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LUBRICANTS AND FUELS CONTAINING BOROXAROPHENANTHRENE COMPOUNDS

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This invention relates to the stabilization of lubricating and fuel compositions. More particularly, it relates to additives for lubricants and fuels which are particularly capable of inhibiting the oxidative deterioration of these materials.

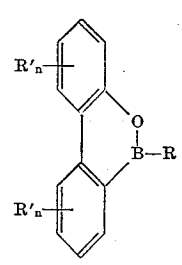
It is well known that lubricating oil fractions are subject to oxidative deterioration under conditions of use such as in modern internal combustion engines. Oxidation products are formed in the oil which products are acidic in nature and exert an oxidative effect on metal parts with which the oil comes in contact. Furthermore, these oxidation products produce formations of varnish and sludge on the engine surfaces. This tends to lower the operating efficiency of the engine. The proper lubrication of engine parts is further hampered due to the detrimental effect of oxidation on the viscosity of the oil. Similarly, it is known that the oxidation of fuels particularly during storage causes gum formation and layer deposits which tend to cause operating malfunctions.

In order to overcome, insofar as possible, these undesirable effects, additives known as antioxidants are normally added to the lubricants and fuels. For example, phenolic or amine compounds are commonly employed as such additives. Modern technology, however, requires lubricants and fuels possessing increased resistance to oxidation.

It is therefore an object of the present invention to provide novel additives for lubricant and fuel compositions. Another object is to provide a new class of additive agents for lubricants and fuels which additives are capable of inhibiting the oxidative deterioration of such materials in an improved manner. A further object is to provide lubricating compositions and fuel compositions which are highly stabilized against oxidation. Further objects of the invention and some advantages thereof will become apparent hereinafter.

In accordance with the present invention, it has been found that certain compounds which may be characterized as 9,10-boroxarophenanthrenes are capable of improving the oxidative resistance of lubricant and fuel compositions in an improved and unexpected manner.

These 9,10-boroxarophenanthrene compounds may be represented by the general formula:



where R represents hydroxy, hydrocarbyl, oxy-hydrocarbyl, halogen, halogenated hydrocarbyl, halogenated oxy-hydrocarbyl groups or, in the case of the anhydride, an oxy-9,10-boroxarophenanthrene group; R' represents the same or different hydrocarbyl, halogen or halogenated

hydrocarbyl groups; and *n* is zero or an integer from 1 to 4, preferably 1 or 2.

As used herein, by the term "hydrocarbyl" is meant groups composed of carbon and hydrogen atoms such as aliphatic, aryl, aliphatic-aryl, both alkaryl and aralkyl, and cycloaliphatic groups.

Suitable substituents for R include the above-mentioned hydroxy group as well as alkyl groups, both straight-chain and branched-chain, such as methyl, ethyl, propyl, isopropyl, tert.-butyl, octyl, dodecyl, hexadecyl, octadecyl, tetracosyl triacontyl etc.; aryl groups such as phenyl, naphthyl, etc.; aliphatic-aryl groups including tolyl, amylphenyl, phenyloctyl, and the like; cycloaliphatic groups such as cyclohexyl; oxy-hydrocarbyl groups such as any of the aforementioned hydrocarbyl groups attached to an oxygen atom, e.g., alkoxy, aryloxy groups, etc.; halogens such as chlorine, bromine iodine; halogenated hydrocarbyl and halogenated oxy-hydrocarbyl groups additionally containing one or more halogen atoms. The R' substituents may be selected from any of the hydrocarbyl, halogen, and halogenated hydrocarbyl groups hereinabove described as suitable for R.

Hydrocarbyl, oxy-hydrocarbyl, halogenated hydrocarbyl and halogenated oxy-hydrocarbyl groups containing from 1 to about 30, particularly from 1 to about 18 carbon atoms are preferred substituents.

Some examples of the 9,10-boroxarophenanthrene compounds used in accordance with the present invention are:

9-hydroxy-9,10-boroxarophenanthrene,
di-octadecyl-9-hydroxy-9,10-boroxarophenanthrene,
the anhydride of 9-hydroxy-9,10-boroxarophenanthrene,
9-tert.-butoxy-9,10-boroxarophenanthrene,
9-methoxy-9,10-boroxarophenanthrene,
9-chloro-9,10-boroxarophenanthrene,
9-phenyl-9,10-boroxarophenanthrene,
the 1,1,7-trihydroperfluoro-heptyl ester of 9-hydroxy-9,10-boroxarophenanthrene,
the 2,2-difluoro-dodecyl ester of 9-hydroxy-9,10-boroxarophenanthrene,
1,3-dibromo-9-hydroxy-9,10-boroxarophenanthrene, and
1,3,7-tribromo-9-hydroxy-9,10-boroxarophenanthrene.

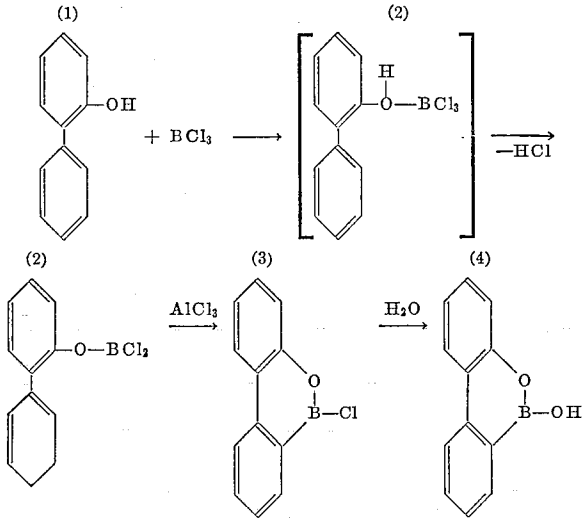
The 9,10-boroxarophenanthrene compounds of the present invention possess surprisingly effective antioxidant properties and, indeed, they are superior in antioxidant properties to several widely used, commercial antioxidants.

While organo boron compounds have been employed heretofore as antioxidants, these prior art materials were of the borate-type. Such borates were hydrolytically unstable and exhibited only moderate antioxidant properties. The 9,10-boroxarophenanthrene compounds of this invention are not borates. For example, 9-hydroxy-9,10-boroxarophenanthrene, a preferred compound of this invention, may be described as internal ester of 2-(2-hydroxy phenol)-phenylboronic acid wherein the ring system containing the boron possesses an unusual degree of stability due to its aromaticity. The anhydride of 9-hydroxy-9,10-boroxarophenanthrene is hydrolytically stable.

The preparation of the 9,10-boroxarophenanthrenes of the invention is, in general, known to the art. For example, the methods described by Dewar and Dietz, Journal Chemistry Society (London), 1344 (1960), may be employed.

The preparation of 9-hydroxy-9,10-boroxarophenanthrene is exemplary of these procedures. Briefly, orthophenylphenol (1) is reacted with excess boron trichloride. The intermediate product (2) from this reaction is then heated in the presence of aluminum chloride to give 9-chloro - 9,10 - boroxarophenanthrene (3). This chloro compound is then treated with water to give the desired 9-hydroxy - 9,10 - boroxarophenanthrene (4). Although the present invention is not limited to any particular

theory, it is believed that the above reactions may be represented as follows:



Although the antioxidant compounds of the invention are referred to herein as boroxarophenanthrenes, according to "Chemical Abstracts" this type of structure may also be termed the dibenz [c,e] [1,2] oxaborin system. Thus, based on the "Chemical Abstracts" nomenclature, the above-described 9-hydroxy-9,10-boroxarophenanthrene is 6-hydroxy-dibenz [c,e] [1,2] oxaborin.

Further details regarding the invention and some of the advantages thereof will become apparent from the following specific embodiments.

EXAMPLE 1

Boron trichloride (235 g., 2.0 moles) was bubbled into a 1-liter flask containing 200 ml. of dry methylene chloride at —70° C. The flask had been purged with nitrogen prior to the addition of the boron trichloride. A solution of 170 g. (1 mole) of o-phenyl-phenol in 200 ml. of methylene chloride was added dropwise to the flask. During this addition the flask contents were stirred, blanketed with nitrogen, and the temperature was kept at —50° C. to —70° C. After the addition was completed (1.5 hours), the mixture was stirred at —70° C. for 30 minutes and then allowed to warm gradually to room temperature (about 26° C.). Hydrogen chloride evolved during the warming. The hydrogen chloride was trapped in a caustic solution. The mixture was stirred at room temperature for 1 hour and then excess boron trichloride and the solvent were removed at 25° C. at 0.2 mm. Hg. A brown, viscous liquid was obtained. The residue was dissolved in 200 ml. of hexane, 5 g. of aluminum chloride was added, and the mixture was heated to 50° C. Hydrogen chloride evolved continuously. The mixture was heated at 50° C. for 24 hours. At this time, hydrogen chloride evolution had subsided. The product was filtered and 200 ml. of ether was added to the filtrate. The resulting solution was charged to a separatory funnel containing 400 ml. of water. The funnel contents were shaken, allowed to settle and the organic layer was isolated. The organic layer was concentrated under reduced pressure. A solid was obtained. Recrystallization from benzene gave a crystalline material, with a melting point of 210° C. (uncor.). The ultra-violet spectrum of the crystalline product was identical to that reported by Dewar and Dietz (J. Chem. Soc. (London) pages 1344–47, 1960). The calculated boron content for the product, $C_{12}H_9O_2B$, is 5.5%; while 5.9% boron was found upon analysis.

In order to evaluate the antioxidant properties of the boroxarophenanthrenes herein described oil compositions containing these compounds are subjected to a non-catalytic oxidation test and a catalytic oxidation test. The tests procedures are as follows:

Non-catalytic oxidation test

This test is conducted in an oxygen circulation apparatus of the type described by Dornte (Ind. Eng. Chem., 28, 26–30, 1936) modified so that the rate of oxygen absorption can be recorded automatically. In general, a tube containing an oil sample and additive is placed in a heater thermostatted at 302° F. After thermal equilibrium is established the sample tube is connected with the closed oxygen circulating system. Oxygen is circulated through a fritted glass disk near the bottom of the sample tube at a rate of 5 liters per hour. The time required for the absorption of 50 millimoles of oxygen per 100 grams of sample is taken as the induction period. The longer the induction period the greater is the oxidative resistance of the oil sample.

Catalytic oxidation test

This test determines the effectiveness of an additive in preventing the catalyst oxidation of the oil sample under oxidizing conditions. The test procedure is as follows. In a 200 mm. x 25 mm. test tube is placed a 25 gram sample of a test oil having emersed therein (a) 15.6 sq. in. of sand-blasted iron wire, (b) 0.78 sq. in. of polished copper wire, (c) 0.87 sq. in. of polished aluminum wire and (d) 0.167 sq. in. of a polished lead specimen. The oil sample is heated to a temperature of 325° F. and maintained at this temperature while dry air is passed therethrough at the rate of 10 liters per hour for 40 hours. Upon expiration of the test period, the neutralization number (mg. KOH/g. sample) of each sample is determined. Several additives were tested at various concentrations and the minimum effective concentration necessary to limit the increase in neutralization number to a value of 2 was determined graprically. The lower the amount of additive required to maintain the neutralization number below the value of 2, the more effective is the antioxidant properties of this additive.

The results obtained are reported in Tables 1 and 2.

Table 1

NON-CATALYTIC OXIDATION TEST

Test No.	Additive	Conc. (Weight Percent)	Induction Period (Hours)
1	Oil,[1] none		0.9
2	Oil plus 2, 6-di-tert-butyl-p-cresol	0.1	18
3	Oil plus phenyl-α-naphthylamine	0.1	61
4	Oil plus 9-hydroxy-9, 10 boroxaro-phenanthrene.	0.1	354
5	Oil plus 9-methoxy-9, 10-boroxaro-phenanthrene.	0.1	270
6	Oil plus anhydride of 9-hydroxy-9, 10-boroxarophenanthrene.	0.095	351
7	Oil plus 1,1, 7-trihydroperfluoro-heptyl ester of 9-hydroxy-9, 10-boroxaro-phenanthrene.	0.26	193
8	Oil plus 9-tert-butoxy-9, 10-boroxaro-phenanthrene.	0.129	463

[1] A white oil KV at 210° F.=8 cs.

Table 2

CATALYTIC OXIDATION TEST AT 325° F. 40 HOURS

Test No.	Additive	Min. Effective Conc. (Wt. Percent). Required to Limit Δ (NN) to a Value of 2
1[2]	Oil plus phenyl-α-naphthylamine	3.3
2	Oil plus 2, 6-di-tert-butyl-p-cresol	>4.0
3	Oil plus 9-hydroxy-9, 10-boroxaro-phenanthrene.	0.25
4	Oil plus dioctadecyl-9-hydroxy-9, 10-boroxarophenanthrene.	1.00
5	Oil plus 2, 2-difluoro-dodecyl ester of 9-hydroxy-9, 10-boroxarophenan-threne.	0.70
6	Oil plus anhydride of 9-hydroxy-9, 10-boroxarophenanthrene.	0.20
7	Oil plus 9-tert-butoxy-9, 10-boroxaro-phenanthrene.	0.16

[1] Δ (NN) of base oil without additive=16.
[2] KV at 210° F.=4.90 cs.

It is noted from Table 1 that the antioxidant compounds of this invention are markedly superior to well known, commercially available antioxidants such as 2,6-di-tert-butyl-p-cresol (Test 2) and phenyl-α-naphthylamine (Test 3). Thus, the oil samples containing these commercial antioxidants had low oxidation resistance as shown by their low induction periods of 18 hours and 61 hours respectively. By contrast, the samples containing 9,10-boroxarophenanthrene antioxidants required from 193 hours (Test 7) to 463 hours (Test 8) to absorb the measured amount of oxygen thereby demonstrating the superior antioxidant properties of these compounds.

It will be seen from Table 2 that 3.3 wt. percent (Test 1) and greater than 4.0 wt. percent (Test 2) of the commercial antioxidants was necessary to limit the neutralization number Δ(NN) of the oil samples to a value of 2. On the other hand, as little as 0.16 to 1.0 wt. percent (Tests 3, 4, 5, 6 and 7) of the instant 9,10-boroxarophenanthrenes achieved the same result.

The 9,10-boroxarophenanthrene antioxidants of this invention are extremely effective in reducing and preventing oxidation, particularly at elevated temperatures, in a variety of lubricating compositions and fuels.

Thus, these compounds may be employed in lubricating compositions containing mineral oils from a variety of different crudes, both solvent and acid refined, hydrocracked etc.; as well as those containing synthetic base oils, i.e., synthetic hydrocarbons, synthetic esters, silicones etc.; including hydrogenated polyolefins, polyalkylene oxides, alkyl benzenes, various phosphorus acid esters, di-2-ethylexyl sebacate, di-octyl adipate, trimethylol propane trioctanoate, and the like. The 9,10-boroxarophenanthrenes, for example, may be advantageously used in automotive engine and gear oils, aviation lubricants including jet engine oils, various hydraulic and transmission fluids, industrial and marine oils, etc.

The fuels, the oxidation resistance of which is improved in accordance with the invention, in general, may be characterized as liquid hydrocarbon fuels. Such fuels include hydrocarbon fractions having initial boiling points from about 70° F. and final boiling points to about 750° F., and include gasolines, kerosines, fuel oils etc.

The amount of 9,10-boroxarophenanthrene employed will depend on various factors such as the nature of lubricating or fuel composition, its intended use, the presence or absence of other additives, etc. It is, however, a particular advantage of the antioxidants of this invention that they are effective in extremely low concentrations of the order of 0.001% or lower. In general, the 9,10-boroxarophenanthrenes are used in amounts by weight from about 0.001% to about 10%, preferably from about 0.01% to about 5% by weight in lubricants; and from about 0.001% to about 3%, preferably from about 0.01% to about 1% in fuels.

The lubricants and fuels of the present invention may, of course, also contain effective quantities of various typical additives normally used to improve such compositions and including detergents, rust and corrosion inhibitors, V.I. improvers, sludge inhibitors, other antioxidants, octane improvers, anti-icing agents, etc.

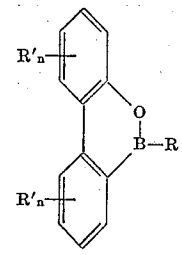
It will, of course, be appreciated that various modifications may be practiced without departing from the scope and spirit of the present invention.

Having fully described the invention, what we desire to secure and claim by Letters Patent is:

1. An organic composition selected from the group consisting of lubricants and fuel compositions containing an effective amount, sufficient to improve the oxidation resistance thereof, of a 9,10-boroxarophenanthrene compound.

2. A lubricating composition containing a minor amount

of a 9,10-boroxarophenanthrene compound of the formula:



where R is selected from the class consisting of hydroxy, hydrocarbyl, oxy-hydrocarbyl, halogen, halogenated hydrocarbyl, halogenated oxy-hydrocarbyl, and oxy-9,10-boroxarophenanthrene groups; R' is selected from the class consisting of hydrocarbyl, halogen and halogenated hydrocarbyl groups; and *n* is selected from the class consisting of zero and an integer from 1 to 4.

3. The lubricating composition of claim 2 which contains a major proportion of a lubricating oil.

4. The lubricating composition of claim 2 wherein the said boroxarophenanthrene compound is present in an amount from about 0.001 to about 10 weight percent.

5. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is 9-hydroxy-9,10-boroxarophenanthrene.

6. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is the anhydride of 9-hydroxy-9,10-boroxarophenanthrene.

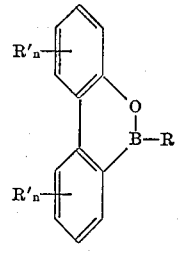
7. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is di-octadecyl-9-hydroxy-9,10-boroxarophenanthrene.

8. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is 9-methoxy-9,10-boroxarophenanthrene.

9. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is the 1,1,7-trihydroperfluoro-heptyl ester of 9-hydroxy-9,10-boroxarophenanthrene.

10. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is the 2,2-difluorododecyl ester of 9-hydroxy-9,10-boroxarophenanthrene.

11. A hydrocarbon fuel composition containing a minor amount of a 9,10-boroxarophenanthrene compound of the formula:



where R is selected from the class consisting of hydroxyl, hydrocarbyl, oxy-hydrocarbyl, halogen, halogenated hydrocarbyl, halogenated oxy-hydrocarbyl groups, and oxy-9,10-boroxarophenanthrene groups; R' is selected from the class consisting of hydrocarbyl, halogen and halogenated hydrocarbyl groups; and *n* is selected from the class consisting of zero and an integer from 1 to 4.

12. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is present in an amount from about 0.001 to about 3 weight percent.

13. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is 9-hydroxy-9,10-boroxarophenanthrene.

14. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is the anhydride of 9-hydroxy-9,10-boroxarophenanthrene.

15. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is di-octadecyl-9-hydroxy-9,10-boroxarophenanthrene.

16. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is 9 - methoxy - 9,10-boroxarophenanthrene.

17. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is the 1,1,7-trihydroperfluoro-heptyl ester of 9-hydroxy-9,10-boroxarophenanthrene.

18. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is the 2,2-difluorododecyl ester of 9-hydroxy-9,10-boroxarophenanthrene.

19. The fuel composition of claim 11 wherein said boroxarophenanthrene compound is 9 - tert. - butoxy-9,10-boroxarophenanthrene.

20. The lubricating composition of claim 2 wherein said boroxarophenanthrene compound is 9 - tert. - butoxy-9,10-boroxarophenanthrene.

References Cited by the Examiner

Dervar et al.: "Jour. Am. Chem. Soc.," vol. 84 (1962), pages 395–398.

Dervar et al.: "Jour. Chemical Society" (London) (1960), pages 1344–1347 (Part 1).

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