PATENT SPECIFICATION

NO DRAWINGS

822,279

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Index at acceptance:—**Classes 2(3),** C3A13E; **and 91,** G1A1.

International Classification:—**C07d. C10g.**

COMPLETE SPECIFICATION

Organic Boron Compounds and Liquid Leaded Motor Fuel containing the same

We, THE STANDARD OIL COMPANY, of Midland Building, Cleveland 15, Ohio, United States of America, a Company incorporated under the Laws of the State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to organic boron compounds and to liquid leaded motor fuels comprising organic boron compounds incorporated therein.

It is well known that during the operation of an initially clean internal combustion engine, deposits form progressively and accumulate on the surfaces within the combustion zone, *i.e.*, on the cylinder head, piston top, spark plug, and the intake and exhaust valves. As the operation continues, the amount of the deposits reaches a level after which there is no appreciable further increase in the amount of the deposits. The engine is then regarded as having deposit equilibrium and old deposits flake off as fast as new deposits form.

The deposit problem is aggravated when tetraethyl lead is contained in the fuel because the deposits are then no longer essentially carbonaceous, but comprise appreciable quantities of lead and lead compounds generally mixed in with the carbonaceous material. Despite the fact that one or more organic halides are included in the fuel with the tetraethyl lead to serve as a scavenging agent, the lead is not all removed. A carbonaceous deposit with lead is often more tenacious and troublesome than a pure carbonaceous deposit. The fact that this deposit is partially metallic in character is thought to give it a catalytic activity which modifies the action of the deposit in affecting engine operation. Furthermore, since the lead is intimately mixed in with the carbonaceous material, the lead in the deposit is difficult to reach by means of scavengers or material reactive therewith to eliminate or modify it, especially in engines which have been in operation and which have such deposits built up in them over a long period of time.

These deposits have a number of adverse effects upon engine operation, but with available fuels they cannot be avoided and are inherent in present day operation of internal combustion engines. One adverse effect of the deposits is manifested most clearly to the operator of the engine, particularly an automobile engine, by the fact that the presence of the deposits in the engine requires a fuel having a higher octane rating in order not to knock than is required by a new or clean engine. This requirement for a fuel of higher octane number, as the engine becomes progressively dirtier, persists until the deposits reach equilibrium, and is known as octane requirement increase (ORI). Another factor to be considered is the reduction in the volume of the combustion zone equivalent to the volume of the deposits and the consequent increase in compression ratio which aggravates the above manifestation.

Another adverse effect of the deposits is characterised by uncontrolled ignition, either pre-ignition or post-ignition. This is explained by the fact that the deposits, or portions of them become heated to incandescence and ignite the hydrocarbon either before or after the portion in the cycle at which the charge would be ignited by the spark of the spark plug. This manifests itself in various ways characterised as "roughness," "rumble," various forms of knocking, and a general lack of smoothness in engine operation.

Another adverse effect of the deposits is on

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the spark plug, particularly when the deposits contain lead which results in spark plug fouling with resultant loss in power or reduced spark plug life.

Still another adverse effect of the deposits is the result of their thermal insulating property. They are poorer conductors than the metal parts of the engine and as a result they interfere with proper cooling and temperature maintenance of the engine parts. This is particularly true in the case of the exhaust valves which become overheated and burn or otherwise deteriorate as the result of the deposits. A serious adverse effect of the deposits is the channeling of exhaust valves. This is explained by the fact that the deposits flake off as fast as they are formed once the deposit equilibrium is reached, and the flakes leave through the exhaust valves. The glowing deposits expelled from the silencer have been seen by all who drive at night. As these deposits leave through the exhaust valve they may lodge between the valve and the seat, thereby interfering with the proper closing of the valve. The hot exhaust gases passing between the valve and the seat result in channeling. Failure of the valve to seal the combustion chamber properly results in loss of acceleration, power and mileage. Somewhat analogous results occur in connection with the inlet valves, but because these valves are cooler the character of the deposits is often different, and while not as severe, is nevertheless a problem in engine operation. The action of fuel and the deposits on valve life and condition has been largely overlooked or minimised in evaluating fuels, and since the valve action is vital to proper engine operation, this phase of the matter deserves special attention.

It is an object of this invention to provide novel organic boron compounds which may be incorporated in leaded liquid motor fuels with a view to mitigating the beforementioned problems.

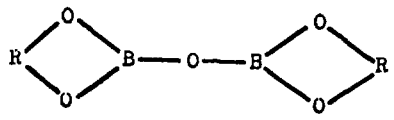
Organic boron compounds, if they are stable under many conditions of use, are usually of relatively high molecular weight and have a relatively low boron content. As such, they are not adapted for many uses where their suitability depends on a high proportion of boron in the compound. In addition, organic boron compounds which do have a substantial boron content, as a class, are generally unstable and do not satisfactorily resist oxidation or hydrolysis.

The novel boron compounds provided according to the present invention have the advantage of a relatively high boron content and, at the same time, are particularly resistant to oxidation and are resistant to hydrolysis to form boric acid, a property not possessed by the common organic esters of boric acid. Whilst the compounds of this invention may hydrolise *in situ* they yield boron-containing hydrolysis products which still have the desired effect and are stable against further hydrolysis.

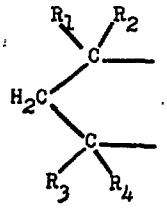
In addition, the organic boron compounds of the invention, together with their hydrolysis products, are moderately soluble in hydrocarbons as well as water and their hydrolysis products do not precipitate from gasoline in which the compounds are dissolved even though such gasoline is stored for long periods in contact with water. This is to be contrasted with many boron compounds which hydrolyse so readily that they would be eliminated from gasoline when the latter is stored in contact with water as is usually the case at bulk storage plants and in the tanks of individual cars.

Thus, the boron compounds of the invention have such desirable characteristics as solubility, volatility, and chemical structure as to make them both soluble in the fuel, and effective in the combustion chamber.

The present invention provides novel boron compounds of the general formula:

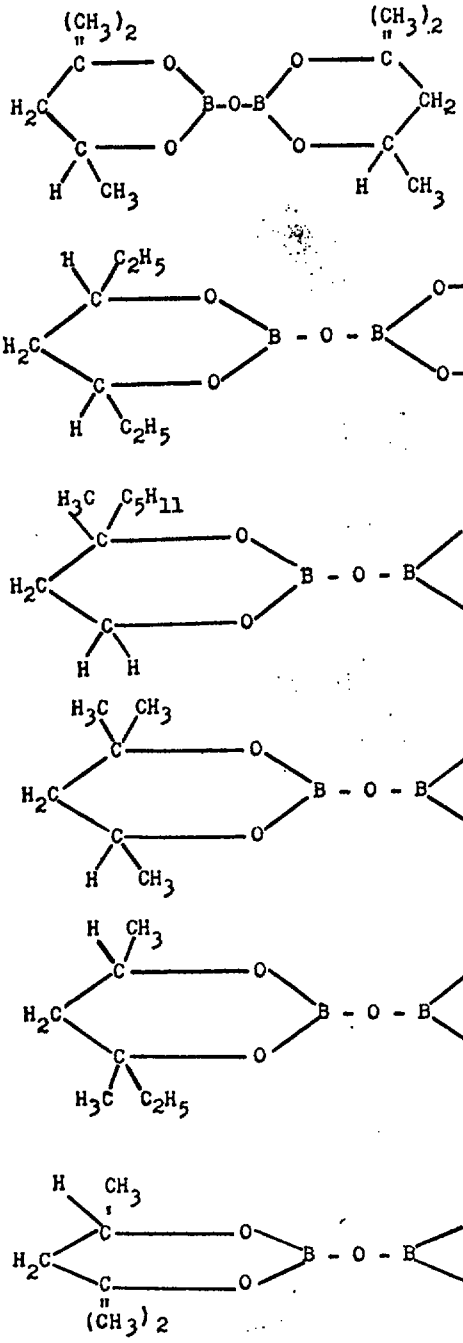


wherein each R is an alpha or beta alkylene radical having 3 to 20 carbon atoms, such compounds having not more than 25 carbon atoms in the molecule. In a sub-group within this novel class of compounds each R represents a radical of the general formula:

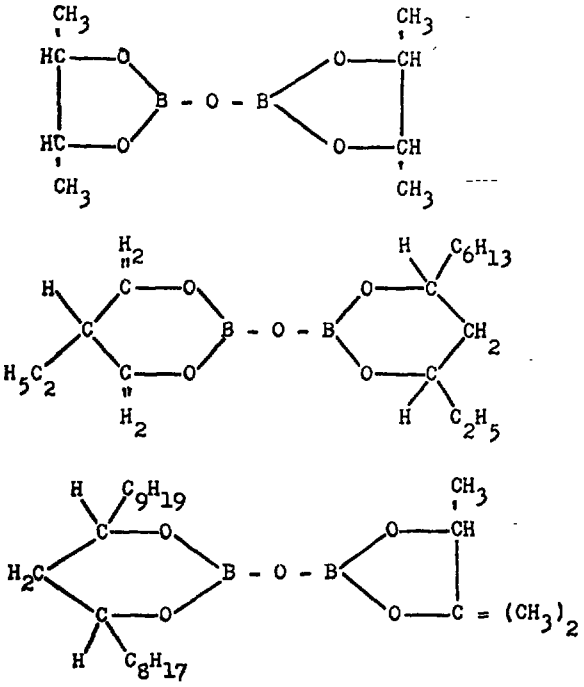


wherein R_1, R_2, R_3 and R_4 are the same or different and are each a hydrogen atom or an alkyl group having 1 to 6 carbon atoms. Said alkyl groups are preferably methyl groups.

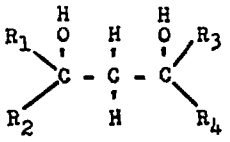
Examples of boron compounds within this sub-group are as follows:



Examples of other boron compounds according to the invention are as follows:



The invention also includes a process for producing such boron compounds which comprises mixing in a 1:1 molar ratio boric acid and an alpha or beta glycol having 3 to 20 carbon atoms, or an equimolar mixture of two glycols, heating the resulting mixture until liquid and continuing the heating to vaporise out, 2½ moles of water, said glycol or glycols being such that the compound produced will not have more than 25 carbon atoms in the molecule. To produce compounds within the sub-group referred to above, the glycol or glycols to be used are of the general formula:



wherein R_1, R_2, R_3 and R_4 have the meanings defined above.

Of course, in the case of the production of asymmetric boron compounds, equimolar quantities of the two appropriate glycols will be used in admixture, instead of using a single glycol as in the preparation of symmetrical compounds. The materials are reacted at mildly elevated temperatures until the water of reaction which is required to be split off is vaporised from the reaction mixture. All the water can be removed by simple boiling. However, because of the low boiling points of many of the compounds a certain amount thereof may be lost due to volatilisation during the removal of water. For this reason the complete removal of water from the reaction system may preferably be effected by means of fractional distillation or azeotropic fractional distillation which permits the removal of the water with a minimum loss of the reaction product. The water of reaction removed from the reaction system may be accurately measured so that the formation of the ester anhydrides of the present invention, rather than the corresponding ester acids, may be readily controlled.

Our invention also includes gasoline to which has been added up to 6 cc. per United States gallon of tetraethyl lead, a halide scavenging agent, and a boron compound of this invention, the amount of said boron compound added to the gasoline being equivalent to 0.002 to 0.1% by weight boron. Advantages of the boron compounds of this invention are that they are liquid and that they react readily with water, unlike their hydrolysis products which are solids and do not readily hydrolyse further. The boron compounds of this invention, being themselves liquid, can readily be added as such to gasoline by conventional metering and blending operations, without the necessity of first dissolving them in a solvent; furthermore, they will react with any water present in the gasoline, so removing such water therefrom, without precipitation of the hydrolysis product which although normally solid is also soluble in the gasoline.

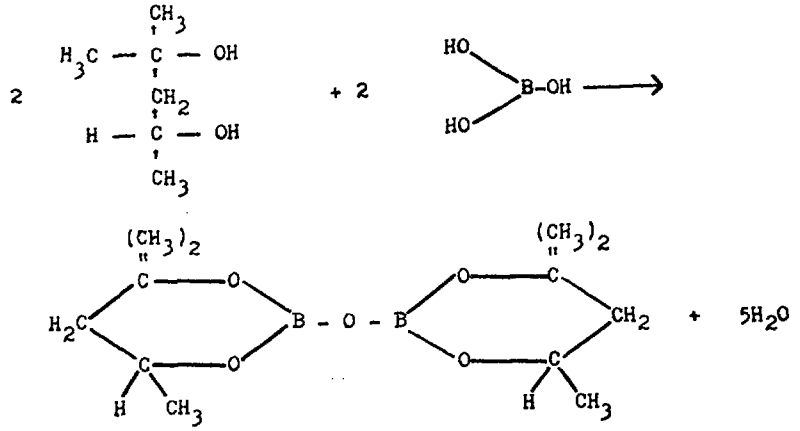
The compounds of this invention when in pure form may, on exposure to moisture, form a certain amount of solid product and even though this product is soluble in gasoline, the presence of solids would make it more difficult to blend the boron additive into the gasoline. For this reason it may be desirable to incorporate a certain proportion of solvent therewith during or before blending them with gasoline, so as to maintain the boron-containing component in a liquid form, whereby it may the more easily be metered and blended into gasoline; such solvent may for example be toluene, methanol or hexylene glycol. However, the greater the bulk of the supply of liquid boron compound the less is there a call for the use of an auxiliary solvent.

The following Examples illustrate the production of the compounds of the present invention.

EXAMPLE 1.

49.5 Grams of dry orthoboric acid and 94.5 grams of 2-methyl-2,4-pentanediol (a 1:1 molar ratio) were mixed together. Upon mixing, the temperature dropped approximately 8 to 10° C. and upon additional stirring, the temperature then rose rapidly to and slightly above the initial temperature, at which time the mixture became solid. The mixture was then heated and became completely liquid at about 70 to 75° C. 100 cc. of benzene was added and the water formed was removed

azeotropically by distillation with the benzene over a period of several hours. The reaction proceeds in accordance with the following equation:



and the product may be named bis-(1,1,3-trimethyltrimethyleneoxy) boric oxide. The compound of this Example was found to be a colourless liquid of medium viscosity. It is miscible in hydrocarbons, and particularly in gasoline, and the common organic solvents in all proportions, and has a higher boron content in liquid form than any known boron compound which will not precipitate boric acid when added to wet gasoline. It has the following additional properties, prior to purification by repeated fractional distillation as mentioned below:

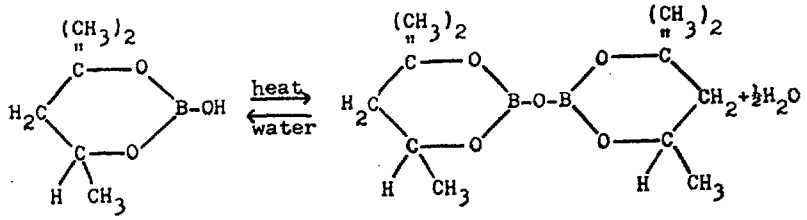
Boiling point:	Approximately 275° C. at atmospheric pressure and 140—142° C. at 1 mm. Hg.
n_D^{25}	1.4310
Molecular weight	Calculated 269.9, found 246.5.
Per cent. boron	Calculated 8.01, found 7.41.

The boron determination was made by titration with mannitol, and the molecular weight was done cryoscopically in benzene. Infra red analysis confirmed the absence of the hydroxyl group, and repetition under conditions permitting recovery of the water of reaction showed that two and one-half moles of water were formed for each mole of glycol and boric acid reacting.

The above compound was twice distilled at a pressure less than 1 mm. Hg. The narrow boiling heart cut was submitted to analysis. The following composition was found:

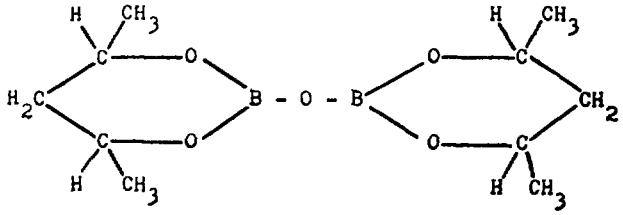
%	Calculated	Found by Analysis
Carbon	53.39	53.42
Hydrogen	8.96	9.02
Boron	8.01	7.79

The liquid anhydride product is very hydroscopic and readily reacts with water to form the compound shown below, from which it can also be prepared by dehydration, by heating or desiccation. This reversible reaction is represented by the following equation:

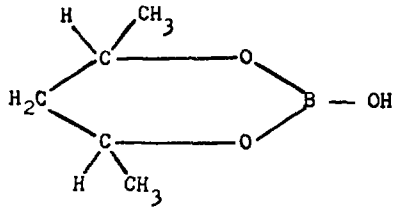


EXAMPLE 2.

52 Grams pentanediol-2,4 is reacted with 31 grams of dry orthoboric acid under the same conditions as those of Example 1. The product was a clear, colourless, viscous liquid having a boiling point of 114° C. at 1 mm. Hg. It has the formula



The yield was 61 grams, which was vacuum distilled at 1 mm. Hg. to give a yield of 55.8 grams. The compound reacts with water to give a product that is crystalline solid, having a melting point of 76° C. and which has the formula



Gasoline solutions containing up to 3 cc. per gallon of tetraethyl lead and to which the anhydrides mentioned above had been added in an amount to provide 0.002 to 0.1% boron were stored in open beakers in a humidity chamber for several months at 75° F. No crystals were formed, and analysis of the gasoline before and after the test showed the boron content to be the same. No precipitation occurred when the samples were stored at −10° F. for several months, and the boron content was the same before and after the test.

Fuel containing the boron compound should be and is sufficiently stable to be stored in contact with moisture for three months without loss of boron content.

The gasoline base stocks to which the boron compounds are added may be any of those conventionally used in making motor gasoline (gasoline for use in an automobile).

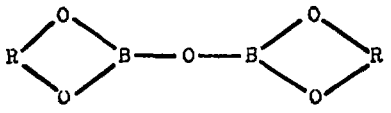
The gasoline of the invention also contains tetraethyl lead in amounts up to 6 cc., but usually from ½ cc., per United States gallon, and a halide scavenging agent. The latter may be 1 theory of ethylene dichloride and ½ theory of ethylene dibromide (the so-called "motor mix" or MM) or 1 theory of ethylene dibromide (the so-called "aviation mix" or AM). By "theory" is meant the stoichiometric amount of the ethylene dihalide for combination with all of the lead as lead halide. The AM is preferred since in combination with the boron compound there results a better overall effect in engine performances. The gasoline may contain any of the usual adjuncts such as anti-oxidants, dyes, solvent oils or alcohols.

The amount of the boron compound added to the fuel may vary and the amount is preferably expressed in terms of boron. Generally an amount of the compound to provide 0.002% by weight of boron (based on the total fuel) is the smallest amount that will give any significant effect. Amounts between 0.004% and 0.008% by weight are preferred. Use of amounts in excess of 0.1% usually cannot be justified economically.

The specification of our copending Application No. 26073/55 (Serial No. 822,278) sets out in detail the results of tests carried out on gasolines containing the product of the hydrolysis of the compound of Example 1 hereof. Such results also indicate the advantages of the use of the compounds of this invention, which compounds hydrolyse in wet gasoline to give such hydrolysis products.

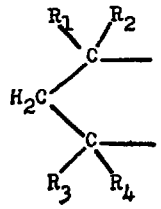
WHAT WE CLAIM IS:—

1. Compounds of the general formula:



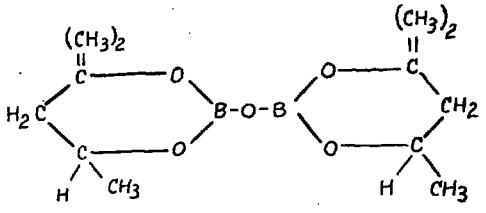
wherein each R is an alpha or beta alkylene radical having 3 to 20 carbon atoms, such compounds having not more than 25 carbon atoms in the molecule.

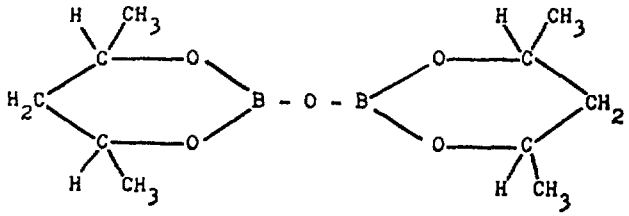
2. Compounds according to claim 1, wherein each R represents a radical of the general formula:



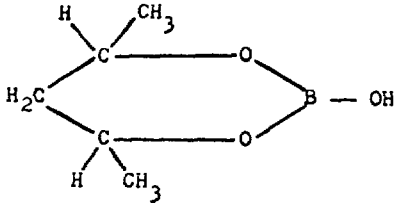
wherein R_1, R_2, R_3 and R_4 are the same or different and are each a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

3. The compound of the formula:





The yield was 61 grams, which was vacuum distilled at 1 mm. Hg. to give a yield of 55.8 grams. The compound reacts with water to give a product that is crystalline solid, having a melting point of 76° C. and which has the formula



Gasoline solutions containing up to 3 cc. per gallon of tetraethyl lead and to which the anhydrides mentioned above had been added in an amount to provide 0.002 to 0.1% boron were stored in open beakers in a humidity chamber for several months at 75° F. No crystals were formed, and analysis of the gasoline before and after the test showed the boron content to be the same. No precipitation occurred when the samples were stored at −10° F. for several months, and the boron content was the same before and after the test.

Fuel containing the boron compound should be and is sufficiently stable to be stored in contact with moisture for three months without loss of boron content.

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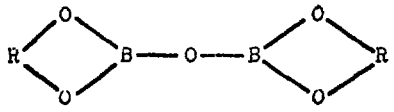
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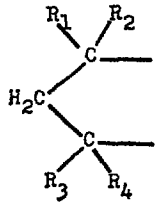
WHAT WE CLAIM IS:—

1. Compounds of the general formula:



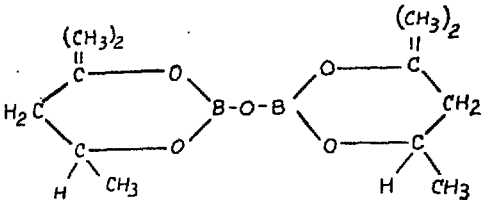
wherein each R is an alpha or beta alkylene radical having 3 to 20 carbon atoms, such compounds having not more than 25 carbon atoms in the molecule.

2. Compounds according to claim 1, wherein each R represents a radical of the general formula:



wherein R_1, R_2, R_3 and R_4 are the same or different and are each a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

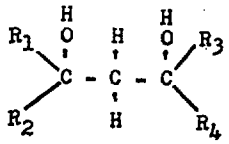
3. The compound of the formula:



4. The compounds according to claim 1 hereinbefore specifically referred to.

5. A process for the production of the compounds claimed in any of the preceding claims, which comprises mixing in a 1:1 molar ratio boric acid and an alpha or beta glycol having 3 to 20 carbon atoms, or an equimolar mixture of two such glycols, heating the resulting mixture until liquid and continuing the heating to vaporise out 2½ mols of water, said glycol or glycols being such that the compound produced will not have more than 25 carbon atoms in the molecule.

6. A process according to claim 5, wherein said glycol or glycols have the general formula:



wherein R_1, R_2, R_3 and R_4 have the meanings defined in claim 2.

7. A process for the production of the compound claimed in claim 3, which comprises mixing one mole of orthoboric acid with one mole of 2-methyl-2,4-pentanediol, heating the resulting mixture until liquid and continuing the heating to vaporise out 2½ moles of water.

8. A process for the production of boron compounds of the general formula defined in claim 1, substantially as described with reference to either of the Examples.

9. Boron compounds whenever made by a process as claimed in any of claims 5 to 8.

10. Gasoline to which has been added up to 6 cc. per United States gallon of tetraethyl lead, a halide scavenging agent, and a boron compound as claimed in any of claims 1, 2, 3, 8 and 9, the amount of said boron compound added to the gasoline being equivalent to 0.002 to 0.1% by weight boron.

11. Gasoline as claimed in claim 10, in which the scavenging agent is one theory of ethylene dibromide per theory of tetraethyl lead.

12. Gasoline as claimed in claim 10, or 11, wherein the boron compound is one in which each R as defined in claim 1 is an alkylene radical having not more than 4 carbon atoms.

13. Gasoline as claimed in claim 12, wherein each R is a straight chain alkylene radical having 4 carbon atoms.

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* C L M S *