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ACETYLENIC LEAD COMPOUNDS AND GASOLINE COMPOSITIONS THEREOF

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This invention relates to an improved gasoline composition. More particularly, the invention is concerned with a superior new hydrocarbon fuel of the gasoline boiling range containing propynyl trimethyl lead or butynyl trimethyl lead. This invention also relates to new lead compounds; specifically new lead acetylides, such as propynyl trimethyl lead and butynyl trimethyl lead.

Gasoline compositions of high octane number are commonly required for modern spark ignition internal combustion automobile and aircraft engines. Engines of these types in general used today are designed with high compression ratios for more efficient operation. Since the present trend is toward engines of still higher compression ratios for increased power and improved performance, there is constant demand for gasoline compositions of even higher octane number.

Many materials have been added to the gasoline base stocks, and additives such as lead tetraethyl have been employed to meet the demands for higher octane number gasoline compositions. However, it has been generally realized that there is at present a limit to the improvement in octane number either by means of blending or addition of additives. New gasoline base stocks with the combination of different additives are needed. Consequently, to avoid present limitations and provide new approaches, new gasoline compositions have been provided.

Thus, an object of the present invention is to provide new lead compounds suitable for improving octane ratings of hydrocarbon base fuels boiling in the gasoline range. Another object is to provide new propynyl trimethyl lead and butynyl trimethyl lead compounds. As one of the aspects of the invention, the new lead compounds are useful for study of combustion properties of hydrocarbons, especially in respect to the antidetonating properties. As a further aspect of the invention, the new lead compounds are useful to produce trimethyl lead hydroxide, e.g., upon introducing propynyl trimethyl lead compound into water. Other objects and aspects of the invention will be apparent from the description of the invention herein.

It has now been found that hydrocarbon base fuel boiling in the gasoline boiling range containing propynyl trimethyl lead or butynyl trimethyl lead, novel and effective lead compounds in amounts sufficient to improve the octane number, preferably, at least 0.5 ml./gal. of base fuel provides greatly improved octane ratings. Generally, the compounds are added to the gasoline mixture in an effective amount from about 1 ml. to about 7 ml./gal. of base fuel.

The superior new gasoline compositions of the invention show improved high octane numbers compared to the unleaded hydrocarbon base fuels. The novel propynyl trimethyl lead or butynyl trimethyl lead and mixtures thereof in accordance with the invention provide a new class of organo lead compounds useful as octane improving agents for gasolines as well as for other purposes.

The invention as to the lead compounds is best exemplified by the members selected from the group consisting of propynyl trialkyl lead and butynyl trialkyl lead wherein the alkyl is methyl, ethyl and propyl, and mixtures thereof. Examples of these compounds are propynyl methyl ethyl propyl lead, propynyl dimethyl ethyl lead, propynyl dimethyl propyl lead, propynyl diethyl methyl lead, propynyl diethyl propyl lead, propynyl trimethyl lead, propynyl triethyl lead, propynyl tripropyl lead, propynyl dipropyl methyl lead, propynyl dipropyl ethyl lead and the above corresponding alkyl derivatives of butynyl, pentynyl and hexynyl lead. The preferred embodiments are propynyl trimethyl lead and butynyl trimethyl lead compounds.

Known inorganic acetylides are invariably either salt-like, e.g., sodium acetylide, or highly explosive solids, e.g., silver acetylide. The new lead compounds, on the other hand, fall into neither category as they are liquid and thermally stable. It is most unexpected that the properties of the compounds are so different from those of other acetylides.

Although the mechanism by which the propynyl trimethyl lead or butynyl trimethyl lead compounds operate in a detonating hydrocarbon base fuel is not known, it is believed that the lead compound undergoes a unique rate controlling step in the detonation reaction and at some point is in a form which inhibits the "wild" detonating side reactions which cause the knock in the modern engines.

The hydrocarbon base fuel of the compositions according to the invention are prepared by conventional refining and blending processes. They normally contain straight-chain paraffins, branched-chain paraffins, olefins, aromatics and naphthenes. Since straight-chain paraffins have a tendency adversely to affect octane number, the content of such hydrocarbons is ordinarily low.

As already mentioned, the base fuel is a hydrocarbon fuel boiling in the gasoline boiling range. Generally described, such fuels have an ASTM (D-86) distillation with initial boiling point of about 100° F. and a final boiilng point of about 425° F. Preferably the unleaded base fuel has a Research octane number of at least 85, as determined by the accepted CFR engine test methods. Also, the base fuel preferably contains at least 20% by volume of aromatic hydrocarbons. Less than 30% by volume of olefinic hydrocarbons are present in the fuel. The total paraffin and naphthene hydrocarbon content of the preferred fuel may be as much as 80% by volume. For best overall engine performance, fuels containing in the range of 20–60% by volume of paraffinic and naphthenic hydrocarbons are preferred by volatility and other desirable characteristics. The more preferred hydrocarbon base fuels are those which contain from 20–60% by volume aromatic hydrocarbons and from 0–30% by volume of olefinic hydrocarbons. Most preferably, a gasoline having all-round desirable characteristics has a clear octane number of at least 95 and contains about 50–60% by volume of paraffin and naphthene hydrocarbons, about

30–40% aromatic hydrocarbons and about 5–15% olefinic hydrocarbons.

For practical purposes, not more than about 7 ml. of lead compound per gallon is ordinarily used in the compositions. If desired, other octane improving additives may be employed in addition to propynyl trimethyl lead or butynyl trimethyl lead. These include other lead compounds such as lead tetraethyl, carbonyl derivatives of iron and cyclopentadienyl derivatives of metals, such as manganese or iron. Other gasoline additives such as scavengers like ethylene chloride or bromide, oxidation inhibitors, corrosion inhibitors, surface ignition suppressants like phosphorus compounds, detergents, and the like may be present.

The following examples illustrate the preparation of propynyl trimethyl lead and butynyl trimethyl lead in accordance with the invention. Unless otherwise specified, the proportions are on a weight basis.

EXAMPLE 1

A solution of n-butyl lithium (0.2 mol) in 200 cc. mixed pentane-hexane was mixed with 250 ml. of diethyl ether in a 1-liter, 3-necked flask fitted with a reflux condenser, stirrer and gas inlet tube. This solution was cooled in ice, stirred, and methyl acetylene (propyne) was bubbled through. A white suspension of propynyl lithium rapidly formed. As soon as evolution of heat ceased, indicating completion of the reaction, the passage of the gas was stopped. 57.6 g. (0.2 mol) of trimethyl lead chloride was then added to the suspension and the mixture was heated. Since both reactants have a low solubility in ether, 100 ml. of dioxane was added to improve the solubility, and the heating was continued for 3 to 4 hours. The mixture was left overnight and the ether was removed by stripping under a vacuum. The residue was distilled at 100° C. under a pressure of 40 mm. of mercury with the addition of a small amount of mineral oil to assist the final removal of the distillate. Most of the dioxane and lead compound were collected in an ice-cooled trap, and the ether was condensed in a Dry Ice trap. The material in the ice-cooled trap was fractionated to remove dioxane which distilled at 28° C. under a pressure of 45 mm. of mercury, and the residue distilled entirely at 65.5° C. under a pressure of 16 mm. of mercury. The product was a colorless liquid (density, 1.82 g./ml. at 23° C.) having good thermal stability. The yield was 15.8 g. corresponding to 27%. The infrared spectrum showed a strong absorption peak at 2130 $cm.^{-1}$ due to the —C≡C— stretching frequency. The bond is alpha to the lead atom.

EXAMPLE 2

4.6 g. (0.2 mol) of sodium chips were added gradually to 250 cc. of mechanically stirred liquid ammonia in a suitable reaction vessel. Throughout the addition of the sodium, a stream of gaseous ethyl acetylene (butyne-1) was introduced. The blue color produced by the addition of each piece of sodium was rapidly discharged, and when all the sodium had been used, a white suspension was obtained. 50.9 g. (0.176 mol) of trimethyl lead chloride were added portionwise to this liquid and a vigorous reaction occurred. Following this, 200 ml. of ethyl ether were added and the ammonia was allowed to evaporate. The ether extract was washed with water and dried over anhydrous magnesium sulfate. After removal of the ether, fractionation yielded 6 g. (11%) of a liquid boiling at 54° C. at a pressure of 4 mm. of mercury. The infrared spectrum showed a peak at 2130 $cm.^{-1}$ due to the —C≡C— stretching mode. The bond is alpha to the lead atom.

In further illustration of the superior new gasoline composition of the invention, several compositions and tests thereon are given in the following additional examples. These tests show the improved effect of the combination of the hydrocarbon base fuel with propynyl trimethyl lead or butynyl trimethyl lead as compared with fuels without lead compounds.

The following table is a summary of the pertinent data of the examples. The type of compositions of the hydrocarbon base fuel is shown with respect to the normal octane rating. The number is the clear octane rating of an unleaded premium and primary reference base gasolines. This octane number, as already mentioned, is the accepted Research octane number which is usually employed in designating a given gasoline. This method is described as Research Method D–908 in ASTM "Manual of Engine Test Methods for Rating Fuels." According to this method, the octane numbers are also designated "F–1 Octane Numbers."

The table also shows the effects on octane number of the base fuel by the addition of propynyl trimethyl lead or butynyl trimethyl lead according to the Motor Method D–357 of the "ASTM Manual of Engine Test Methods for Rating Fuels." This method is designated as "F–2 Method" and is more stringent than the Research Method. It illustrates more accurately the desirable qualities of the improved gasoline composition of the invention. In both F–1 and F–2 methods, the compositions were blended to give the customary lead concentration equivalent to about 3 cc. of TEL. The data of the examples are presented in Table I.

Table I

OCTANE NUMBERS OF GASOLINE WITH ALKYNYL TRIMETHYL LEADS

Compound	Conc., g./gal.	Base gasoline	Octane number	
			F-1	F-2
Propynyl trimethyl lead	0	Premium	96.5	82.5
Do	4.5	do	100.2	86.6
Do	0	Primary reference*	80.0	
Do	4.5	do	94.9	
Butynyl trimethyl lead	0	Premium	96.5	82.5
Do	4.75	do	100.8	87.4

*Primary reference mixture: 80% 2,2,4-trimethyl pentane, 20% n-heptane.

The examples summarized in the above table show that gasoline compositions of the invention containing propynyl trimethyl lead or butynyl trimethyl lead are decidedly better on the basis of octane number ratings than comparable unleaded gasoline compositions.

As many apparently widely different embodiments of this invention may be made by one skilled in the art without departing from the spirit and scope of the invention, it is to be understood that the invention is not limited to the specific embodiments except as defined in the appended claim.

I claim:

A hydrocarbon fuel of the gasoline boiling range adapted for use as a fuel for spark ignition internal combustion engines having a clear Research octane number of at least about 85 and containing at least 20% by volume of aromatic hydrocarbons, not more than 30% by volume of olefinic hydrocarbons and not more than 60% by volume of paraffinic and naphthenic hydrocarbons, said hydrocarbon fuel having incorporated therein from about 1 ml. to about 7 ml. of butynyl trimethyl lead per gallon of said fuel.

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