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MOTOR FUELS

Fred S. Arimoto, New Castle, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to motor fuels for spark ignition engines and to anti-knock compositions for use in such motor fuels.

In operating internal combustion engines, particularly the modern engines with high compression ratios, it has been found that the tendency for the fuel mixture to pre-ignite increases as the engine is operated. Also, the octane value of the fuel required to prevent knock must be increased after the engines have been in operation for some time and this so-called octane demand increases until a fairly constant value is reached. It is believed that both these effects are closely related to the formation of solid deposits in the engine, although the present invention does not depend on any theory for the cause of the increased octane demand and increased pre-ignition tendency.

It has been reported by Hughes et al. in *Industrial and Engineering Chemistry*, 43, 2841-2844 (1951) that alkyl borates of the formula $B(OR)_3$, such as triethyl and triisobutyl borates, and alkyl borines of the formula R_3B , such as normal and tertiary butyl borines, incorporated in the gasoline used, reduce the increase in octane requirement. Compounds of these types, however, cannot be used under actual practical conditions because of their reactivity. Thus, the borines are very readily oxidized, even at the dilution at which they would be used in gasoline, and some are even spontaneously inflammable in pure form. The borate esters show an equally serious sensitivity to hydrolysis and are rapidly attacked by the small amount of water always present in commercial gasoline. Even when they are used in dried gasoline in experimental engine tests, they are hydrolyzed by atmospheric moisture in the carburetor and in a fairly short time clog its passage with solid hydrolysis products.

It is an object of the present invention to provide improved motor fuels for spark ignition engines. Another object is to provide motor fuels for spark ignition engines which minimize the tendency of deposits to promote pre-ignition during continued engine operation. A further object is to provide new and improved anti-knock compositions for addition to motor fuels for spark ignition engines. A still further object is to provide anti-knock compositions which, when added to motor fuels for spark ignition engines, cause the motor fuels to minimize the tendency of deposits to promote pre-ignition during continued engine operation. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished by my invention which comprises hydrocarbon motor fuels for spark ignition engines which contain tetraethyl lead and, for each gallon of motor fuel, from 0.1 to about 3 ml. of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 15 carbon atoms and wherein each R is a hydrocarbon radical of 2 to 7 carbon atoms, and anti-knock mixtures comprising tetraethyl lead and between 2 and 0.02 volumes of such boronate esters for each volume of tetraethyl lead.

The boronate esters of my invention are very effective

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in reducing the tendency of deposits to promote pre-ignition of motor fuels, containing tetraethyl lead, in spark ignition engines during continued engine operation. By pre-ignition is meant ignition of the fuel-air mixture in the engine cylinder by hot deposit surfaces. My boronate esters have the unpredictable and unobvious advantage, over other boron compounds previously proposed for this purpose, of being very stable toward oxygen and moisture when dissolved in hydrocarbon motor fuels and in tetraethyl lead anti-knock compositions, so that they are quite satisfactory for use under the conditions encountered in practice; that is, they are highly resistant to oxidation and to hydrolysis in such solutions at atmospheric temperatures over long periods of time and under the conditions prevailing in the carburetors and intake manifolds of spark ignition engines. Also, they are soluble in the hydrocarbon motor fuels and in the anti-knock mixtures, at least to the extent required for the purposes of my invention. Such boronate esters do not affect appreciably the octane numbers of the motor fuels. Neither do they deleteriously affect the stability of the motor fuels but usually improve the stability of the motor fuels, particularly in the absence of substantial amounts of water.

The motor fuels will, preferably, be gasoline, but may be any other combustible liquids of suitable volatility commonly employed as fuels for spark ignition engines, including paraffinic, naphthenic and aromatic hydrocarbons, isooctane and mixtures of isooctane with other suitable liquid hydrocarbons. Such motor fuels may also contain antioxidants, stabilizers, dyes, or other compounds which are commonly employed in motor fuels.

The motor fuel will contain tetraethyl lead in a proportion of from about 0.5 ml. to about 5 ml. per gallon of the motor fuel. The concentration of tetraethyl lead in the motor fuel will be varied as is usual with the engine and its use. In automotive engines, the concentration of tetraethyl lead is usually in the range of from about 1.5 ml. to about 3.0 ml. per gallon of motor fuel. In light airplane engines, the concentration of tetraethyl lead is usually in the range of from about 1 ml. to about 2 ml. per gallon of motor fuel. However, larger high output aircraft engines usually require from about 2.5 ml. to about 5 ml. of tetraethyl lead per gallon of motor fuel.

The motor fuel may contain a halo-hydrocarbon lead scavenging agent in an amount up to about 5 theories, usually from about 1 to about 5 theories, and preferably from about 1 to about 2 theories, based on the tetraethyl lead. One theory of a scavenging agent is that quantity which provides 2 atoms of active halogen per atom of lead in the tetraethyl lead. The class of halo-hydrocarbon scavenging agents is well known and a great many of them have been disclosed in prior patents and in the literature. Generally, they are hydrocarbons in which at least one hydrogen has been replaced by chlorine or bromine or both. The most commonly employed scavenging agents are ethylene dichloride and ethylene dibromide, and they are preferred scavenging agents in the compositions of my invention. Of the lead compounds found in the engine deposits, the lead halides, such as $PbCl_2$ and $PbBr_2$, formed by the reaction of lead with the scavenging agents, appear to be the most active in promoting preignition. Hence, it is desirable to use the minimum permissible amount of scavenging agent so as to further reduce the tendency for preignition.

The boronate esters of my invention have the formula $RB(OR)_2$ wherein each R is a hydrocarbon radical of 2 to 7 carbon atoms and contain a total of from 10 to 14 carbon atoms. The total number of carbon atoms in the boronate esters is that required to provide compounds having a volatility roughly approximating that of tetraethyl lead. Preferably, the boronate esters will

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contain from 12 to 14 carbon atoms. The R's in the formula may be the same or different and may be alkyl, alkylene, aryl, aralkyl, alkaryl or cycloaliphatic radicals. The alkyl radicals may be primary, secondary or tertiary, and straight or branched chain radicals. Ordinarily, each R is a monovalent radical, but two R's may together represent a divalent radical such as a polymethene radical. Preferably, one R will be an alkyl radical of 4 to 5 carbon atoms and each of the other R's will be a hydrocarbon radical of the class of alkyl radicals of 3 to 5 carbon atoms, and aryl radicals of 6 to 8 carbon atoms. More particularly, I prefer the boronate esters which contain 12 to 14 carbon atoms and in which each R is an alkyl radical of 4 to 5 carbon atoms, such as di-n-butyl n-amy-l-boronate, di-n-butyl n-butylboronate, di-isobutyl t-butylboronate, di-isobutyl n-butylboronate, di-n-butyl t-butylboronate, and diamyl amylboronates. The most preferred boronate esters are di-n-butyl n-butylboronate and di-isobutyl n-butylboronate. Other boronate esters, within the scope of my invention, are:

Diethyl phenylboronate
Di-isobutyl ethylboronate
Diallyl n-butylboronate
Di-n-butyl propylboronate
Di-isobutyl phenylboronate

The boronate esters and methods of making them are, in general, known to the art. Those specifically disclosed herein were made either by esterifying the corresponding free boronic acid, made by the method of Snyder, Kuck and Johnson disclosed in J. A. C. S., 60, 105 (1938), or by reacting equivalent amounts of the required Grignard reagent and the borate ester.

The boronate esters of my invention will be employed in a concentration of from 0.1 ml. to about 3 ml. per gallon of motor fuel, and preferably in a concentration of from about 0.1 ml. to about 1 ml. per gallon.

Ordinarily, tetraethyl lead is sold in the form of an anti-knock mixture for addition to motor fuels. Such anti-knock mixtures usually consist essentially of tetraethyl lead, the desired proportion of halo-hydrocarbon lead scavenging agent, a dye for identifying the composition and the motor fuel containing it, and a small amount of a liquid hydrocarbon diluent. While the boronate esters of my invention may be added to the motor fuel separately from the tetraethyl lead, it is desirable to add them to the anti-knock mixture in a proportion to provide the desired amount in the motor fuel when the mixture is added to the motor fuel.

Thus, an important feature of my invention is an anti-knock mixture consisting essentially of tetraethyl lead and between 2 and 0.02 volumes of a boronate ester of my invention per volume of tetraethyl lead. Usually, such mixtures will contain the desired scavenging agents. The boronate esters are miscible with the tetraethyl lead and with mixtures thereof with the scavenging agents. Preferably, the boronate ester will be in the proportion of from about 0.5 to about 0.03 volume per volume of tetraethyl lead. Also, preferably, the scavenging agent will be in a proportion of from about 1 to about 2 theories. Usually, it will be desirable to include in the anti-knock mixture a dye for the purpose of identifying the mixture and the motor fuel containing it, and the usual liquid hydrocarbon diluent. The resulting compositions are stable, homogeneous liquid compositions which are particularly suitable for addition to motor fuels for the purpose of preventing knocking and of reducing the tendency of the motor fuel to create combustion chamber deposits prone to cause pre-ignition during continued operation of the engine with such motor fuel.

In order to more clearly illustrate my invention, preferred modes of carrying the same into effect and the advantageous results to be obtained thereby, the following examples are given:

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Example I

One gram (about 0.005 mole) of di-n-butyl n-butylboronate was shaken in a flask with 50 ml. isooctane (94 ml. of boronate per gallon of isooctane) and 20 ml. water for 4 hours at room temperature. At the end of this time, no acid was found in the water layer as determined by titration with caustic indicating negligible hydrolysis. When tri-n-butyl borate was treated in a similar manner, 4.6% of the ester was hydrolyzed under these mild conditions.

Example II

About 0.002 mole (0.4 gr.) of various boronate esters were agitated with 25 ml. of 85 octane number reference fuel consisting of 85 vol. % isooctane and 15 vol. % n-heptane (75 ml. of boronate per gallon of fuel) and 20 ml. water for 30 minutes at 50° C. The approximate per cent of the boronate ester, which was hydrolyzed to acid, was determined by titration of the water layer with caustic. The results are shown in the following table:

Compound	No. of Carbons	Percent Hydrolyzed
Diethyl phenylboronate.....	10	94
Diisobutyl ethylboronate.....	10	87
Diallyl-n-butylboronate.....	10	84
Di-n-butyl propylboronate.....	11	72
Diisobutyl phenylboronate.....	14	62
Diisobutyl tert.-butylboronate.....	12	54
Diisobutyl-n-butylboronate.....	12	53
Di-n-butyl-n-butylboronate.....	12	53
Di-n-butyl-n-amy-lboronate.....	14	22

Similar experiments with tri-n-butylborate showed that hydrolysis takes place faster than the ester can pass from the fuel into the water phase, and appears to be complete in less than 5 minutes.

This example shows clearly that rather drastic conditions of concentration and temperature (never experienced in gasoline storage) are required to hydrolyze the boronate esters, whereas the borates are hydrolyzed almost immediately. While even the least stable boronate esters are sufficiently stable for use under practical conditions, those which hydrolyze to the extent of less than 60% under the conditions of this example are preferred.

Example III

Diisobutyl n-butylboronate was evaluated as a fuel additive in 60 octane number (O. N.) primary reference fuel (60% isooctane and 40% n-heptane by volume) both with and without tetraethyl lead by the standard knock rating procedures in a Cooperative Fuel Research engine. With the research method (ASTM D908-47T) and with the motor method (ASTM D357-47), the following results were obtained:

	Octane Numbers	
	Research Method	Motor Method
60 O. N. ref. fuel.....	60.0	60.0
60 O. N. ref. fuel +3 ml. boronate/gal.....	59.6	59.5
60 O. N. fuel +3 ml. TEL/gal.....	84.5	83.0
60 O. N. fuel +3 ml. TEL/gal. +3 ml. boronate/gal.....	84.6	84.3

Example IV

A standard Oldsmobile "Rocket" engine (compression ratio 7.5:1) was operated under low duty cyclic conditions using a fuel consisting of catalytic cracked gasoline (containing 0.1% organic sulfur), 3.0 ml. of tetraethyl lead per gallon (plus 1.0 "theory" of ethylene dichloride and 0.5 "theory" of ethylene dibromide), and 1.0 ml. of diisobutyl n-butylboronate. At the end of about 60 hours and continuing for 110 hours additional, the pre-ignition requirement of this engine was approximately

81 octane numbers, as determined under retarded spark conditions so that knock would not interfere with the pre-ignition determination. At the end of this 170 hour period, the engine operation was continued using the above leaded fuel without the boronate ester additive and the pre-ignition requirement increased to 85-86 octane numbers within 20 hours and remained at that level for at least 90 hours more.

When an attempt was made to test tributyl borate under the same conditions, the carburetor passages became clogged with hydrolysis products and a new carburetor had to be installed after 12 hours operation.

Example V

Several commercial gasolines were mixed with 1.0 ml. per gallon of diisobutyl n-butylboronate and stored at 110° F. over a layer of water to determine their stability in the presence of the boronate ester. The gasoline's stability was measured by means of induction period (for oxygen absorption) and by ASTM gum determinations, in mg. of gum per 100 ml. of the gasoline. The results are shown below (averages of two determinations each):

Gasoline	Induction Period (Fresh), min.	ASTM Gum (Fresh)	ASTM Gum (10 days storage)
Gasoline A	359	9.6	13.0
Gasoline A + boronate	417	7.8	7.9
Gasoline B	603	6.6	4.5
Gasoline B + boronate	497	4.8	2.0
Gasoline C	387	2.2	2.6
Gasoline C + boronate	353	3.3	nil
Gasoline D	285	5.0	5.5
Gasoline D + boronate	303	4.5	5.9

This example clearly shows that the boronate ester exerts no deleterious effect on the stability of the commercial gasoline. In fact, in storage tests at room temperature with a typical catalytic cracked gasoline, the boronate appeared to impart superior stability to the gasoline, as is shown in Example VI.

Example VI

A typical catalytic cracked gasoline, mixed with diisobutyl n-butylboronate ester and/or tetraethyl lead, containing 1 theory of ethylene dichloride and 0.5 theory of ethylene dibromide, as indicated below, was stored at room temperature for one month both in the presence and in the absence of water. ASTM gum determinations were made on the gasoline. The water layers from the stored samples were titrated with standard sodium hydroxide to determine the liberated acid. The results are indicated below in which the gum is given in mg. per 100 ml. of the gasoline:

Cat. cracked fuel plus	ASTM Gum (no H ₂ O layer present)	ASTM Gum (H ₂ O layer present)	Millequiv. acid in H ₂ O layer
(Control)	26	7.6	21×10 ⁻²
3.0 ml./gal. TEL	2.2	3.0	22×10 ⁻²
0.5 ml. boronate/gal.	1.4	1.8	0.4×10 ⁻²
0.5 ml. boronate/gal. plus 3.0 ml./gal. TEL	0.4	3.6	2.5×10 ⁻²

In addition to their effect upon pre-ignition, the boronate esters of the present invention have also been observed to have a desirable effect upon the increase in the octane demand which takes place as an engine is operated. In other words, it has been observed that the octane number of the fuel, required to operate an engine without knocking after it has been in operation for some time, is less if the engine has been operated over this period with a fuel containing a boronate ester. However, the effect of the boronate esters on pre-ignition, as shown in Example IV, is of greater practical significance,

particularly in the types of high compression engines now being developed.

The boronate esters of my invention have the formula $RB(OR)_2$ and hence structurally are somewhat similar to the borines, which have the formula R_3B . Since the borines are extremely susceptible to oxidation at atmospheric temperatures, tending to catch fire spontaneously, it would be expected that the boronate esters would also be quite susceptible to oxidation, particularly at the elevated temperature present in the carburetors and the intake manifolds of spark ignition engines, and over long periods of storage. However, diisobutyl n-butylboronate, for example, has stood in contact with air and inflammable material for several days without evidence of combustion. Also, when a motor fuel, containing a boronate ester, was used in the operation of an automobile engine over long periods of time as in Example IV, there was no evidence of any oxidation of the boronate ester, such as the deposition of non-volatile oxidation products in the carburetor and other parts of the intake system of the engine.

Since the boronate esters of my invention contain ester groups, and since the borate esters, having the formula $B(OR)_3$, are very susceptible to hydrolysis in the presence of moisture at atmospheric temperatures, it would be expected that the boronate esters of my invention would also be quite susceptible to hydrolysis in the presence of water or water vapor at atmospheric temperatures and particularly at the elevated temperatures present in the carburetors and the intake manifolds of spark ignition engines, and over long periods of storage. However, as shown in the examples, motor fuels containing the boronate esters could be used or stored over long periods of time without difficulty, whereas a motor fuel containing a borate ester (tributyl borate) could not.

It will be understood that the preceding examples are given for illustrative purposes solely, and that my invention is not limited to the specific embodiments disclosed therein. On the other hand, it will be apparent to those skilled in the art that, within the scope of the general description, variations can be made in the boronate esters, in the proportions thereof employed in the motor fuels and in the anti-knock mixtures, in the composition of the motor fuels, in the composition of the anti-knock mixtures, in the engines, and in the techniques employed, without departing from the spirit or scope of my invention.

It will be apparent that, by my invention, I have provided novel motor fuels for spark ignition engines and novel anti-knock mixtures useful for making such motor fuels, whereby the tendency for pre-ignition during continued operation of the engines therewith is materially reduced by means which are practical. Therefore, it is obvious that my invention constitutes a valuable advance in and contribution to the art.

I claim:

1. A hydrocarbon motor fuel for spark ignition engines containing, for each gallon thereof, from about 0.5 to about 5 ml. of tetraethyl lead and from 0.1 to about 3 ml. of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 14 carbon atoms and wherein each R is a hydrocarbon radical of 2 to 7 carbon atoms at least two of which are aliphatic.

2. A hydrocarbon motor fuel for spark ignition engines containing, for each gallon thereof, from about 0.5 to about 5 ml. of tetraethyl lead and from 0.1 to about 3 ml. of a boronate ester of the formula $RB(OR)_2$ which contains 12 to 14 carbon atoms and wherein each R is an alkyl radical of 4 to 5 carbon atoms.

3. A hydrocarbon motor fuel for spark ignition engines containing, for each gallon thereof, from about 0.5 to about 5 ml. of tetraethyl lead and from 0.1 to about 3 ml. of di-n-butyl n-butylboronate.

4. A hydrocarbon motor fuel for spark ignition engines containing, for each gallon thereof, from about 0.5 to about 5 ml. of tetraethyl lead and from 0.1 to about 3 ml. of diisobutyl n-butylboronate.

5. An anti-knock mixture consisting essentially of tetraethyl lead and between 2 and 0.02 volumes per volume of tetraethyl lead of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 14 carbon atoms and wherein each R is a hydrocarbon radical of 2 to 7 carbon atoms at least two of which are aliphatic.

6. An anti-knock mixture consisting essentially of tetraethyl lead and between 2 and 0.02 volumes per volume of tetraethyl lead of a boronate ester of the formula $RB(OR)_2$ which contains 12 to 14 carbon atoms and wherein each R is an alkyl radical of 4 to 5 carbon atoms.

7. An anti-knock mixture consisting essentially of tetraethyl lead and between 2 and 0.02 volumes per volume of tetraethyl lead of di-n-butyl n-butylboronate.

8. An anti-knock mixture consisting essentially of tetraethyl lead and between 2 and 0.02 volumes per volume of tetraethyl lead of di-isobutyl n-butylboronate.

9. An anti-knock mixture consisting essentially of tetraethyl lead, from about 1 to about 5 theories of a halo-hydrocarbon scavenging agent, and from about 0.5 to about 0.03 volume per volume of tetraethyl lead of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 14 carbon atoms and wherein each R is a hydrocarbon radical of 2 to 7 carbon atoms at least two of which are aliphatic.

10. An anti-knock mixture consisting essentially of tetraethyl lead, from about 1 to about 5 theories of a halo-hydrocarbon scavenging agent, and from about 0.5 to about 0.03 volume per volume of tetraethyl lead of a boronate ester of the formula $RB(OR)_2$ which contains 12 to 14 carbon atoms and wherein each R is an alkyl radical of 4 to 5 carbon atoms.

11. An anti-knock mixture consisting essentially of tetraethyl lead, from about 1 to about 5 theories of a halo-hydrocarbon scavenging agent, and from about 0.5 to about 0.03 volume per volume of tetraethyl lead of di-n-butyl n-butylboronate.

12. An anti-knock mixture consisting essentially of tetraethyl lead, from about 1 to about 5 theories of a halo-

hydrocarbon scavenging agent, and from about 0.5 to about 0.03 volume per volume of tetraethyl lead of di-isobutyl n-butylboronate.

13. A hydrocarbon motor fuel for spark ignition engines containing, for each gallon thereof, from about 0.5 to about 5 ml. of tetraethyl lead and from 0.1 to about 3 ml. of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 14 carbon atoms and wherein the R attached to the boron atom is a hydrocarbon radical of the class consisting of alkyl radicals of 3 to 5 carbon atoms and a phenyl radical and each of the other R's is an alkyl radical of 4 to 5 carbon atoms.

14. An anti-knock mixture consisting essentially of tetraethyl lead and between 2 and 0.02 volumes per volume of tetraethyl lead of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 14 carbon atoms and wherein the R attached to the boron atom is a hydrocarbon radical of the class consisting of alkyl radicals of 3 to 5 carbon atoms and a phenyl radical and each of the other R's is an alkyl radical of 4 to 5 carbon atoms.

15. An anti-knock mixture consisting essentially of tetraethyl lead, from about 1 to about 5 theories of a halo-hydrocarbon scavenging agent, and from about 0.5 to about 0.03 volume per volume of tetraethyl lead of a boronate ester of the formula $RB(OR)_2$ which contains 10 to 14 carbon atoms and wherein the R attached to the boron atom is a hydrocarbon radical of the class consisting of alkyl radicals of 3 to 5 carbon atoms and a phenyl radical and each of the other R's is an alkyl radical of 4 to 5 carbon atoms.

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