United States Patent Office 3,073,853 Patented Jan. 15, 1963



3,073,853

# TRIMETHYL LEAD METHYL SULFIDE

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No Drawing. Filed Sept. 30, 1960, Ser. No. 59,519
1 Claim. (Cl. 260—437)

This invention relates to a novel organometal compound. More particularly, the invention is concerned with a superior new lead sulfide antiknock compound for hydrocarbon fuels of the gasoline boiling range.

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 use 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 a constant demand for gasoline compositions of even higher octane number.

Improved methods of refining and blending 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 that can be obtained by such conventional methods and additives. New gasoline base stocks with the combination of different additives are greatly needed, therefore, to avoid present limitations and provide gasoline compositions of high octane number for future use in automobile and aircraft engines.

It has now been found that a superior new gasoline composition of high octane number is provided by a hydrocarbon base fuel boiling in the gasoline boiling range, containing trimethyl lead methyl sulfide, a novel lead compound, in amounts sufficient to improve the octane number, preferably, at least 0.5 milliliter per gallon of base fuel.

The improved gasoline compositions containing the new antiknock compound of the invention show unexpectedly high octane numbers. Hydrocarbon base fuels, together with trimethyl lead methyl sulfide and mixtures thereof in accordance with the invention, have octane numbers which are practically equivalent to similar base fuels employing the conventional lead tetraethyl additive in the same lead content. This is surprising since it has been generally accepted heretofore that other lead compounds are distinctly less efficient than lead tetraethyl with respect to octane number improvement. Furthermore, it has been widely recognized that sulfur is ordinarily antagonistic to lead antidetonants.

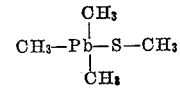
The hydrocarbon base fuel of the composition, according to the invention is prepared by conventional refining and blending processes. It normally contains straight-chain paraffins, branched-chain paraffins, olefins, aromatics and naphthenes. Since straight-chain paraffins have a tendency to adversely 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 an initial boiling point of about 100° F. and a final boiling 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 method. Also, the base fuel preferably contains at least 20 percent by volume of aromatic hydrocarbons. Less than 30 percent 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 percent by volume. For best over-all engine performance,



fuels containing in the range of 20 to 60 percent by volume of paraffinic and naphthenic hydrocarbons are preferred for volatility and other desirable gasoline characteristics. The more preferred hydrocarbon base fuels are also those which contain from 20 to 60 percent by volume aromatic hydrocarbons and from 0 to 30 percent by volume of olefinic hydrocarbons. Most preferably, a gasoline having all-around desirable characteristics has a clear octane number of at least 95 and contains about 50 to 60 percent by volume of paraffin and naphthene hydrocarbons, about 30 to 40 percent aromatic hydrocarbons and about 5 to 15 percent olefinic hydrocarbons.

The trimethyl lead methyl sulfide is illustrated by the general formula



For practical purposes, not more than about 4 milliliters of lead compounds per gallon is ordinarily used in the compositions. If desired, other octane-improving additives may be employed in addition to trimethyl lead methyl sulfide. 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 composition of trimethyl lead methyl sulfide in accordance with this invention. Unless otherwise specified the proportions are on a weight basis.

## EXAMPLE I

This example shows the preparation of trimethyl lead methyl sulfide. Twenty-four grams (0.5 mole) of methyl mercaptan are cooled to 0° C. and dissolved in 500 ml. of 4 N sodium hydroxide at 0° C. To this solution is added with stirring a solution of 144.0 g. (0.5 mole) of trimethyl lead chloride in water. On standing for one-half hour, a heavy liquid separates and is removed in a separatory funnel, dried with calcium chloride, and fractionated to a pat temperature of 70° C. at a pressure of 1 mm. of mercury. The boiling point is found to be 43° C. at a pressure of 0.75 mm. of mercury. The refractive index $n_D^{20}$ is 1.6116. The infrared spectrum checks that of the predicted compound by comparison with the spectra of known alkyl lead compounds, alkyl sulfides, and mercaptides.

In further illustration of the superior new gasoline antiknock compound of the invention, several compositions and tests thereon are given in the following examples. These tests show the improved effect of the combination of particular hydrocarbon base fuels with trimethyl lead methyl sulfide.

The following table is a summary of the pertinent data of the examples. The hydrocarbon base fuel contains 51 percent by volume of the paraffins and naphthenes, 25 percent olefins, and 24 percent aromatics. The fuel has a sulfur content of about 0.06 percent by weight. The table shows the effect on octane number by the addition of trimethyl lead methyl sulfide compared with lead tetraethyl. The octane numbers in this comparison are based on the Research Method D-908 and the Motor Method D-357 of the "ASTM Manual of Engine Test Methods for Rating Fuels." The latter method, which is more stringent than the research method, illustrates more accurately the desirable qualities of the improved gasoline composition of the invention.

In the table, the effect of trimethyl lead methyl sulfide and lead tetraethyl is based on gasoline compositions con-

taining an equal lead concentration. For the purpose of practical comparison this is 3.17 grams of lead per gallon. Such amounts are equivalent to the 3 cc. of tetraethyl lead per gallon employed in many gasolines. The gasolines containing the trimethyl lead methyl sulfide have approximately 0.02 percent of leadbound sulfur in addition to the sulfur already present.

*Table*

| Example No. | Lead Compound | Research Octane | Motor Octane |
|---|---|---|---|
| II | None—base fuel | 94.4 | 82.5 |
| III | Tetraethyl Lead | 99.2 | 87.7 |
| IV | Trimethyl lead methyl sulfide | 99.1 | 87.5 |

The examples summarized in the above table show that the improved gasoline composition of the invention containing the novel trimethyl lead methyl sulfide of the invention is surprisingly comparable on the basis of octane number rating to gasoline compositions of the type preferred heretofore.

The organolead compounds of this invention are also



useful wherever oil-soluble lead compounds are desired. For example, fine particle dispersions of lead may be obtained by thermal decomposition of the trialkyl lead sulfide dissolved in liquid hydrocarbon, such as isooctane. Such fine metal dispersions of lead are useful as catalysts for certain reactions. The fine lead particles may be converted to lead oxides which are useful as lubrication agents. The lead compound of the invention may also be used as a free radical initiator in polymerization reactions.

I claim:

Trimethyl lead methyl sulfide.

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