any positions of the phenoxy group that do not include both the 2-position and the 6-position.

Broadly stated the present invention comprises substantially water stable boron esters in which boron is linked to at least one phenoxy group which is at least substituted at the 2-position and at the 6-position by tertiary alkyl radicals.

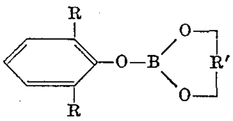
From the foregoing broadly stated paragraph it will be seen that the esters of the present invention can be a metaborate ester as shown by the general formula



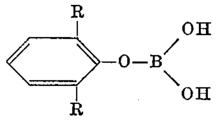
where R is any tertiary alkyl radical. The tertiary radicals may be the same or different, as for example R can be tertiary butyl at the 2 and 6-positions, or R can be tertiary butyl at the 2-position and teritary amyl at the 6-position. Or the present compositions can be an orthoborate mixed ester in which a boron atom is linked by esterification with both aroxy and alkoxy radicals as shown by the general formula



where R is any tertiary alkyl radical which may be the same or different; R′ is any alkyl, alkenyl or alkynyl radical, and also may be the same or different radicals; and *n* is an integer from 1 to 2. Or the mixed esters can be of the type where the boron atom is linked to only one phenoxy radical and joined by the other two ester bonds to a glycol, as shown by the formula



where R is a tertiary radical as in the foregoing general formulae and R′ is a glycol. Still further, the present compositions can be an ester of the type where the boron atom is linked to a phenoxy radical and linked by the other two bonds to hydroxyl groups,



where R is a tertiary radical as in the foregoing formula.

Thus it is again emphasized that the present compositions are esters wherein boron is linked to at least one phenoxy radical and the phenoxy radical must be substituted at the 2-position and at the 6-position with tertiary alkyl radicals. While the tertiary alkyl radicals may contain any number of carbon atoms, in the preferred embodiment of our invention we use tertiary alkyl radicals each containing from four to ten carbon atoms.

Many phenols have been reported to react with orthoboric acid (H_3BO_3) to produce the corresponding orthoborate, containing three moles of phenol per mole of the boric acid. However, such orthoborates are not hydrolytically stable. So far as we have ascertained, phenols that are substituted at the 2- and 6-positions with tertiary alkyl radicals do not react, like most other phenols, with orthoboric acid to give the orthoborate. However, we have successfully reacted 2,6-di-tertiary alkyl phenols with boric acid, metaboric acid, or boric oxide to produce the corresponding esters containing only one mole of phenol per mole of boric acid. Such boron esters, whether in monomeric or trimeric form, will be referred to throughout the present specification and claims as metaborates. The resulting substituted phenyl metaborates are remarkably resistant to wetting by water, and can be brought into direct contact with water without appreciable hydrolysis.

Phenyl metaborates of the described type can also be produced by reaction of 2,6-di-tertiary alkyl phenols with a suitable organo-boron compound, such, for example, as a trialkoxyboroxine.

Although, as already indicated, substituted triphenyl orthoborates do not result from reaction of orthoboric acid and 2,6-di-tertiary alkyl phenols, it is possible to produce mixed esters containing one or two substituted phenoxy groups of the described type and containing also two or one alkoxy groups. For example, such mixed esters may be produced by transesterification of an alkyl substituted phenol of the special type described and an aliphatic orthoborate. The resulting mixed substituted phenyl alkyl boron esters are found to be remarkably stable. The diphenyl alkyl esters of the invention are extremely resistant to wetting by water and can be brought into contact with water substantially without hydrolysis; and the substituted phenyl dialkyl esters are remarkably stable to hydrolysis. As a result of their unusual stability, the mixed aryl-alkyl boron esters of the invention are especially useful for many purposes in which they may come in contact with water, including, in particular, the important field of utility as additives for improving the combustion properties of hydrocarbon fuels.

Previous attempts to produce individual mixed boron esters involving hydrocarbon groups of both aryl and alkyl type have not been successful, largely because the products, if formed, were not thermally stable and hence, for example, they could not be isolated by distillation. At the temperatures required for distillation, and even for initial production, of such previously known mixed aryl-alkyl boron esters, the latter tend to be converted into a mixture of tri-aryl borate and tri-alkyl borate.

Another important advantage of the new mixed boron esters is the fact that they are effectively stable thermally. Individual species can therefore be isolated by distillation without disproportionation. The thermal stability of the new mixed esters is associated with the presence of tertiary alkyl radicals at both the 2-position and the 6-position of the phenoxy group, or of both phenoxy groups if there are two. Thus, for example, it is possible to separate by distillation 2,6-di-t-butylphenyl di-n-butyl borate and di-(2,6-di-t-butylphenyl)-n-butyl borate without appreciable disproportionation, leading to satisfactory isolation of those two compounds. However, when a mixture of 2,6-diisopropylphenyl di-n-butyl borate and di-(2,6-diisopropylphenyl)-n-butyl borate, for example, is distilled, disproportionation prevents effective isolation of either component of the mixture.

Moreover, the 2,6-di-tertiary alkyl substitution of the phenoxy groups not only leads to stability in the presence of water of the boron-aroxy linkage, as in the 2,6-substituted phenyl metaborates already mentioned, but also leads to remarkably great hydrolytic stability of the boron-alkoxy linkages. That is true even for alkyl radicals for which the tri-alkyl borate hydrolyzes almost immediately. Thus, for example, tri-n-propyl borate hydrolyzes in only a few seconds; but in 2,6-di-t-butylphenyl di-n-propyl borate the ester bonds between the boron atom and the alkoxy radicals are effectively stable in the presence of water. Thus the present compounds provide for the first time a means of producing hydrolytically stable ester bonds between boron and a wide variety of alkoxy radicals.

A particularly useful group of mixed esters of the type just described are those in which the boron atom is linked to only one phenoxy radical, and is joined by the other two ester bonds to a glycol. Compounds of this type can be made from the following glycols: ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, hexylene glycol (2-methyl-2,4-pentanediol), and 1,4-butanediol.

While the compounds of the invention are particularly characterized by the described substitution of tertiary alkyl radicals at the 2- and the 6-positions of the phenoxy groups, the phenoxy groups may also be further substituted at the 3-, 4-, and 5-positions by similar tertiary alkyl radicals or by other radicals such, for example, as normal alkyl, isoalkyl, phenyl and the like, without appreciably affecting the described properties of thermal and hydrolytic stability. In particular, two molecules comprising stable ester linkages of the described type may be joined either directly or via an alkyl group at the 4-positions of their respective phenoxy groups. An example of such a configuration, in which the linking alkyl group is methyl, is 4,4′ - methylene bis-(2,6 - di-t-butylphenyl di-n-butyl borate). Esters of that general type are useful when a compound is desired which has an appreciably higher molecular weight with substantially the same percentage content of boron.

A full understanding of the invention and of its further objects and advantages will be had from the following examples of particular manners in which it may be carried out. Those examples, however, are intended only as illustration and not as a limitation upon the scope of the invention, which is defined in the appended claims.

Example 1.—A reaction vessel was charged with 2,6-di-t-butylphenol and boric acid (H_3BO_3) in a molar ratio of 3.3 to 1 and about 300 ml. of xylene per mole of the phenol. The reaction mixture was stirred at reflux temperature, and released water was removed as an azeotrope with xylene and measured in a water trap. Other azetroping solvents, such as benzene, for example, may be substtiuted for the xylene. After removing the azeotroping agent the reaction product was dissolved in acetone and the precipitated residual B_2O_3 was removed by filtration. Evaporation of the acetone yielded, 2,6-di-t-butylphenyl metaborate, a white crystalline solid, melting at 310–323° C. Analysis indicated that the product contained 4.55% boron, as compared to a theoretical value of 4.66%. In spite of the initial presence of more than 3 moles of phenol per mole of boric acid, no indication was found of any production of the orthoborate.

Example 2.—The process of Example 1 was repeated with the orthoboric acid replaced by a correspoding quantity of anhydrous boric oxide (B_2O_3). A correspondingly smaller quantity of water was removed. The product was 2,6-di-t-butylphenyl metaborate, as in Example 1.

Example 3.—A reaction vessel was charged with 2,6-di-t-butylphenol and n-butyl metaborate (tri-n-butoxyboroxine) in a molar ratio of about 3.3 to 1. The mixture was heated to 255 to 300° C. as three moles of n-butyl alcohol were distilled. After removal of the excess phenol the product, 2,6-di-t-butylphenyl metaborate, was purified as in Example 1. The reaction of Example 3 can also be carried out in an azeotroping solvent, such as xylene, for example. In this case the mixture is heated to remove the n-butanol-xylene azeotrope at about 117° C.

Example 4.—The procedure of Example 1 was repeated, with the phenol replaced by a corresponding quantity of 2,6-di-t-butyl-4-methylphenol. The resulting product was 2,6-di-t-butyl-4-methyl-phenyl metaborate, a white crystalline solid melting at 246 to 268° C. Analysis indicated that the product contained 4.46% boron (theoretical value 4.40%). As in Example 1, no indication was found of any production of the orthoborate.

2,6-di-t-butyl-4-methylphenyl metaborate has also been produced by procedures corresponding to Examples 2 and 3.

Other 2,6-di-tertiary alkyl phenols may be reacted with boric acid, with boric oxide or with a tri-alkoxy boroxine to produce the corresponding phenyl metaborates. The following metaborates are illustrative of those which may be prepared in that manner and which are highly resistant to wetting by water:

2,4,6-tri-t-butylphenyl metaborate;
2,6-di-t-hexyl-4-n-octylphenyl metaborate;
2,6-di-t-decylphenyl metaborate;
2,6-di-t-amyl-3,4-di-ethylphenyl metaborate;
2,6-di-t-octyl-4-isobutylphenyl metaborate.

Example 5.—A 12-liter reaction vessel equipped with a 3-foot packed column with stillhead and receiver was charged with 24 moles of 2,6-di-t-butyl-4-methylphenol and 12 moles of tri-n-butyl borate. Heat was applied and 12.43 moles of n-butanol was removed as distillate, the head temperature being held at about 117° C., the boiling point of n-butanol. Analysis of the distillate for boron indicated the presence of about 0.05 mole of tri-n-butyl borate.

The heat was then removed and the packed column replaced by an 18-inch Vigreux column. The excess unreacted phenol was then distilled at 113 to 160° C. at a pressure of 1 mm. of Hg. 2,6-di-t-butyl-4-methylphenyl di-n-butyl borate was then distilled at 167 to 171° C. at 1 mm. of Hg. The yield of the ester, which was a colorless liquid, was about 7.1 moles, or 59% of the theoretical yield based on the initial tri-n-butyl borate. Analysis for boron by Parr bomb fusion gave 2.95% boron (theoretical value 2.88%).

A further fraction, distilled at 231 to 246° C. at 1 mm. of Hg, was melted and poured into acetone. Di-(2,6-di-t-butyl-4-methylphenyl) n-butyl borate precipitated as a white crystalline solid, which was removed by filtration, washed with acetone and dried under vacuum. The resulting product, which melted at 159 to 176° C., was analyzed for boron by Parr bomb fusion, giving a boron content of 2.10% (theoretical value 2.07%). The total yield of the diphenyl butyl borate was approximately 0.7 mole. That yield can be increased relative to the yield of the phenyl di-butyl borate by appropriate increase of the reaction time and of the initial ratio of phenol to tributyl borate.

Procedures corresponding generally to Example 5 have been carried out with other 2,6-di-tertiary alkyl phenols and also with other tri-alkyl borates as initial reactants, leading to the following illustrative mixed esters which are substantially thermally and hydrolytically stable and were found to exhibit the properties indicated:

2,6-di-t-butylphenyl di-n-butyl borate, a pale yellow liquid, boiling at 150 to 154° C. at 1 mm. of Hg;
Di-(2,6-di-t-butylphenyl)-n-butyl borate, a white crystalline solid;
2,6-di-t-butylphenyl di-n-propyl borate, a colorless liquid boiling at 182 to 184° C. at 18 mm. of Hg;
2,6-di-t-butylphenyl diisopropyl borate, a colorless liquid boiling at 155 to 161° C. at 18 mm. of Hg;
Di-(2,6-di-t-butylphenyl) isopropyl borate, a yellow crystalline solid boiling at 176 to 191° C. at 1 mm. of Hg;
2,6-di-t-butyl-4-methylphenyl di-n-propyl borate, a colorless liquid boiling at 193 to 195° C. at 18 mm. of Hg;
Di-(2,6-di-t-butyl--4-methylphenyl) isopropyl borate, a white crystalline solid melting at 152 to 172° C. and boiling at 217 to 235° C. at 1 mm. Hg;
2,6-di-t-butyl-4-methylphenyl diisopropyl borate, a white crystalline solid boiling at 173 to 175° C. at 18 mm. of Hg;
Di-(2,6-di-t-butyl-4-methylphenyl) isopropyl borate, a white crystalline solid melting at 161 to 177.5° C. and boiling at 217 to 235° C. at 1 mm. of Hg;
2,4,6-tri-t-amylphenyl di-n-butyl borate, a pale yellow liquid boiling at 160 to 164° C. at 1 mm. of Hg.

Example 6.—A reaction vessel provided with a 3-foot packed column with stillhead and receiver was charged with 4,4-methylene bis-(2,6-di-t-butylphenol) and tri-n-butyl borate in a molar of 1 to 3. Heat was applied and about 2.1 moles of n-butanol were removed by distillation at a head temperature of about 117° C. The packed column was then replaced with an 18-inch Vigreux column and the reaction mixture was distilled at a pressure of 1 mm. of Hg. The unreacted tri-n-butyl borate was distilled at 85 to 92° C./1 mm. An intermediate fraction, consisting of about 150 grams was distilled at 130 to 147° C./1 mm. The temperature then rose to about 220° C./1 mm., in which range a further 30 grams of material was distilled. The reaction product remaining in the pot was 4,4′-methylene bis-(2,6-di-t-butylphenyl di-n-butyl borate). It was a clear orange liquid while hot and solidified to a clear orange glassy solid on cooling to room temperature. Analysis for boron by sodium carbonate fusion gave a boron content of 2.84% (theoretical value 2.94%).

Example 7.—A one liter reaction vessel equipped with a one-foot packed column with stillhead and receiver was charged with two moles (412.6 g.) of 2,6-di-tert-butylphenol (100% excess) and one mole (182 g.) of triallyl borate. Heat was applied and 41.8 g. of allyl alcohol was removed as distillate (theory 58.1 g.) in 4.5 hrs. The head temperature was held at about 97° C., the boiling point of allyl alcohol. The heat was then removed and the packed column replaced by a one-foot Vigreux column. The unreacted triallyl borate distilled at 79–82° C./18 mm. and the excess phenol distilled at 87–93° C./0.5 mm. The product, 2,6-di-tert-butylphenyl diallyl borate, was then distilled at 104 to 110° C./0.2 mm. The yield of ester, which was a colorless liquid, was 152 g. (46% yield based on triallyl borate). Analysis for boron by Parr bomb fusion gave 3.20% boron (theoretical value 3.28%).

Example 8.—A one liter reaction flask equipped with a one-foot packed column with stillhead and receiver was charged with one mole of 2,6-di-tert-butylphenyl-di-n-butyl borate (362.4 g.) and one mole of n-octanol (130.2 g.). Heat was applied and 67 g. of n-butanol were removed as distillate (theory 74.1 g.) in three hours. The head temperature was held at about 117° C., the boiling point of n-butyl alcohol. The heat was then removed and the packed column was replaced by a one-foot Vigreux column. A small amount of unreacted n-octanol distilled at 57–65° C./1 mm. and a small amount of unreacted 2,6-di-tert-butylphenyl di-n-butyl borate distilled at 150–158° C./1 mm. The product 2,6-di-tert-butylphenyl n-butyl n-octyl borate was then distilled at 181–190° C./1 mm. yielding 310 g. (74% yield) of a pale yellow liquid which analyzed 2.62% boron by sodium carbonate fusion (theory 2.59%). A higher boiling fraction which distilled at 205–210° C./1 mm. was obtained. This fraction was 62 g. of a pale yellow liquid which analyzed 2.31% boron by sodium carbonate fusion. Theory for boron for the compound 2,6-di-tert-butylphenyl di-n-octyl borate is 2.28%.

Example 9.—A 125-ml. Erlenmeyer flask containing 32 g. (1 mole) of anhydrous methanol was cooled in an ice water bath, and 30 g. (0.105 mole) of 2,6-di-tert-butylphenoxy boron dichloride was added. The mixture reacted exothermically to give a homogeneous solution from which the odor of hydrogen chloride could be detected. On cooling the reaction mixture to room temperature, the product 2,6-di-tert-butylphenyl dimethyl borate crystallized as white needles. The reaction mixture was cooled in an ice water bath for one hour and the crystalline ester was filtered on a Buchner funnel and dried under vacuum to give 14.6 g. of ester. The filtrate was reduced in volume under vacuum and on cooling yielded a second crop of ester which after filtering and drying weighed 6.1 g. The total weight of product was 20.7 g. (72% yield). A portion of the product after recrystallizing twice from methanol analyzed 3.82% boron by Parr bomb fusion (theory 3.90%) and melted at 72.4–74.0° C.

Example 10.—A 500-ml. Erlenmeyer flask containing 69 g. (1.5 moles) of absolute ethanol was cooled in an ice water bath and 60 g. (0.21 mole) of 2,6-di-tert-butylphenoxy boron dichloride was added. The mixture reacted exothermically to give a homogeneous solution from which the odor of hydrogen chloride could be detected. The reaction mixture was transferred to a 300-ml. round-bottomed flask equipped with a one-foot Vigreux column with a stillhead and receiver. Heat was applied and the excess ethanol distilled at 78° C. When all the ethanol was removed, the remaining material was distilled under pump vacuum. The product 2,6-di-tert-butylphenyl diethyl borate distilled at 114–115° C./1 mm. yielding 60.3 g. (94% yield) of a colorless liquid which analyzed 3.48% boron by Parr bomb fusion (theoretical percent boron, 3.53).

Example 11.—A reaction vessel was charged with 2,6-

di-t-butyl-4-methylphenol and hexylene glycol monoborate (2-hydroxy-4,4,6-trimethyl-1,3,2-dioxaborinane) in a molar ratio of approximately 1:1 and about 300 ml. of xylene per mole of the phenol. Water was removed as an azeotrope with xylene, and the reaction product was isolated as described in Example 1. The product was 2,6-di-t-butyl-4-methylphenyl hexylene glycol borate, a white crystalline solid melting at 100.6 to 102.0° C. and boiling at 200 to 202° C. at 21 mm. of Hg.

The same product was produced also by reaction of 2,6-di-t-butyl-4-methylphenyl di-n-butyl borate, produced, for example, as described in Example 5, and hexylene glycol (2-methyl-2,4-pentanediol) in the presence of an azeotroping solvent.

Many other hydrolytically stable mixed aryl-alkyl boron esters may be produced in accordance with Examples 5 to 10 by replacing the specific initial ingredients of those examples by other combinations of 2,6-di-tertiary alkyl phenols and tri-alkyl borates or glycol borates. The following are illustrative of hydrolytically stable mixed boron esters that may be produced in accordance with the invention:

2,4,6-tri-t-amylphenyl di-n-amyl borate;
2,6-di-t-amylphenyl di-2-octyl borate;
Di-(2,6-di-t-butyl-4-methylphenyl)-n-decyl borate;
Di-(2,6-di-t-decylphenyl) diisobutylcarbinyl borate;
2,6-di-t-amylphenyl hexylene glycol borate;
4,4'-methylene-bis-(2,6-di-t-amylphenyl hexylene glycol borate);
2,6-di-t-decylphenyl di-n-octyl borate;
Di-(2,6-di-t-octyl-4-isopropylphenyl)-t-butyl borate;
2,6-di-t-heptylphenyl dimethyl borate.

In addition, the following is illustrative of hydrolytically stable partial esters that may be produced in accordance with the present invention: 2,6-di-t-butylphenoxy dihydroxyborane.

As an example of the substantial stability of the described 2,6-di-tertiary alkyl phenyl metaborates when in contact with water, a weighed sample of 2,6-di-t-butyl-4-methylphenyl metaborate was dropped into 100 ml. of water and boiled for 20 minutes. The sample showed no tendency to melt or dissolve in the water. After cooling to room temperature and addition of mannite and phenolphthalein, the sample was titrated with 0.1 N sodium hydroxide. It was found that only 20% of the sample had hydrolyzed when in contact with water at 100° C. for 20 minutes. That value is typical of the 2,6-di-tertiary alkyl phenyl metaborates that have been described.

As an example of the substantial stability of the mixed di-(2,6-tertiary alkyl phenyl) alkyl boron esters of the invention when in contact with water, a weighed sample of di-(2,6-di-t-butyl-phenyl)-n-butyl borate was boiled in water for 20 minutes, and the resulting hydrolysis was determined in the manner just described. It was found that only 1.65% of that typical diphenyl alkyl boron ester had hydrolyzed.

As an example of the substantial stability against hydrolysis of the described mixed esters in which boron is linked to one 2,6-di-tertiary alkyl phenoxy radical and to two alkoxy radicals, a weighed sample approximating 1 gram of 2,6-di-t-butylphenyl di-n-butyl borate was completely dissolved in 100 ml. of 90% by volume aqueous dioxane. The solution was maintained at 25° C. in a constant temperature bath. At definite time intervals 10 ml. aliquots of solution were removed and added to 50 ml. of water, causing the ester to precipitate so that hydrolysis was virtually stopped. Mannite and phenolphthalein were then added and the mixture titrated with standard base to determine the percentage of the ester that had hydrolyzed in the sample. From a series of such determinations the half-life of 2,6-di-t-butylphenyl di-n-butyl borate in 90% aqueous dioxane at 25° C. was found to be 60 days.

That value is included in the following table, which lists the observed values, obtained in the manner just described, for the half-lives of several illustrative mixed substituted phenyl dialkyl esters of the invention in 90% aqueous dioxane at 25° C.

Table

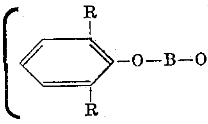
Ester:	Observed half-life (days)
2,6-di-butylphenyl di-n-propyl borate	100
2,6-di-t-butylphenyl di-isopropyl borate	460
2,6-di-t-butylphenyl di-n-butyl borate	60
2,6-di-t-butyl-4-methylphenyl di-n-propyl borate	130
2,6-di-t-butyl-4-methylphenyl di-isopropyl borate	375
2,6-di-t-butyl-4-methylphenyl di-n-ibutyl borate	80
2,6-di-t-butyl-4-methylphenyl hexylene glycol borate	90
2,4,6-tri-t-amylphenyl di-n-butyl borate	130

The compounds of the present invention are particularly useful as additives for hydrocarbon fluids such as fuels and lubricating compounds. The combustion properties and stability of hydrocarbon fuels are improved by addition of the present boron-containing compounds in suitable proportions. The additives are useful for that purpose in concentrations from about 0.005 to about 5%. For example, when 2,6-di-t-butylphenyl metaborate is added to JP-5 jet fuel in a preferred concentration between 0.01 and 0.1% a distinct improvement in combustion properties and thermal stability is observed.

Other modes of applying the principle of the invention may be employed provided the features stated in any of the following claims or the equivalent of such be employed.

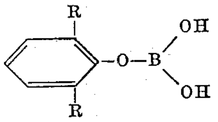
We, therefore, particularly point out and claim as our invention:

1. A substantially water stable boron ester having the formula



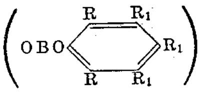
where R represents tertiary alkyl radicals.

2. A substantially water stable boron ester having the formula



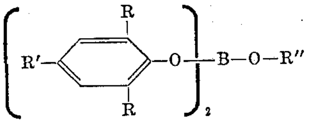
where R represents tertiary alkyl radicals.

3. A trimeric metaborate ester of the formula



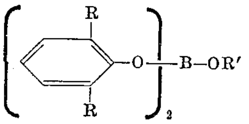
wherein R is a tertiary alkyl radical and R_1 is selected from the group consisting of hydrogen and alkyl radicals.

4. A borate ester of the general formula



where R represents a tertiary alkyl radical, R' is selected from the group consisting of hydrogen and lower alkyl radicals and R'' represents a lower alkyl radical.

5. A substantially water stable boron ester of the formula



where R is tertiary alkyl and R′ is selected from the group consisting of alkyl, alkenyl and alkynyl.

6. 2,6-di-t-butylphenyl-di-alkenyl borate.

7. 2,6-di-t-butylphenyl metaborate.

8. Di-(2,6-di-t-butylphenyl)alkyl borate.

9. Di-(2,6-di-t-butylphenyl)alkenyl borate.

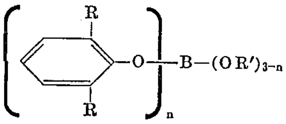
10. 2,6-di-t-butyl-4-methylphenyl metaborate.

11. Di-(2,6-di-t-butyl-4-methylphenyl)-n-butyl borate.

12. 2,6-di-t-butylphenyl diallyl borate.

13. 2,6-di-t-butylphenoxy dihydroxyborane.

14. The method of producing a mixed boron ester of the formula



where R is tertiary alkyl, R′ is selected from the group consisting of alkyl, alkenyl and alkynyl, and *n* is an integer selected from 1 and 2, said method comprising reacting a phenol that is substituted at the 2-position and at the 6-position by tertiary alkyl radicals and a tri-alkyl borate and separating the resulting di-phenyl alkyl borate and the phenyl di-alkyl borate by fractional distillation.

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