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MOTOR FUEL

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This invention relates to improvement of low boiling mineral oil products, such as gasoline, motor benzol, kerosene, and similar hydrocarbon fractions used as internal combustion engine fuels. It is concerned more particularly with control of oxidation tendencies of motor fuels by blending agents.

As is well known, extensive chemical refining of motor fuels to eliminate unstable compounds, which normally during usual conditions of storage, develop gum and color bodies by absorbing oxygen, involves added expense and results in considerable loss of reactive but useful motor fuel components. Therefore, it has been found desirable to employ anti-oxidant blending agents to inhibit oxidation of the unstable fuel components during storage.

It is an object of this invention to provide motor fuels with the type of blending agent which is sufficiently soluble, stable, and reactive in hydrocarbon oils to stabilize a motor fuel toward oxidation or to inhibit gum formation therein under storage conditions.

Another object of this invention is to provide a method of treating motor fuels with an addition agent that suppresses undesirable oxidation of motor fuel hydrocarbons under storage conditions with suitable effects on the combustion of the fuel within internal combustion engines. A still further object of this invention is to stably blend with a motor fuel a substance which is capable of effecting improvement in color stability of a fuel and elimination of corrosive components from the fuel.

Other objects are apparent from the following description:

According to this invention, organic compounds of boron constitute blending agents which satisfactorily retard oxidation of motor fuel hydrocarbon components and inhibit gum formation by these components. Organic compounds of boron in which the boron constituent is joined directly to carbon atoms of organic groups are highly useful in this respect. They are formulated generally as follows:

$$R_nBX_m$$

wherein R represents organic groups and X represents an inorganic function or a molecule containing such a function which may or may not be present. The subscript n denotes the number of organic groups, such as aliphatic or aromatic groups linked through carbon to boron, B, and the subscript m denotes the number of X groups attached to the boron atom, the sum of the numerical values for n and m being such as to satisfy the valence of the boron.

The efficacy of particular organo-boron compounds for the purpose in hand depends on their composition and constitution. In accordance with the present invention, important factors have been discovered with regard to activity, stability, and solubility of these compounds.

The alkyl and aryl borines represented by the following formula:

$$R_3B$$

wherein R represents alkyl groups, aryl groups, or both, were found to be sufficiently soluble in hydrocarbon oils and reactive for inhibiting oxidation of hydrocarbon components which are highly susceptible to oxidation. But many of these compounds of boron, particularly the alkyl borines of low molecular weight, were found difficult to handle for usual applications on account of their instability. In certain instances, some of the borines may be employed as motor fuel blending agents. However, as a class, the borines are useful in the preparation of more stable organo-boron compounds which have been found to be excellent motor fuel addition agents.

The alkyl borines, represented by trimethyl boron, $B(CH_3)_3$, are prepared according to methods described in the article of E. Krause and R. Nitsche, Berichte 54, 2784 (1921). The boiling points of these compounds increase with increasing molecular weight; thus, the boiling point of trimethyl boron is —20.2° C. at 760 mm. pressure and the boiling point of $B(C_2H_5)_3$, is 95° C., the tripropyl boron boils at 156° C., and tri-isobutyl boron boils at 188° C.

The aryl borines, such as triphenyl boron, are prepared according to the method of E. Krause and H. Polack described in Berichte 59, 777 (1926). A variety of other organo-boron compounds are obtainable, such as those in which the boron constituent is attached to both hydrocarbon groups and inorganic groups, for example, tolyl boron dichloride, diphenyl boron chloride, alkyl borates, alkyl boric acids, etc.

In accordance with the chief object of the present invention, it has been found that normally unstable borines can be stabilized by combination with ammonia or organic bases to obtain substances which are very effective oxidation inhibitors. In general, the stabilized organo-boron compounds are addition products in which boron is linked to three univalent hydrocarbon radicals and to ammonia or an organic nitrogen base such as a primary, secondary, or tertiary

amine, including aniline, pyridine, phenyl hydrazine, piperidine, or the like. The manner in which these addition products are formed is described by E. Krause in Berichte 57, 813 (1924). These addition compounds come under the general type formulae:

$R_3B \cdot NH_3$ $R_3B \cdot RNH_2$ $R_3B \cdot R_2NH$ $R_3B \cdot R_3N$

wherein R represents organic groups in general, including hydrocarbon groups such as alkyl, aryl, alkaryl, or aralkyl radicals. In the addition compound, a simple borine molecule is considered to have a coordinate valence linkage with the base molecule, which may be the ammonia molecule, e. g. as in triphenyl borine amine, $(C_6H_5)_3B \cdot NH_3$, or an aliphatic amine, e. g. in triethyl borine-ethyl amine, $(C_2H_5)_3B \cdot C_2H_5NH_2$ or some other base, like those mentioned. It has been observed that these addition compounds are generally more stable and less volatile when they include an aryl radical and that some have more solubility in mineral oils when they include alkyl radicals.

While the exact properties of these various compounds and mechanisms by which they improve a motor fuel are not fully understood, it has been observed that the stabilized organo-boron compounds, when present in a motor fuel in very small quantities, caused the fuel to resist appreciable chemical changes for long periods when exposed to an atmosphere of oxygen under conditions more drastic than are encountered during normal storage. No exact explanation of this behavior is intended to be presented, but it has been observed that the alkyl and aryl borine addition products with ammonia and organic ammonia derivatives slowly over long periods tend to disintegrate to liberate ammonia or amino compounds and to provide the highly reactive borines which serve as excellent oxidation inhibitors. The ammonia or amino compounds, liberated in a nascent state, combine with acidic components of the fuel which tend to be injuriously corrosive and to discolor the fuel.

The concentrations of the borine addition agents which are used to improve the stability of a motor fuel are, in all instances, minute, as little as 0.001 to 0.005% by weight of the fuel producing noticeable effects. It is generally desirable, however, to use about 0.01% to about 0.1% of the addition agent.

These organo-boron addition agents are effective in many different types of petroleum products having boiling ranges as low as that of a light fraction of gasoline or as high as the boiling range of kerosene irrespective of the type or source, whether derived from paraffin, naphthene, asphalt, or various mixed base crudes, and whether obtained by cracking, reforming, alkylating, or polymerizing processes.

Prior to the addition of the blending agents, the motor fuel may be given some degree of chemical purification so that the fuel has initially a desired color and low contents of corrosive components, gum forming components, and preformed gum. Any of the known refining processes may be used, as, for example, treatments which employ acid, clay solvent extraction, hydrogenation, etc. However, these treatments may be omitted.

In order to illustrate the merits of the organo-boron compounds as inhibitors, results from the following tests are presented.

Breakdown tests were carried out according to the following A. S. T. M. procedure:

25 ml. of a fuel sample to be tested were enclosed in a bomb together with oxygen under a pressure of 100 pounds per square inch, the bomb being attached to a pressure recording instrument. The bomb was placed in a steam bath into which steam was led at a sufficient rate to bring the temperature of the bomb to 212° F. in about 2 minutes. The pressure within the bomb gradually reached equilibrium at the bath temperature. The time was noted when the bomb pressure dropped 2 pounds per square inch from the observed equilibrium pressure. The time (in minutes) which elapsed between the start of the heating of the bomb by the steam and the drop in pressure below the equilibrium pressure was noted as the induction period, which is a measure of the stability of the fuel. The data appearing in the following table were obtained by testing a sample of raw, cracked gasoline from a debutanizer tower. One portion of the sample was tested without an addition agent, another portion was tested after being blended with a specific proportion of a triaryl borine and a third portion was tested after being blended with an addition product of the triaryl borine and an alkyl amine.

Table I

Motor fuel composition	Breakdown induction period
	Minutes
Blank fuel	30.0
Blank fuel+0.05% triphenyl borine	78.0
Blank fuel+0.05% triphenyl borine-ethyl amine	81.0

It was found possible to determine the effect of the borine-amine addition compounds in a refined mineral oil boiling above the gasoline range, i. e. substantially above 200° C., by a dynamic oxidation rate test. In this test, the rate of oxidation was determined by passing oxygen at a constant rate through a 10 cc. sample of the fuel composition maintained at a temperature of 200° C. and measuring the amount of oxygen absorbed by the fuel during successive 15 minute intervals. Representative results from these tests are illustrated in the following table:

Table II

Composition	Oxygen absorption rate, cc. of O_2/10 cc. of fuel/15 min. intervals		
Blank mineral oil	190	80	63
Blank mineral oil+0.2% triphenyl borine-ethyl amine	7	18	15

Still another test demonstrating the effectiveness of the stabilized organo-boron compounds in decreasing gum formation in a gasoline motor fuel is the copper dish gum test, in which the fuel is subjected to less drastic oxidizing conditions than in the aforementioned breakdown and dynamic oxidation rate tests. In brief, the copper dish gum test consists in placing 100 cc. of the fuel to be tested in a 3½ inch diameter spun copper dish which is heated on a steam bath to evaporate off the volatile material. The test result is expressed in milligrams of gum finally left in the dish after the evaporation of the volatile material. It was found that the copper dish gum value of a refined gasoline was decreased from 13.5 mg. to 10.5 mg. by the presence

of less than about .01% triphenyl borine-ethyl amine in the fuel.

From such results, it is concluded that the organo-boron compounds are effective for protecting a hydrocarbon fuel from the deleterious action of air (or oxygen) even under exceedingly drastic oxidation conditions and that the stable borine addition products with ammonia or organic bases are more useful and efficacious than the less stable borines.

In the practice of this invention, the organo-boron compounds which can be most safely and conveniently handled are preferably selected. As already mentioned, such compounds, in general, are addition products of an organo-boron compound with a nitrogen base. These addition products have noticeably less sensitivity to decomposition by air than the borines in which boron is connected only to hydrocarbon radicals. The selection of a particular compound or combination of compounds to be blended with a hydrocarbon fuel is dependent on the particular use of the fuel composition. For more volatile fuels, such as gasoline which is to be used in a high compression spark-ignition engine, it is desirable to use organo-boron compounds, which have a low sensitivity to decomposition by air, in minimal amounts, which are sufficient to produce the desired oxidation inhibiting effects without adversely affecting the anti-knock properties of the fuel. With less volatile fuels, the addition agent is permissibly more sensitive to oxidation, particularly if the fuel composition is protected from air prior to use. Additional benefits are experienced from the addition of the organo-boron compounds to less volatile fuels by reason of the fact that these compounds can be used in sufficient amounts to promote ignition and complete combustion of the high boiling hydrocarbon components of the fuels.

Although the organo-boron compounds set forth herein are especially suitable for stabilizing cracked gasoline or blends of cracked and straight gasoline to oxidation, they have other useful functions as have been indicated in such fuels and other hydrocarbon containing motor fuels. They act as anti-oxidants in higher boiling petroleum fractions, such as heavy naphtha, kerosene, or the like.

Other additive agents may be incorporated in the fuel compositions together with the selected organo-boron compounds, e. g. agents which aid in further solubilizing and stabilizing the organo-boron compounds, oiliness agents, dyes, soaps, thickeners, anti-knock agents, corrosion inhibitors, and oxidation inhibitors of other types.

The present invention is not limited to any particular addition agent, nor to any theory on the effect of these substances, nor to the particular amounts described for the purpose of illustration. Any modification or variation which conforms to the spirit of the invention is intended to be included within the scope of the claims.

I claim:

1. A motor fuel comprising a gasoline hydrocarbon fuel and a minor proportion of a hydrocarbon borine-amine addition product.

2. A composition in accordance with claim 1, in which said addition product contains boron joined directly to the carbon atom of an aromatic radical.

3. A composition according to claim 1, in which said addition product is the addition product of an alkyl borine and an amino compound.

4. A composition according to claim 1, in which said addition product is the addition product of an aryl borine and an amino compound.

5. A motor fuel comprising unsaturated gasoline hydrocarbons and containing, as an oxidation inhibitor, from 0.001 to 0.1% of a hydrocarbon borine-amine addition product.

6. A composition according to claim 5, in which said addition product is an aryl borine-amine.

7. A composition according to claim 5, in which said addition product is an alkyl borine-amine.

8. A method for improving a gasoline hydrocarbon motor fuel which comprises blending with said fuel a small amount of a hydrocarbon borine-amine addition product of the type $R_3B \cdot X$, wherein R represents hydrocarbon radicals and X represents an amine molecule.

9. A method for improving a gasoline hydrocarbon motor fuel which comprises the step of blending with said fuel a small amount of a hydrocarbon borine-amine addition product of the type $R_3B \cdot RNH_2$, wherein R represents hydrocarbon radicals selected from the class consisting of alkyl and aryl radicals.

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