United States Patent Office

2,710,252

Patented June 7, 1955

2,710,252

ALKANEDIOL ESTERS OF ALKYL BORONIC ACIDS AND MOTOR FUEL CONTAINING SAME

Samuel M. Darling, Lyndhurst, Ohio, assignor to The Standard Oil Company, Cleveland, Ohio, a corporation of Ohio

No Drawing. Application May 17, 1954,
Serial No. 430,437

18 Claims. (Cl. 44—76)

The present invention relates to alkanediol esters of alkyl boronic acids and to a liquid hydrocarbon motor fuel containing minor amounts of one or more of said esters.

It is well known that the performance of an internal combustion engine is deleteriously affected during operation by the formation of deposits in the combustion zone and on the piston skirt and the piston rings.

The deposits formed in the combustion zone, particularly on the piston head and the exhaust valves, appear to have the most immediate effects upon engine performance in that their presence requires a fuel having a higher octane rating in order not to knock, than is required by a new or clean engine. This means, in other words, that the octane value of a fuel required by an engine containing deposits in the combustion zone in order not to knock (referred to hereinafter as "octane requirement") is higher than the octane requirement of a clean engine. For example, a clean engine which requires a gasoline having an octane rating of 60 in order not to knock is said to have an octane requirement of 60. If the same engine, when dirty, i. e., with deposits in the combustion chamber, requires a gasoline having an octane rating of 75 in order not to knock, such an engine is said to have an octane requirement of 75, or an "octane requirement increase" of 15. If a clean engine starts to get dirty, the octane requirement rises with continued use. Finally there is no more octane requirement increase with continued use and apparently the engine has then become as dirty as it is ever going to be with continued use or, if it becomes dirtier after a certain point, it does not require a gasoline of greater octane value in order not to knock.

It has previously been found, for example, that the weight of material deposited upon the top or head of the piston reaches a maximum in a single cylinder F–4 engine after approximately 20 hours of operation and that thereafter it decreases slightly, possibly due to a flaking action, until it levels off after about 40 hours of operation. It has also been found that the weight of the material deposited upon the exhaust valves reaches a maximum in the same engine after about 30 hours of operation and thereafter it decreases slightly and levels off after about 40 hours of operation. The fact that the weight of deposits in the combustion zone first reaches a maximum value and then levels off to a somewhat lower value while the octane requirement levels off at the maximum value is believed to disprove the formerly accepted theory that the octane requirement of an engine is proportional to the weight of deposits in the combustion chamber.

The undesirable effects of the deposits in the combustion chamber is further aggravated when tetraethyl lead is contained in the fuel because these deposits then are no longer primarily carbonaceous but contain appreciable quantities of lead. Accordingly, it has been found that the total weight of deposits formed in the combustion zone is appreciably greater when using a leaded fuel than when using a non-leaded fuel. The octane requirement increase of an engine operating on leaded fuel, however, is not in proportion to the difference in deposit weights. From this it is concluded that the octane requirement increase of an engine is determined not so much by the quantity of material deposited as by its presence and character.

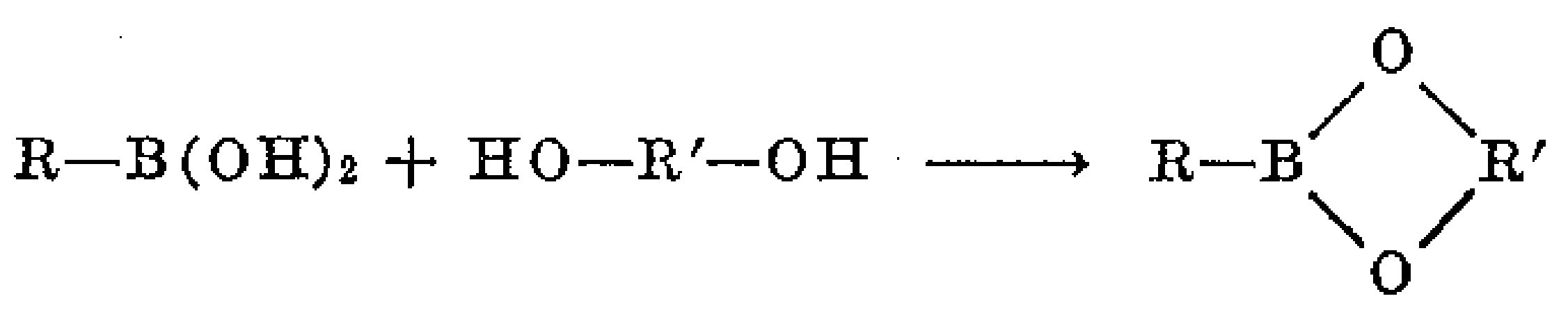
It has also previously been found that the increase in octane requirement resulting from the formation of engine deposits is not attributable to a decrease in the thermal conductivity of the surfaces enclosing the combustion zone.

Since it has been found that the octane requirement increase of an engine is not determined solely by the quantity of material deposited in the combustion zone and that it is not due to a decrease in the thermal conductivity of the surfaces enclosing said zone, it is believed that it is due to a catalytic action wherein the deposits in the combustion zone act as catalysts to accelerate the oxidation of petroleum hydrocarbons. It has, therefore, been suggested that the proper approach to the problem of reducing the octane demand increase of an engine is that of adding to the fuel a substance having an anti-catalytic effect, or, in other words, the effect of suppressing or inhibiting the catalytic properties of the deposits formed, especially the troublesome lead-containing deposits.

In accordance with the aforesaid suggestion it has previously been proposed to add minor amounts of boron in the form of soluble or dispersible boron compounds to the liquid hydrocarbon fuels used in internal combustion engines. Among the compounds previously proposed for such purposes are the tri-alkyl borates and the tri-alkyl borines, e. g., tri-amyl borine and tri-isobutyl borate. Such compounds have been shown to be effective in achieving the desired goal, but their use has been limited to some extent by various deficiencies which generally stem from their susceptibility to oxidation or to hydrolysis by water.

In accordance with the present invention, I have discovered that certain alkanediol esters of alkyl boronic acids are surprisingly stable even in the presence of water, are soluble in liquid hydrocarbon motor fuel, and, when added to such a motor fuel, provide a fuel which is capable of preventing substantial increase in the octane requirement of an engine on prolonged operation.

The alkanediol esters of alkyl boronic acids which form part of the present invention are prepared by reacting an alkanediol having from 2 to 8 carbon atoms with an alkyl boronic acid having from 4 to 10 carbon atoms. While the mechanism of the reaction has not been ascertained with certainty, it is believed that the reactants combine, mol for mol, with the elimination of two molecules of water to form a cyclic compound as illustrated by the following equation:



wherein R represents an alkyl radical of 4 to 10 carbon atoms, and R′ represents a hydrocarbon radical of from 2 to 8 carbon atoms, preferably a radical of 4 to 8 carbon atoms on which the OH groups are substituted on adjacent carbon atoms or on carbon atoms separated by only one carbon atom.

The motor fuel of the invention comprises a liquid hydrocarbon motor fuel which may be either leaded or unleaded and which contains an ester of the above description in an amount to minimize the octane requirement increase of an internal combustion engine operated on the fuel.

The amount of additive to be contained in the fuel is generally very small and is conveniently measured in terms of the amount of boron added to the fuel. For most purposes, I have found that the amount of additive should be such that the fuel will contain between about 0.0002 and about 0.02% by weight of boron. Amounts within the range of about 0.001 to 0.01% are preferred. Reference in this application to boron concentration is intended to refer to the amount of boron in the alkyl boronic acid as a component thereof and not to an amount of boron in its elemental state.

It is to be emphasized at this point that the boron additives described herein, when added to a motor fuel, are not anti-knock agents in the sense that they increase the octane rating of a fuel as is done by the addition of tetraethyl lead or other known anti-knock agents.

In the method of the invention, the optimum results are achieved when operating an initially clean engine but the method also has a gradual beneficial effect in operating a dirty engine. Cleaning of the engine, when desirable, may be accomplished by any of several known techniques such as by disassembly and scraping.

In the preparation of alkanediol esters of alkyl boronic acids of the invention, the preferred procedure comprises refluxing approximately equimolecular quantities of the appropriate alkanediol and alkyl boronic acids in an inert reaction medium such as an aromatic hydrocarbon, e. g., benzene. During the reaction, the water is collected in an azeotropic trap. The preparation of typical alkyl boronic acids which may be utilized as reactants in this process is described in my copending application Serial No. 430,436, filed May 17, 1954. The time of the reaction is generally a few hours; in most cases from 5 to 6 hours are sufficient.

The following examples further illustrate the invention. Parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

A reaction vessel was equipped with a reflux condenser and azeotropic trap. Into the vessel there was placed 26.8 g. of n-octyl boronic acid, 20 g. (0.1692 mol) of 2-methyl-2,4-pentanediol and approximately 200 ml. of benzene. The mixture was heated and allowed to reflux for about 6 hours, water being collected during the reaction in the azeotropic trap. The amount of water so collected was 7 ml., the theoretical amount being 5.8 ml. At the end of the reflux period, the benzene solution was washed five times with 100 ml. portions of water and the benzene was then stripped off by simple distillation keeping the temperature below 75° C. The residue was then placed under vacuum and nitrogen was bubbled through for 15 minutes. A light yellow fluid was obtained, a few white crystals remaining in the flask. The weight of crystals plus fluid was 37.6 g. and the weight of fluid, after filtration, was 36.4 g. This amounted to 95.3% of the theoretical yield. The product analyzed as follows:

	Found	Theory
Molecular Weight	239,240	240.2
Percent Boron	4.15, 4.37	4.50
Density	0.8644	
Refractive Index	1.4309	
Boiling Point (° C.)	150 (2-3 mm.)	

EXAMPLES 2 THROUGH 17

Several other esters were prepared by the procedure of Example 1. The following table shows the reactants and mols thereof utilized in each preparation:

Table I

Example No.	Boronic Acid	Diol	$\frac{\text{Mols Diol}}{\text{Mols Acid}}$
2	n-butyl	2,5-hexanediol	$\frac{0.0029}{0.0025}$
3	do	2,3-dimethyl-2,3-butanediol	$\frac{0.0029}{0.0025}$
4	do	2-methyl-2,4-pentanediol	$\frac{0.0029}{0.0025}$
5	do	2,2-diethyl propanediol	$\frac{0.0029}{0.0025}$
6	do	propylene glycol	$\frac{0.0029}{0.0025}$
7	t-butyl	2-methyl-2,4-pentanediol	$\frac{0.0029}{0.0018}$
8	do	propylene glycol	$\frac{0.0029}{0.0018}$
9	n-hexyl	2,5-hexanediol	$\frac{0.015}{0.011}$
10	do	2,3-dimethyl-2,3-butanediol	$\frac{0.016}{0.011}$
11	do	2-methyl-2,4-pentanediol	$\frac{0.015}{0.011}$
12	do	2,2-diethyl propanediol	$\frac{0.015}{0.011}$
13	do	propylene glycol	$\frac{0.0029}{0.0029}$
14	do	ethylene glycol	$\frac{0.0029}{0.0029}$
15	n-octyl	2,5-hexanediol	$\frac{0.014}{0.011}$
16	do	2,3-dimethyl-2,3-butanediol	$\frac{0.014}{0.011}$
17	do	2,2-diethyl propanediol	$\frac{0.014}{0.011}$

EXAMPLES 18 THROUGH 34

Each of the esters prepared in Examples 1 to 17 was added to iso-octane and to a conventional leaded gasoline in an amount to provide a concentration of 0.004% boron in each fuel. All of the fuels were then examined or tested to determine the resistance to hydrolysis by water of the additive contained therein. In this test, 900 ml. of each motor fuel was placed over the 100 ml. of distilled water and allowed to stand in the dark for 144 hours. At the end of this time, the water layer was analyzed for boron content and this value was then subtracted from the amount of boron originally present in the fuel to determine the amount of boron remaining in the fuel. The results in the hydrolysis test are reported in terms of percent of boron remaining in the fuel compared with the amount originally present.

The following table gives the results of the hydrolysis tests:

Table II

Example No.	Additive of Example No.	Percent Hydrolysis in Iso-octane	Percent Hydrolysis in Gasoline
18	1	0.18	0.26
19	2	86.01	70.7
20	3	1.82	1.46
21	4	1.46	1.46
22	5	8.02	6.2
23	6	37.5	42.6
24	7	3.07	4.1
25	8	24.0	24.5
26	9	14.67	10.77
27	10	1.0	1.05
28	11	0.91	0.91
29	12	1.08	1.12
30	13	8.77	10.71
31	14	15.91	20.45
32	15	0.31	0.90
33	16	0.18	0.25
34	17	0.18	0.29

The results in the table show that the motor fuels of the invention are remarkably resistant to hydrolysis. In view of the known efficacy of boron in preventing octane requirement increase, it is thus indicated that such motor fuels will operate efficiently in minimizing octane requirement increase even in the presence of water. It is also evident that the optimum results are obtained when the glycol from which the additive is prepared contains at least 4 carbon atoms and the OH groups are substituted on adjacent carbons or on carbons separated by only one other carbon atom.

It is to be understood that the liquid hydrocarbon motor fuel of this invention may be any of those ordinarily used for internal combustion engines and may contain other ingredients and additives such as antioxidants, gum inhibitors, solvent oils, upper cylinder lubricants, dyes and perfumes ordinarily added to motor fuels. The presence of these additives and the amounts normally used does not alter the effect of the additive.

It is intended to cover all changes and modifications in the examples of the invention, herein given for purposes of disclosure, which do not constitute departure from the spirit and scope of the appended claims. Further, it is not intended that the scope of the invention be limited by any theory advanced to explain the action of the additive disclosed as effective in reducing the increase in the octane requirement of an internal combustion engine.

I claim:

1. An ester of an alkanediol having from 2 to 8 carbon atoms and an alkyl boronic acid having from 4 to 10 carbon atoms.

2. An ester according to claim 1 in which the alkyl boronic acid is n-octyl boronic acid.

3. An ester according to claim 1 in which the alkyl boronic acid is n-hexyl boronic acid.

4. An ester according to claim 1 in which the alkyl boronic acid is a butyl boronic acid.

5. The 2-methyl-2,4-pentanediol ester of n-octyl boronic acid.

6. The 2,5-hexanediol ester of n-octyl boronic acid.

7. The 2,2-diethyl propanediol ester of n-octyl boronic acid.

8. The 2,3-dimethyl-2,3-butanediol ester of n-octyl boronic acid.

9. The 2,3-dimethyl-2,3-butanediol ester of n-hexyl boronic acid.

10. A liquid hydrocarbon motor fuel containing the ester of claim 1 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

11. A liquid hydrocarbon motor fuel containing the ester of claim 2 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

12. A liquid hydrocarbon motor fuel containing the ester of claim 3 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

13. A liquid hydrocarbon motor fuel containing the ester of claim 4 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

14. A liquid hydrocarbon motor fuel containing the ester of claim 5 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

15. A liquid hydrocarbon motor fuel containing the ester of claim 6 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

16. A liquid hydrocarbon motor fuel containing the ester of claim 7 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

17. A liquid hydrocarbon motor fuel containing the ester of claim 8 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

18. A liquid hydrocarbon motor fuel containing the ester of claim 9 in an amount to minimize octane requirement increase of an internal combustion engine on which said fuel is operated.

References Cited in the file of this patent

UNITED STATES PATENTS

2,257,194 Rosen .... Sept. 30, 1941
2,312,208 Clayton et al. .... Feb. 23, 1943

OTHER REFERENCES

Industrial and Engineering Chemistry, vol. 43, No. 12, Dec. 1951, pp. 2842–2843. (Copy in 44—76.)