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FUEL COMPOSITION

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This invention relates to improved motor fuels for use in internal combustion engines, and more particularly pertains to improved internal combustion engine motor fuels, the anti-detonating qualities or characteristics of which have been improved by the incorporation therein of anti-detonating compounds, such as the metallo-organics exemplified by the well-known organo-lead compounds or complexes.

Leaded gasolines, i. e. gasolines containing organo-lead compounds, to obtain improved anti-detonating characteristics, have been widely accepted by the industry, particularly for use in the operation of internal combustion engines. These lead compounds are usually alkylated lead compounds, and are preferably a tetra-alkyl lead, such as tetra-ethyl lead. When a gasoline containing, as the only additive, one or more of these lead compounds is burned in an internal combustion engine, lead deposits (i. e. high melting point inorganic lead compounds, principally lead oxides and/or lead sulfates) tend to accumulate on the various parts of the combustion chamber, pistons, spark plugs, valves, etc. Such deposits may cause serious deterioration of the spark plugs, sticking of the valves, and other deleterious effects, which all result in poor performance characteristics and decreased efficiency in engine operation. These deleterious effects are particularly pronounced when relatively high concentrations of organo-lead compounds are employed; for instance, the use of gasolines containing between about 4 cc. and about 5 cc. of tetra-ethyl lead (per gallon of gasoline) in aviation engines, particularly under cruising conditions, frequently results in failures of such engines due to deposits, especially on the spark plugs.

In order to minimize these deleterious effects resulting from lead deposits, scavenger compounds are added to such leaded gasolines. A scavenger compound is one which will reduce the quantity, or inhibit the formation, of deposits of lead by reacting, under the high temperature conditions within the engine, with the lead to form relatively volatile lead compounds which will be swept out of the engine with the exhaust gases. All generally known scavengers are halides, usually alkyl halides—the present most widely used scavenger being ethylene dibromide.

It is well known that halogen compounds have relatively corrosive characteristics because of the marked tendency thereof to form highly corrosive halogen acids. These characteristics are exhibited by presently used scavengers, both (1) in the gaseous state during or shortly after burning of the gasoline, particularly when an excess

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of the halogen is present over that required to combine with the lead, and (2) in the liquid state before burning. The latter is of concern due to corrosion of storage and transportation facilities used for the pure scavenger or for mixtures of scavenger and leading compound and/or gasoline. It is of particular importance in the fuel feed and distribution systems of engines, e. g. where small amounts of corrosion can cause faulty carburetion due to clogging of lines by corrosion products and/or by corroding of parts which require close tolerances. In order to avoid these difficulties it has often been necessary to use relatively expensive corrosion-resistant metals and/or alloys, particularly in carburetion systems.

With regard to the corrosion in the gaseous state during burning, it has been previously disclosed (see, e. g., U. S. Patent No. 2,364,921), that in multicylinder engines using fuels containing lead compounds and scavengers having widely divergent boiling points, there is a maldistribution of these components, resulting in an excess of scavenger in some cylinders and a scarcity in others. Not only is the scavenging incomplete where a scarcity exists, but excessive corrosion takes place where an excess of scavenger exists. Consequently, it is highly desirable that a lead compound (anti-detonating agent) and the scavenger therefor should have substantially the same, or very close, boiling points. The presently most widely used leading compound, i. e. tetra-ethyl lead, and the most widely used scavenger, i. e. ethylene dibromide, have boiling points differing by nearly 70° C.

In view of the present trend toward higher octane fuels, obtainable at least in part by the use of relatively large amounts of lead compounds and correspondingly large amounts of scavenger, the above-mentioned difficulties are becoming increasingly serious, so that engine failures occur even when the heretofore known scavengers are used in highly leaded gasoline.

Accordingly, an object of the present invention is to provide new and useful fuel compositions having minimum corrosive properties toward metals. A further object is to provide improved fuel compositions for multicylinder engines. Additional objects are to provide fuel composition additives having properties such that uniform scavenging is achieved in each cylinder of multicylinder engines, and in which additives the scavenger has a minimum corrosive action toward the engine parts. Other objects will become apparent hereinafter.

It has now been found that certain halogen-carbon compounds, as hereinafter defined, have

a greatly reduced corrosive effect upon metals, and when used with leading compounds such as tetra-alkyl leads, as an additive for gasoline fuels, have outstanding scavenging properties. These scavengers exhibit a minimum of chemical interaction in liquid mixtures with fuel leading compounds under usual storage and handling conditions, have no adverse effects upon the stability of finished gasolines, and respond very well to scavenger-stabilizers.

By the expression "halogen-carbon compound," as used herein, is meant a compound consisting only of carbon and halogen atoms. The class of halogen-carbon compounds which are useful according to this invention includes only those consisting of two carbon atoms and at least two halogen atoms per carbon atom, the halogen atoms having an atomic weight between 35 and 81, inclusive. The preferred compounds are tetrabromo- and tetrachloroethene (more commonly named tetrabromo- and tetrachloroethylene) and hexabromo- and hexachloroethane, although compounds having both chlorine and bromine in the same molecule, attached to the same or different carbon atoms, may be used if desired. The following are illustrative examples of compounds of the last-mentioned group:

1,1,2,2-tetrachloro-1,2-dibromo ethane,
1,2,2-trichloro-1,1,2-tribromo ethane,
1,2-dichloro-1,1,2,2-tetrabromo ethane,
1,1-dibromo-2,2-dichloro ethylene,
1,2-dibromo-1,2-dichloro ethylene,
1-chloro-1,2,2-tribromo ethylene, and
1-bromo-1,2,2-trichloro ethylene.

In order to demonstrate the reduced corrosive effects of the scavengers of this invention as compared with commonly used scavengers, the following tests were carried out:

Strips of mild steel were immersed in three different 50 ml. samples of straight-run gasoline containing 1% of tetrabromoethene, 1% of hexachloroethane, and 1% of ethylene dibromide, respectively. The samples were maintained at 120° F. After 3 weeks some corrosion was noted on the steel in ethylene dibromide solution, and after 4 weeks 5% of the surface was corroded. Even after 5 weeks the strips in the hexachloroethane and in the tetrabromoethene solutions showed no signs of any corrosion.

In order to investigate more concentrated solutions of the scavengers, similar tests were made using respectively, 25% solutions of ethylene dibromide and of tetrabromoethene in benzene. In less than 3 weeks the surface of the steel immersed in ethylene dibromide solution was 5% corroded, whereas the same amount of corrosion of the surface of the steel immersed in tetrabromoethene had not occurred until more than 4 weeks had passed.

Thus, it is readily seen that there is a very marked reduction in corrosiveness of the scavengers of the present invention as compared with the usually used ethylene dibromide.

No attempt is made to explain the precise theory underlying these reduced corrosive properties. However, a distinguishing feature in this respect is the absence of hydrogen in the scavengers of this invention. The importance of this was further illustrated by the following tests:

Mild steel strips were immersed, respectively, in (1) a 1% solution of tetrabromoethene in straight-run gasoline, and (2) a 1% solution of tribromoethene in straight-run gasoline, both solutions being maintained at 120° F. At the end of one week, 5% of the surface of the steel strip in the tribromoethene solution was corroded, whereas after 5 weeks no corrosion was visible on the strip immersed in the tetrabromoethene solution.

Thus, it is seen that a scavenger containing even one hydrogen atom per molecule is much more corrosive than one having the same structure except for the absence of hydrogen (bromine substituted therefor).

The scavengers of this invention are at least comparable with the widely used ethylene dibromide in scavenging ability. This was demonstrated by noting the weight of lead deposits resulting from the use of a leaded fuel containing ethylene dibromide in one series of test runs and tetrabromoethene in another series of test runs. All tests were conducted with a special single-cylinder Lauson-type engine having a 2.5 inch bore and 2.5 inch stroke, using as a fuel 80 octane gasoline to which tetra-ethyl lead was added in an amount of 4 cc. per gallon of fuel. During each run the engine was operated for 10 hours at a speed of 1300 R. P. M. and a fuel to air ratio of 0.09. Two runs using a stoichiometric amount of ethylene dibromide as a scavenger resulted in an average lead deposit of 2.702 grams per 10 hours, whereas two runs using equivalent quantities of tetrabromoethene resulted in an average lead deposit of only 2.178 grams per 10 hours.

By the terms "stoichiometric amounts," "equivalent quantities," or terms of similar import, as used herein, is meant the amount of scavenger which contains an amount of halogen required to combine with the lead according to the equation:

$$2\ \text{Halogen} + \text{Pb} \rightarrow \text{Pb}(\text{Halogen})_2$$

that is, two atomic parts of halogen for each atomic part of lead. It is to be understood that there is no intention to imply that the above equation explains the reaction occurring in the combustion zone between the anti-detonating agent and the scavenger agent.

Other highly desirable properties of the scavengers of the present invention are their effect upon stability of finished gasolines, their response to stabilizer action, and the absence of chemical reaction with liquid mixtures of leading compounds.

The effect of scavengers upon the stability of finished gasoline was determined by subjecting high grade aviation gasoline and oxygen in a test bomb to a temperature of 110° C. and a pressure of 100 p. s. i. (gauge) of oxygen and noting the elapsed time at which the total pressure began to decrease due to formation of significant amounts of deterioration products. The results are tabulated in the table.

Table

Scavenger	Time for Initial Deterioration
None	11 hours 50 minutes.
Ethylene dibromide	12 hours 10 minutes.
Tribromoethane	12 hours 30 minutes.
Tetrabromoethene	12 hours 45 minutes.
Trichloroethane	11 hours 0 minutes.
Hexachloroethane	11 hours 30 minutes.

The data in the table show that the scavengers of this invention have no adverse effect upon stability of finished aviation gasoline.

The effect of stabilizer action upon various scavengers was tested by noting the corrosive action toward mild steel of ethylene dibromide and tetrabromoethene in 25% solution in benzene, first with no stabilizer, then with 0.5% of glycidyl phenyl ether (a stabilizer disclosed in the copending patent application Serial No. 58,798, filed November 6, 1949, now abandoned). When the stabilizer was used with ethylene dibromide the time required for initial visible surface corrosion to develop was not noticeably changed from the 2 to 3 weeks' time required for that scavenger without stabilizer. However, when added to solutions of tetrabromoethene, the time for initial visible surface corrosion to develop was increased from 3 weeks to over 5 weeks. Thus, it is seen that while the newly discovered scavengers themselves exhibit less corrosiveness than currently used scavengers, this advantage is even further magnified when used in combination with the scavenger stabilizers.

The scavengers were also shown to be inactive in liquid mixtures of leading compounds by mixing pure equivalent quantities of tetra-ethyl lead with tetrabromoethene and with hexachloroethane. No chemical reaction was detected in either case.

Because of the excellent stability characteristics of these scavengers with leading compounds and/or finished gasolines, the scavengers may be added to the gasoline directly, or may be first mixed with the leading compound and stored or shipped, this mixture being added to the gasoline at some later time. Furthermore, the scavengers of this invention have no adverse effects upon, nor are they adversely affected by, the normally utilized amounts of other gasoline additives such as inhibitors, stabilizers, dyes and the like.

As mentioned above, it is highly desirable to use a scavenger having a boiling point quite close to the boiling point of the leading compound being scavenged. Consequently, the choice of a particular scavenger of this invention to be used in any particular fuel will be influenced by the anti-detonating compound incorporated in that fuel. It has been found that tetrabromoethene is particularly efficacious when used with tetra-ethyl lead, the boiling point of the scavenger being about 26° C. higher than that of the lead (as compared with the fact that ethylene dibromide boils nearly 70° C. below tetra-ethyl lead). It is also contemplated that mixtures of various scavengers of this invention may be used in place of a single scavenger, particularly if mixtures of leading (anti-detonating) agents are used.

In this connection it must be noted that although the present invention has been described with particular reference to gasolines containing tetra-ethyl lead, the invention is intended to include the use of the described class of scavengers in fuel compositions containing other anti-detonating agents, and especially those organo-metallic anti-detonating agents which form volatile salts with the specified scavengers (or products of their decomposition) under the conditions existing in internal combustion engines during their operation.

The quantity of the scavenger, to be used in any fuel or additive composition, will vary depending upon the kind and/or amount of the anti-detonating agent used, as well as the particular scavenger employed. Generally speaking, in view of the effectiveness of the scavengers of the present invention, it will not be necessary to employ these scavengers in amounts greater than a stoichiometric amount (based on the anti-detonant used). In fact, in most cases, such scavengers can be used in approximately a stoichiometric amount; however, in some cases, it may be found desirable or even advantageous to use the scavenger in amounts which are greater or less than the stoichiometric quantity. For instance, with particular reference to gasolines or internal combustion engine fuels containing tetra-ethyl lead, the latter may be employed in anti-detonating amounts of from 0.5 cc. to 6 cc. or 7 cc. per gallon of fuel, although sometimes the lead content may be as high as 10 cc., or higher. With such leaded fuels, the scavengers of the present invention may be employed in approximately stoichiometric amounts, e. g. from about 75% to about 110% (preferably 90%–105%) of the theoretical value; nevertheless the scavenger concentration may be as high as 200%, or even greater.

I claim:

1. A fuel composition suitable for internal combustion engines, which comprises a hydrocarbon fracton boiling within the gasoline range, from about 0.5 cc. to about 6 cc. of tetra-ethyl lead per gallon of fuel composition, and hexachloroethane in an amount approximately stoichiometric with the tetraethyl lead content.

2. A fuel composition suitable for internal combustion engines, which comprises a hydrocarbon fraction boiling within the gasoline range from about 0.5 cc. to about 6 cc. of tetra-ethyl lead per gallon of fuel composition, and tetrabromoethylene in an amount approximately stoichiometric with the tetraethyl lead content.

3. A fuel composition suitable for internal combustion engines, which comprises a hydrocarbon fraction boiling within the gasoline range, from about 0.5 cc. to about 6 cc. of tetra-ethyl lead per gallon of fuel composition, and hexabromoethane in an amount approximately stoichiometric with the tetraethyl lead content.

4. A fuel composition suitable for use in internal combustion engines, which comprises a hydrocarbon fraction boiling within the gasoline range, from about 0.5 to about 6 cc. of tetra-ethyl lead per gallon of fuel composition, and an approximately stoichiometric amount, based on the tetra-ethyl lead, of a halogen-carbon compound consisting only of carbon and halogen atoms and having two carbon atoms per molecule and at least two halogen atoms per carbon atom, said halogen atoms having an atomic weight of between 35 and 81, inclusive.

5. A fuel composition suitable for use in internal combustion engines, which comprises a hydrocarbon fraction boiling substantially within the gasoline range, a minor but anti-detonating amount of a tetra-alkyl lead anti-detonant, and an approximately stoichiometic amount, based on the tetra-alkyl lead, of a halogen-carbon compound consisting only of carbon and halogen atoms and having two carbon atoms per molecule and at least two halogen atoms per carbon atom, said halogen atoms having an atomic weight of between 35 and 81, inclusive.

6. A fuel composition suitable for use in internal combustion engines, whch comprises a gasoline hydrocarbon fraction, a minor but anti-detonating amount of a tetra-alkyl lead anti-detonant, and a halogen-carbon compound consisting only of carbon and halogen atoms and having two carbon atoms per molecule and at least two halogen atoms per carbon atom, said

halogen atoms having an atomic weight of between 35 and 81, inclusive, and said halogen-carbon compound being present in an amount materially in excess of the stoichiometric amount based on the tetra-alkyl lead.

7. A fuel composition suitable for use in internal combustion engines, which comprises a hydrocarbon fraction boiling substantially within the boiling range of gasoline, a minor but effective amount of a tetra-alkyl lead anti-detonant, and a minor but effective scavenging amount of a halogen-carbon compound consisting only of carbon and halogen atoms and having two carbon atoms per molecule and at least two halogen atoms per carbon atom, said halogen atoms having an atomic weight of between 35 and 81, inclusive.

8. The composition of claim 7 in which the tetra-alkyl lead is tetraethyl lead.

9. The composition of claim 7 in which the tetra-alkyl lead is tetraethyl lead and the halogen-carbon compound is hexachloroethane.

10. The composition of claim 7 in which the tetra-alkyl lead is tetraethyl lead and the halogen-carbon compound is tetrabromoethylene.

11. A fuel composition suitable for use in internal combustion engines, which comprises a gasoline hydrocarbon fraction containing an effective amount of a metallo-organic anti-detonant compound, and a minor amount of a halogen-carbon compound consisting only of carbon and halogen atoms and having two carbon atoms per molecule and at least two halogen atoms per carbon atom, said halogen atoms having an atomic weight of between 35 and 81, inclusive.

12. An additive composition suitable for addition to an internal combustion engine motor fuel and adapted to improve the detonating characteristics of said fuel when incorporated therewith, which comprises substantially stoichiometric amounts of tetraethyl lead and of hexachlorethane.

13. An additive composition suitable for incorporation into a motor fuel for internal combustion engines and adapted to improve the detonating characteristics of said fuel when incorporated therewith, which comprises substantially stoichiometric amounts of tetra-ethyl lead and of tetrabromoethylene.

14. An additive composition suitable for incorporation into a motor fuel for internal combustion engines and adapted to improve the detonating characteristics of said fuel when incorporated therewith, which comprises an effective amount each of an alkylated lead anti-detonant compound and a halogen-carbon compound consisting only of carbon and halogen atoms and having two carbon atoms per molecule and at least two halogen atoms per carbon atom, said halogen atoms having an atomic weight between 35 and 81, inclusive.

15. The composition of claim 14 in which the tetra-alkyl lead is tetraethyl lead.

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The following references are of record in the file of this patent:

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