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MOTOR FUEL CONTAINING AN ALKYL BORONIC ACID

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The present invention relates to a liquid hydrocarbon fuel containing minor concentrations of one or more alkyl boronic acids for use in internal combustion engines.

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 found that certain alkyl boronic acids are surprisingly stable even in the presence of water, are soluble in liquid hydrocarbon motor fuels and, when added to such a motor fuel, provide a fuel which is capable of preventing substantial increase in the octane requirement of an internal combustion engine on prolonged operation. The alkyl boronic acids which may be utilized in the invention are those in which the alkyl group contains from 6 to 8 carbon atoms, i. e., hexyl, heptyl and octyl boronic acids in which the alkyl group may be straight or branched chain.

The number of carbon atoms in the alkyl radical is, as indicated by the preceding description, an important factor in determining the suitability of the additives. For example, compounds in which the alkyl radical has 4 carbon atoms are relatively soluble in water and hence are susceptible to being extracted from the gasoline by the small amounts of water which are often present in gasoline. On the other hand, compounds in which the alkyl group has more than 8 carbon atoms in a straight chain have the disadvantage of low volatility and a low boronic content. For this reason, they are not attractive from a practical view. Accordingly, my invention pertains to a liquid hydrocarbon motor fuel containing an alkyl boronic acid of the above description in an amount to minimize the octane requirement increase of an internal combustion engine operated on said fuel. The fuel may be leaded or unleaded and good results have been obtained in either case.

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 be disassembly and scraping.

The alkyl boronic acids used as motor fuel additives in the present invention may be prepared by reacting an alkyl magnesium halide, e. g., an alkyl magnesium bromide, with a tri-alkyl borate at low temperatures and then hydrolyzing the intermediate product with dilute sulfuric acid according to the following illustrative equations:

$$\mathrm{RMgBr} + \mathrm{B(OCH_3)_3} \longrightarrow \mathrm{RB(OCH_3)_3} + \mathrm{MgBr}$$

$$\xrightarrow[\mathrm{H_2SO_4}]{\mathrm{H_2O}} \mathrm{RB(OH)_2}$$

wherein R represents an alkyl radical of 6 to 8 carbon atoms.

The following specifically illustrate typical preparations of the alkyl boronic acids:

PREPARATION A

n-Hexyl boronic acid

A reaction vessel was fitted with a mercury-sealed stirrer, a dropping funnel, thermometer, and a drying tube. Dry nitrogen was allowed to flow through the vessel for approximately ½ hour and then 31 grams of tri-methyl borate (0.3 mol) was quickly added through the dropping funnel and washed into the vessel with 150 ml. of dry ether. The vessel was suspended in a larger vessel containing Dry Ice and acetone and stirred until the temperature of its contents was from about —70 to —80° C. At this point n-hexyl magnesium bromide (0.22 mol) in ether solution was introduced slowly through the funnel over a period of about 5 hours, keeping the temperature below —70° C.

When the addition was complete, the mixture was stirred at —70° C. for about 4 hours and then allowed to stand in the vessel overnight. The next morning the vessel was allowed to warm to —10° C. and there was observed therein a large amount of a heavy white precipitate and a small amount of clear supernatant liquid. Three hundred (300) ml. of a 10% sulfuric acid solution was then added with stirring and cooling.

The liquid layer was then separated and extracted with 30 ml. of ether which was combined with the contents of the vessel. The contents of the vessel was then concentrated on a steam bath, 20 ml. of distilled water was added, and the heating on the steam bath continued until all material volatile at the temperature of the bath had evaporated. At this point there were two clear layers in the vessel, a lower water layer and an upper light-yellow layer. Upon cooling, the upper layer solidified forming a whitish wax-like material which comprised crude n-hexyl boronic acid. The material analyzed 8.02% boron as against a theoretical boron content of 8.3%.

PREPARATION B

n-Octyl boronic acid

The same apparatus described in Preparation A was used. 34.29 grams (0.33 mol) of tri-methyl borate was added to the flask and diluted with 150 ml. of anhydrous ether. When the temperature of the ether solution reached —80° C., 260 ml. of an ether solution of or containing 86.98 grams of alkyl magnesium bromide, i. e., n-octyl magnesium bromide, was added dropwise over a period of 6 hours. The contents of the vessel was then stirred an additional 5 hours and after standing overnight at —70 to —80° C., the mixture was brought to —10° C. and hydrolyzed as in Preparation A. The product was then recovered as in Preparation A and there was obtained 51.7 grams (99.1% of the theoretical yield) of white wax-like crystals of crude n-octyl boronic acid. The crystals analyzed 6.63% boron as compared to a theoretical boron content of 6.83%.

PREPARATION C

2-ethyl hexyl boronic acid

The same apparatus was used as that described in Preparation A except a ground glass stirrer was used in place of the mercury sealed stirrer. After sweeping the system with dry nitrogen for ½ hour, 26 grams (0.25 mol) of trimethyl borate was added to the flask and washed through with 75 ml. of dry ether. As soon as the temperature reached —70° C. 250 ml. of the 2-ethyl hexyl magnesium bromide solution (48.5 grams—0.22 mol) was added drop-wise over a period of 4½ hours, keeping the temperature below —70° C. throughout the addition. The reaction was stirred an additional 6½ hours at this temperature. After standing overnight in the Dewar flask, the reaction flask was removed from the Dewar and allowed to warm up to —10° C. 200 ml. of water containing 20 ml. of concentrated sulfuric acid were added with stirring and cooling. The reaction was then brought to room temperature, the ethereal layer separated, and the water layer extracted with 50 ml. of ether which was combined with the main portion. The ether solution was concentrated on a steam bath, 20 ml. of water was added, and heated until all the material volatile at the temperature of the steam bath was removed. After cooling, a pale yellow wax-like material was recovered. The crude yield was 28.5 grams, 82.1% of theory. The material analyzed 6.42% boron as compared to a theoretical boron content of 6.83%.

In order to further illustrate the invention, the following examples are presented in which parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

A liquid hydrocarbon motor fuel was prepared by dissolving n-hexyl boronic acid in iso-octane to provide a concentration of 0.004% boron based on the total weight of fuel.

EXAMPLE 2

A liquid hydrocarbon motor fuel was prepared by dissolving n-octyl boronic acid in iso-octane to provide a concentration of 0.004% boron based on the total weight of fuel.

EXAMPLE 3

A liquid hydrocarbon motor fuel was prepared by dissolving n-octyl boronic acid in a leaded gasoline to provide a concentration of 0.004% boron based on the total weight of fuel.

EXAMPLE 4

A liquid hydrocarbon motor fuel was prepared by dissolving 2-ethyl hexyl boronic acid in iso-octane to provide a concentration of 0.004% boron based on the total weight of fuel.

EXAMPLE 5

A liquid hydrocarbon motor fuel was prepared by dissolving 2-ethyl hexyl boronic acid in a leaded gasoline to provide a concentration of 0.004% boron based on the total weight of fuel.

EXAMPLE 5A

A liquid hydrocarbon motor fuel was prepared by dissolving n-butyl boronic acid in iso-octane to provide a concentration of 0.004% boron based on the total weight of fuel.

EXAMPLE 5B

A liquid hydrocarbon motor fuel was prepared by dissolving n-butyl boronic acid in a leaded gasoline to provide a concentration of 0.004% boron based on the total weight of fuel.

The motor fuels of Examples 1 through 5B were tested to determine the resistance to hydrolysis by water of the additive contained therein. In each test, 900 ml. of each motor fuel was placed over 100 ml. of distilled water and allowed to stand 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 tests are reported in terms of weight percent of boron remaining in the fuel compared to the amount originally present.

The following table gives the results of the hydrolysis tests:

Table I

Fuel of Example No.	Additive	Fuel	Hydrolysis (Percent)
1	n-hexyl boronic acid	iso-octane	24.27
2	n-octyl boronic acid	do	3.70
3	do	gasoline	13.81
4	2-ethyl hexyl boronic acid	iso-octane	3.67
5	do	gasoline	4.35
5A	n-butyl boronic acid	iso-octane	86.37
5B	do	gasoline	71.06

The results in Table I show that the motor fuels of the invention illustrated by Examples 1 to 5 are surprisingly resistant to hydrolysis. In view of the known ability of boron to reduce octane requirement increase of an internal combustion engine, it is thus indicated that such motor fuels will operate efficiently in preventing octane requirement increase even in the presence of water. On the other hand, Examples 5A and 5B which form no part of the invention and which are included for comparative purposes show that normal butyl boronic acid is not as effective an additive and is relatively amenable to hydrolysis by water and thus lacks the stability ordinarily desired.

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 normally added to motor fuels. The presence of these additives and the amounts normally used does not alter the effect of the alkyl boronic acid.

It is intended to cover all changes and modifications in the examples of the invention, herein given for purposes of illustration, 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 alkyl boronic acids disclosed as effective in reducing the increase in the octane requirement of an internal combustion engine.

I claim:

1. A liquid hydrocarbon motor fuel for an internal combustion engine containing an alkyl boronic acid in which the alkyl group has from 6 to 8 carbon atoms in an amount to minimize octane requirement increase in an engine operated on said fuel.

2. A liquid hydrocarbon motor fuel according to claim 1 in which the alkyl boronic acid is n-hexyl bromic acid.

3. A liquid hydrocarbon motor fuel according to claim 1 in which the alkyl boronic acid is n-octyl boronic acid.

4. A liquid hydrocarbon motor fuel according to claim 1 in which the alkyl boronic acid is 2-ethyl hexyl boronic acid.

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