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DIESEL FUEL

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5 Claims. (Cl. 44—9)

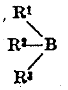
The present invention relates to improvements in compression ignition fuels, and relates more particularly to the use of organic compounds of boron as ignition accelerators for hydrocarbon fuels of the compression ignition type.

This application is a division of my application Serial No. 231,595, filed September 24, 1938 entitled Diesel fuel.

A principal object of this invention is the improvement of Diesel engine fuels, and particularly of fuels adapted for use in high-speed compression ignition engines, whereby there is obtained a reduction in the ignition temperature of the fuel oil and a reduction of the delay period between the injection and ignition of the fuel oil.

According to the present invention, compression ignition fuels, such as Diesel fuel oil having an initial boiling point of at least 300° F., may be altered in combustion characteristics by the addition of relatively small amounts of oil-soluble organic compounds of boron, and particularly oxygen-free boron compounds, the structure of which is such that the boron atom thereof is directly attached to a carbon atom only singly bonded to carbon or other atoms.

More specifically, this invention is concerned with the improvement of the cetane number of compression-ignition fuels such as gas oil by the addition thereto of small amounts of organic borine compounds and derivatives thereof. The borines which may be employed in accordance with this invention may be represented by the formula:



$$\begin{array}{l} R^1\diagdown \\ R^2-B \\ R^3\diagup \end{array}$$

wherein R^1, R^2, and R^3 may be the same or different hydrocarbon radicals. I have found that borines, the structure of which is such that the boron atom thereof is directly attached to a carbon atom only singly bonded to carbon or other atoms, are of particular utility as ignition accelerators for compression ignition fuels. For example, borines containing alkyl groups, cycloparaffin groups, and aryl groups attached to boron through a carbon atom other than a nuclear carbon atom are suitable for use as ignition accelerators, whereas those borines containing aryl groups directly bonded to boron are unsatisfactory for such purpose. I have further found that the branched-chain alkyl borines, such as the iso-alkyl borines, secondary alkyl borines, and, in particular, the tertiary alkyl borines, are superior to the borines containing normal alkyl groups, cycloparaffin groups, or methylene-substituted aryl groups, as ignition accelerators for Diesel fuels. In general, all of the borines which I have found suitable as ignition accelerators or cetane improvers are susceptible to atmospheric oxidation to a greater or lesser extent. Such susceptibility may be markedly decreased, and in many cases entirely eliminated, by forming addition compounds of the borines with ammonia or substituted ammonias such as amines and nitrogenous organic bases, without decreasing the effectiveness of the borines as ignition accelerators.

Among the borine compounds and addition products thereof which may be employed in accordance with this invention are tri-methyl borine, tri-ethyl borine, tri-n-propyl borine, tri-isopropyl borine, tri-n-butyl borine, tri-isobutyl borine, tri-secondary butyl borine, tri-tertiary butyl borine, tri-n-amyl borine, tri-isoamyl borine, tri-secondary amyl borine, tri-tertiary amyl borine, the hexyl borines, the heptyl borines, the octyl borines, and the higher members of this homologous series. Borines containing cycloparaffin groups, such as tri-cyclopentyl borine, tri-cyclohexyl borine, tri-cycloheptyl borine, and tri-cyclo octyl borine, as well as the methylene substituted aryl borines such as tri-benzyl borine, tri-mono-methyl benzyl borine, tri-dimethyl benzyl borine, and the like, may be employed in accordance with my invention. Any of the specific borines above mentioned or others of similar type may be converted into borine-amine addition products of increased stability by treating the borines with organic amines. The borine-amine addition compounds may be prepared by admixing the borine and amine, preferably diluted with an inert, low boiling solvent, heating the mixture at the refluxing temperature thereof to accelerate the formation of the addition compound, and thereafter removing the solvent by evaporation. Equimolecular quantities of the borine and of the amine may be employed, although it is preferable to use a slight excess of amine to insure complete conversion of the borine to the borine-amine compound. Excess amine may be removed from the product by evaporation, together with the solvent aforementioned. Such addition products may be exemplified by tri-methyl borine butylamine, tri-ethyl borine butylamine, tri-propyl borine butylamine, tri-butyl borine amylamine, tri-amyl borine amylamine, tri-hexyl borine amylamine, tri-heptyl borine hexylamine, tri-octyl borine amylamine, tri-cyclohexyl borine amylamine and tribenzyl borine amylamine. The amines to be employed are preferably those which have a carbon chain of sufficient length to enhance the solubility of the borines in fuel oil, without detracting from their efficiency as ignition accelerators.

The following examples are illustrative of the results which may be obtained in the practice of the present invention. The cetane number of the fuel is employed herein as an index of the ignition characteristics of the fuel, and an improvement with respect to ignition characteristics is expressed by an increase in the cetane number. In the table given below there are included, for purposes of comparison, several organic compounds of boron other than the borines. The base fuel oil to which the various boron compounds were added was a hydrocarbon oil having an A. P. I. gravity of 38.0° and a distillation range of from 330° F. to 561° F.

The tri-n-butyl borine n-amylamine product referred to in the following table was prepared as follows:

14.3 parts by weight of tri-n-butyl borine in solution in 107 parts by weight of diethyl ether was added to a solution of 8 parts by weight of n-amylamine in 36 parts by weight of diethyl ether. Upon addition of the one solution to the other, a slight evolution of heat occurred, and the mixture was thereafter heated at refluxing temperature (35 C.-40 C.) for about 50 minutes. The ether and excess n-amylamine were then removed by evaporation, whereby the addition product, i. e., tri-n-butyl borine n-amyl-amine, was obtained as a yellow oil which would not solidify even when cooled to 0° F. The addition product was readily soluble in hydrocarbon oil and was stable to atmospheric oxidation at room temperature.

Compound added	Weight percent added	Cetane No. of blend	Cetane No. of base fuel	Cetane No. increase
	0.00	--------	43.7	--------
Tri-n-butyl borine	0.50	49.1	43.7	5.4
Do	1.00	55.2	43.7	11.5
Do	2.50	65.7	43.7	22.0
Tri-n-butyl borine n-amylamine	0.74	49.2	43.7	5.5
Tri-isobutyl borine	1.00	55.6	43.7	11.9
Tri-tertiary butyl borine	1.00	56.7	43.7	13.0
Tri-secondary octyl borine	1.00	57.5	43.7	13.8
Tri-cyclohexyl borine	1.00	54.5	43.7	10.8
Tri-benzyl borine	1.00	55.2	43.7	11.5
Tri-phenyl borine	1.00	44.3	43.7	0.6
Tri-naphthyl borine	1.00	43.9	43.7	0.2
Tri-n-butyl borate	1.00	44.4	43.7	0.7
Di-n-butyl boric acetate	1.00	43.9	43.7	0.2

It will be seen from the above examples, that a marked increase in cetane number of compression ignition fuel is obtained by the addition thereto of small amounts of oxygen-free organic compounds of boron, the structure of which is such that the boron atom thereof is directly attached to a carbon atom only singly bonded to the other atoms, and particularly the borines other than the tri-aryl borines. And of the borines, it is to be noted that the branched-chain alkyl borines, and especially the secondary and tertiary alkyl borines are superior to the straight-chain alkyl borines, the cycloparaffin borines and the methylene-substituted aryl borines. The true aryl borines, such as triphenyl borine and tri-naphthyl borine, as well as the esters of boric acid and alkyl boric acids are of little or no value as cetane improvers and are not considered within the scope of my invention.

Among the advantages which accrue from the use of organic borines and derivatives thereof as ignition accelerators in compression ignition fuels may be mentioned:

(1) Elimination of knocking and rough-running by decreasing the ignition lag.

(2) Easier starting due to the reduced spontaneous ignition temperatures of the blended fuel.

(3) Possibility of using inferior grade of fuel oil. By the addition of the accelerator, low grade fuels which at present are unsuitable for use in compression ignition engines, may be rendered equal or superior to high grade unblended fuels.

The fuel oils which are employed in accordance with this invention are hydrocarbon oils having an initial boiling point of at least 300° F., and a distillation range of the order of from about 300° F. to about 750° F. Such fuel oils are those suitable for combustion in compression ignition or Diesel engines, and include kerosene, gas oil, and higher boiling oil fractions, or mixtures thereof.

The above description and examples are to be taken as illustrative only and not as limiting the scope of the invention. Any modification or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What I claim is:

1. A compression ignition fuel comprising fuel oil having an initial boiling point of at least 300° F. and an organic borine in quantity sufficient to substantially increase the cetane number of said fuel oil, said borine containing at least one branched-chain hydrocarbon radical.

2. A compression ignition fuel comprising fuel oil having an initial boiling point of at least 300° F. and a secondary alkyl borine in quantity sufficient to substantially increase the cetane number of said fuel oil.

3. A compression ignition fuel comprising fuel oil having an initial boiling point of at least 300° F. and a tertiary alkyl borine in quantity sufficient to substantially increase the cetane number of said fuel.

4. A compression ignition fuel comprising fuel oil having an initial boiling point of at least 300° F. and secondary octyl borine in quantity sufficient to substantially increase the cetane number of said fuel.

5. A compression ignition fuel comprising fuel oil having an initial boiling point of at least 300° F. and tertiary butyl borine in quantity sufficient to substantially increase the cetane number of said fuel.

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