PATENT SPECIFICATION

NO DRAWINGS

822,280

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International Classification:—C07d. C10g.

COMPLETE SPECIFICATION

Gasoline Containing Organic Boron Compounds

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 gasoline containing organic boron compounds.

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 reached 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 the spark plug, particularly when the deposits contain lead which results in a 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

[*Price 3s. 6d.*]

Price 4s 6d

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 flowing 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 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.

With a view to mitigating the beforementioned problems, it is an object of this invention to provide leaded liquid motor fuels to which have been added organic boron compounds not hitherto used for the purpose.

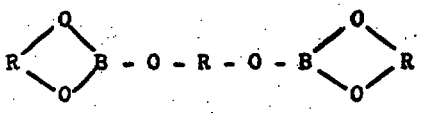
Organic boron compounds, if they are stable under many conditions of use, are usually of relatively high molecular weight and have a relatively low boron content. As such, they are not adapted for many uses where their suitability depends on a high proportion of boron in the compound. In addition, organic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

The boron compounds proposed for use in accordance with 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 to be used according to this invention may hydrolyse *in situ* they will yield boron-containing hydrolysis products which still have the desired effect and are stable against further hydrolysis.

In addition, the organic boron compounds employed in 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.

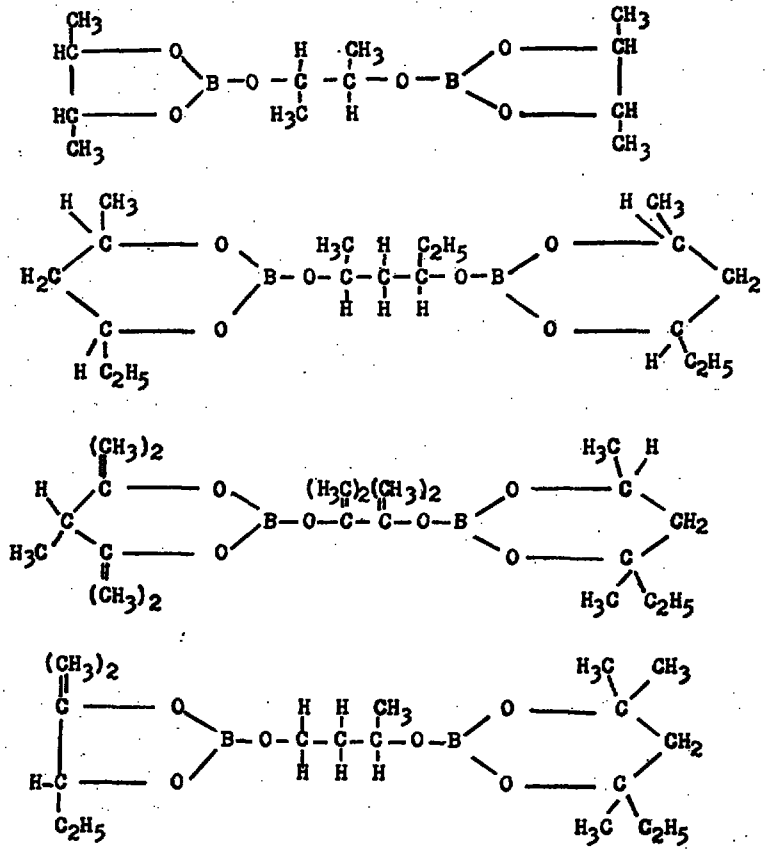
Thus, the boron compounds to be used according to the invention have such desirable characteristics as solubility, volatility and chemical structure as to make them both soluble in the fuel, and effective in the combustion chamber.

The present invention provides 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 having the general formula:

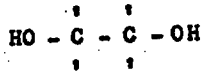


wherein R represents alpha or beta alkylene radicals each having 3 to 20 carbon atoms, said boron compound having not more than 25 carbon atoms in the molecule, the amount of said boron compound added to the gasoline being equivalent to 0.002 to 0.1% by weight of boron.

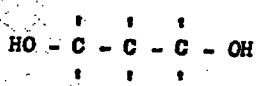
Boron compounds illustrative of those which may be used in accordance with the present invention are as follows:



The compounds used in the fuel of the invention may be made by reacting two mols of boric acid with three mols of the corresponding alpha glycol having the formula



or the beta glycol having the formula



in which formulae the unattached valencies are linked to hydrogen or to the straight chain or branched alkyl radicals, to provide a total of 3 to 20 carbon atoms in the glycol.

Of course, in the case of the asymmetric boron compounds, either equimolar quantities of three glycols or a 2:1 molar mixture of two glycols will be reacted with boric acid instead of using a single glycol as in the preparation of compounds in which each R has the same significance.

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 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 may be accurately measured so that the formation of the desired compound may be readily controlled.

Advantages of the boron compounds to be used according to this invention are that they are liquids 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 necessiy 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.

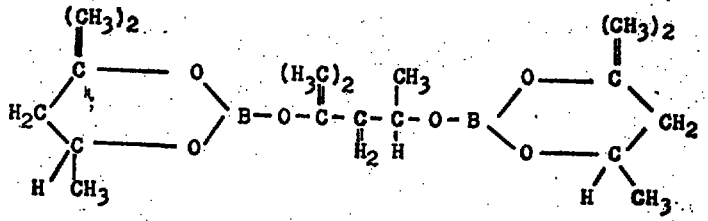
The compounds of this invention when in pure form, may, on exposure to moisture form a certain amount of solid product and even though this product is soluble in gasoline, the presence of solids would make it more difficult to blend the boron additive into the

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 is 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 to be used in the present invention:

EXAMPLE 1.

Dry orthoboric acid (2 moles) and 2-methyl-2,4-pentanediol (3 moles) are mixed together. Upon mixing the temperature dropped and upon additional stirring the temperature 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. A sufficient volume of benzene was then added and the water formed was removed azeotropically with the benzene over a period of several hours until 6 moles of water of reaction had been removed. The resulting boron compound was a colourless liquid having the formula:



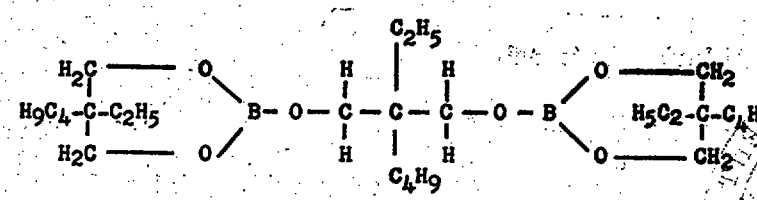
The compound was found to have the following properties:

Boiling point: 154—162° C. at 1 mm. Hg.
n_D^{25}: 1.4388
Molecular weight:
Calculated 370.7; found 330,329
Percent. boron:
Calculated 5.83; found 5.21, 5.29.

The boron determination was made by titration with mannitol, and the molecular weight was determined cryoscopically in benzene.

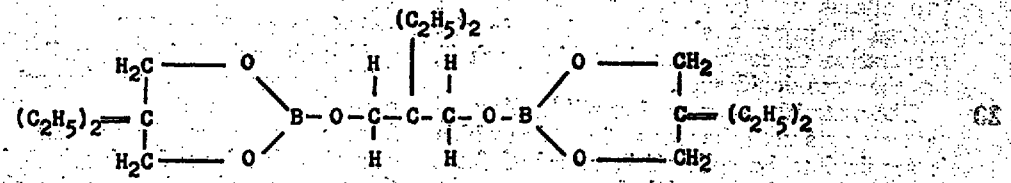
EXAMPLE 2.

40 G. of 2-ethyl-2-butyl-propane-1,3-diol and 10.5 g. of boric acid were heated in 250 ml of benzene. The molar glycol to boric acid ratio was 1.5. The reaction mixture was heated for six hours. The azeotrope distilled at 71° C. 9 Ml. of water were obtained in the distillation. The excess benzene was distilled off at atmospheric pressure. The residue was blown with N_2 to remove all the benzene. The product was a colourless viscous liquid. The yield was 40 g. Analysis showed 4.3 and 4.4% boron. The calculated amount of boron was 4.5%. The product has the formula:



EXAMPLE 3.

40 G. of 2,2-diethylpropane-1,3-diol and 11 g. of boric acid were heated in 250 ml. of benzene (molar glycol to boric acid ratio 1.5). The water was removed as an azeotrope. The latter distilled at 71° C. 11 Ml of water was obtained. The excess benzene was distilled off at atmospheric pressure. The product was a viscous light yellow liquid. Yield was 43 g. Analyses gave 4.6 and 4.8% for the boron content. Corresponding calculated value was 5.2%. The product has the formula:



Gasoline solutions containing up to 3 cc. per United States gallon of tetraethyl lead and to which the boron compounds 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.

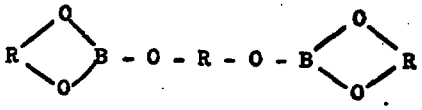
The gasoline base stocks to which the boron compounds are added may be any of those conventionally used in making motor gasoline (gasoline for use in an automobile).

The gasoline of the invention also contains tetraethyl lead in amount up to 6 cc., but usually from 1/2 cc., per United States gallon, and a halide scavenging agent. The latter may be 1 theory of ethylene dichloride and 1/2 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.

WHAT WE CLAIM IS:—

1. 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 having the general formula:



wherein R represents alpha or beta alkylene radicals each having 3 to 20 carbon atoms, said boron compound having not more than 25 carbon atoms in the molecule, the amount of said boron compound added to the gasoline being equivalent to 0.002 to 0.1% by weight boron.

2. Gasoline as claimed in claim 1, wherein each R is an alkylene radical having not more than 4 carbon atoms.

3. Gasoline as claimed in claim 1 or 2, wherein each R is a straight chain alkylene radical having 4 carbon atoms.

4. Gasoline as claimed in claim 1, 2 or 3 in which the scavenging agent is one theory of ethylene dibromide per theory of tetraethyl lead.

5. Gasoline as claimed in any of the preceding claims, in which the boron compound is one of the boron compounds hereinbefore specifically referred to.

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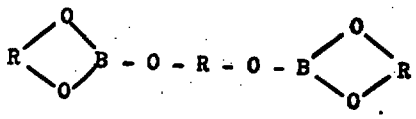

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* C L M S *