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MOTOR FUEL AND ANTIKNOCK AGENT

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6 Claims. (Cl. 44—69)

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The present invention is concerned with an improved motor fuel and an improved antiknock agent therefor. The invention is more particularly concerned with an improved motor fuel adapted for use in aviation engines. In accordance with the present invention, a high quality motor fuel is secured by using an alkyl lead compound in the fuel and employing in conjunction therewith a selected sulfur compound. A preferred adaptation of the present invention comprises an improved motor fuel which is secured by utilizing tetra ethyl lead and a critical quantity of an alkyl sulfate or an alkyl thiophene in conjunction with an organic halide type of lead scavenging agent.

It is well known in the art that sulfur in its various forms has long been considered an objectionable constituent of fuels for spark ignition reciprocating engines. This is due to the fact that the sulfur compounds in general have an unpleasant odor, tend to increase corrosion and exert an adverse effect on the antiknock quality and lead susceptibility of the fuel. It has now been discovered, however, that certain sulfur compounds, rather than being harmful in a motor fuel, actually are of benefit in a motor fuel containing alkyl lead constituents. It has been found that distinct advantages are obtained by including certain sulfur compounds selected so as to have a minimum interference with the antiknock action of the alkyl-lead as well as a minimum corrosive effect on engine parts. While there are a number of individual sulfur compounds that can be found to satisfy these requirements, it has been found that sulfur compounds selected from the class of alkyl sulfates and alkyl thiophenes are especially desirable. This is particularly true when a relatively high concentration of the alkyl lead compound, as, for example, tetra ethyl lead, is employed.

When relatively high concentrations of tetra ethyl lead are employed, it is known that lead residues are deposited in the combustion zone of the engine. These lead residues are harmful to exhaust valves and spark plugs since they cause corrosion and fouling of the metal parts. Various attempts have been made to eliminate or minimize the adverse effects of undesirable lead deposits on the metal parts. One method is to use so-called lead scavenging agents which may

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comprise a halogen compound, as, for example, ethylene dibromide. The added scavenging agent provides available halogen, such as bromine to combine with the lead after combustion to form lead bromide in preference to lead oxide. The lead bromide being a relatively volatile salt is more easily scavenged from the engine with the exhaust gases than is the relatively high boiling lead oxide. Actually, the halogen compound, which, in the case of aviation gasoline, is usually employed in a concentration of one theory of halogen per atom of lead, does not react quantitatively with the alkyl lead compound with the result that the lead residues are not completely removed. Furthermore, other reactions occur resulting in the deposition of lead oxide and certain complex lead salts such as lead oxybromides.

With respect to the deposit which occurs due to the use of an alkyl lead compound, it is known that of the lead compounds deposited in engine combustion chambers, the most harmful to the exhaust valves is lead oxide. On the other hand, from the standpoint of failure of spark plugs in aircraft engines, the most harmful deposits are lead oxide and lead oxybromides.

It has now been discovered, as pointed out heretofore, that the weight of deposit in the combustion chamber is appreciably reduced by increasing the sulfur content of a leaded gasoline to a higher concentration than is normally present. Furthermore, the total quantity of lead in the combustion chamber deposit is also appreciably reduced thereby. Various types of sulfur compounds may be added to the leaded gasoline to obtain a beneficial effect on lead scavenging. However, the type of sulfur compounds used governs their corrosive effect on engine parts and their interference with the antiknock action of the alkyl lead. The particular sulfur compounds used should also preferably have boiling points similar to that of the alkyl lead antiknock agent employed, so as to follow the lead alkyl in proportional amounts to each engine cylinder under conditions of imperfect cylinder-to-cylinder lead alkyl distribution that occurs with multi-cylinder spark-ignition engines.

The alkyl thiophenes and alkyl sulfates have minimum effects on corrosion and antiknock performance of motor fuels and thus are particularly well suited for use with this invention. How-

ever, any non-corrosive acting sulfur compounds having minimum adverse effect on fuel antiknock quality may be used, and this invention is proposed to cover the use of any and all of such compounds.

The present invention may be more readily understood by the following example illustrating embodiments of the same.

EXAMPLE I

A number of tests were made wherein leaded fuels of widely varying sulfur contents were tested, both in the presence and absence of an organic bromide lead scavenging agent. These tests were run in a single cylinder Lauson engine, model LF-22, under the following conditions:

Engine speed	1,800 R. P. M.
Intake air	120° F.
Jacket temperature	212° F.
Oil temperature	165° F.
Air fuel ratio	13.5
Brake load	Approximately ¾ full load
Fuel consumed	Approximately 10 gallons
Test duration	40 hours

At the end of 40 hours operation, the engine was dismantled and inspected. The condition of the combustion zone was noted, after which the deposits were removed, weighed and analyzed. The average results of two tests on each fuel are summarized in the following two tables.

Influence of fuel sulfur content on combustion chamber deposit

[1. Fuels (boiling between 80° F. and 325-380° F.) contain 4 cc. pure TEL/gallon and 1-theory of bromo-xylenes scavenging agent.]

Fuel	A	B	C	D
Wt. Per Cent Combined Sulfur in Fuel (comprising thiophenes, thiols, sulfides, and disulfides)	.0003	.005	.027	.215
Combustion Chamber Deposit—Grams	10.9	11.1	8.6	7.3
Wt. of Lead in Combustion Chamber Deposit—Grams	7.6	7.1	5.1	4.0
Lead Distribution in Deposit:				
Wt. Per Cent Pb combined with Bromine	43	50	54	48
Wt. Per Cent Pb combined with Sulfur	2	7	16	44
Wt. Per Cent Pb combined with Oxygen	55	43	30	8
Spark Plug Deposit—Grams	0.55	0.46	0.22	0.31

[2. Fuels (boiling between 80° F. and 325-380° F.) contain 4 cc. pure TEL/gallon and no organic halide lead scavenging agent.]

Fuel	A	E	D
Wt. Per Cent Combined Sulfur in Fuel (comprising thiophenes, thiols, sulfides and disulfides)	0.0003	0.031	0.215
Combustion Chamber Deposit—Grams	6.2	6.2	4.8
Wt. of Lead in Combustion Chamber Deposit Grams	5.3	4.4	2.6
Lead Distribution in Deposit:			
Wt. Per Cent Pb combined with Bromine	0	0	0
Wt. Per Cent Pb combined with Sulfur	4	42	88
Wt. Per Cent Pb combined with Oxygen	96	58	12
Spark Plug Deposit—Grams	0.50	0.55	0.55

The types of sulfur present in the fuels used in the foregoing engine tests comprise thiophenes, thiols, sulfides and disulfides. However, as heretofore pointed out, the combustion zone deposits are related to the total sulfur content of the fuels, regardless of its organic form. This is confirmed by the fact that the combustion chamber deposit analyses given in the foregoing table correlate with fuel sulfur content even though different types of sulfur compounds are present in the test fuels. For example, based on a Bureau of Mines report dated December 1946 on "Sulfur in Petroleum" by Haines, Wenger, Helm and Ball, the following types of sulfur compounds are present in the test fuels.

Fuel	Fuel Description	Type of Sulfur Compounds Present
A	Isooctane	Unknown.
B	Aviation Fuel (Straight run+alkylate).	Major—Alkanethiols.
C, E	Motor Fuel (Straight Run+Cracked).	Alkanethiols. Benzenethiol. Alkane and cyclic sulfides. Thiophene and alkyl thiophenes. Disulfides.
D	Motor Fuel	Alkanethiols. Benzenethiol. Alkane and cyclic sulfides. Thiophene and alkyl thiophenes. Disulfides.

The invention is broadly concerned with a motor fuel composition comprising an alkyl lead compound and a sulfur compound which is preferably selected from the class consisting of alkyl sulfates and alkyl thiophenes. An organic halide lead scavenging agent may or may not be present along with these constituents. The invention is more specifically directed to improve aviation fuel by adding sulfur compounds boiling above the boiling range of the fuel.

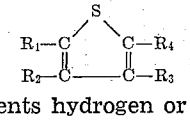
The motor fuel base may comprise hydrocarbon fractions boiling in the range from about 80° F. to 420° F. and higher, but it is preferred that the base motor fuel boil in the range from about 100° F. to 325° F.

The alkyl lead compound may be any suitable antiknock constituent, but preferably comprises tetra-ethyl lead. In general, the alkyl lead compounds should have a total of between 4-12 carbon atoms per molecule, as for example, dimethyl diethyl lead, diethyl dipropyl lead and tetrapropyl lead.

The invention is particularly applicable in motor fuels which contain 4 to 5 cc. of tetra alkyl lead per gallon.

When a lead scavenging agent is employed in conjunction with this invention, it may comprise any suitable scavenging agent. Desirable scavenging agents are, for example, organic halides, preferably those selected from the class of organic bromides and organic chlorides. Aliphatic halides such as ethylene dibromide and ethylene dichloride are two compounds suitable as lead scavenging agents, while 1-4 dichloro butane and acetylene tetra bromide are also satisfactory. Other suitable scavenging agents for use in conjunction with the present invention are aryl halides, as, for example, bromoxylene, dibromo benzene, bromo toluene, or dibromo toluene as well as the corresponding chlorine substituted compounds.

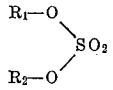
As pointed out heretofore, the sulfur compounds utilized in the present invention are selected from the class of sulfur compounds which do not tend to cause corrosion and which also have a minimum adverse effect on the lead susceptibility of the fuel. Desirable sulfur compounds are those whose molecular structure correspond to the formula



where R represents hydrogen or an alkyl group. Especially desirable compounds are those where the total number of carbon atoms in the alkyl groups is not less than 4 or more than 6. Specif-

ic of this category are, for example, tetra methyl thiophene, diethyl thiophene, diethylene thiophene, mono butyl thiophene and dimethyl ethyl thiophene. These compounds may be prepared by any suitable method.

Other suitable sulfur compounds are alkyl sulfates represented by the formula



where R_1 and R_2 represent alkyl groups of 1 or 2 carbon atoms per molecule. Especially useful compounds of this character are dimethyl sulfate, diethyl sulfate and methyl ethyl sulfate.

In general, the sulfur compounds should boil in the range from about 325° F. to 425° F. and preferably in the range from about 340° F. to 390° F. The amount of sulfur compound utilized may be varied appreciably and is, in general, a function of the amount of lead utilized. The amount of lead utilized may vary in the range from .05 to 5 cc. of tetra ethyl lead per gallon of gasoline. Under these conditions, the amount of sulfur added should be such as to give from about 0.2 to 5 atoms of sulfur per atom of lead present. Particularly desirable results are secured when the amount of sulfur present is from about 0.5 to 2.5 atoms of sulfur per atom of lead.

Having described the invention, it is claimed:

1. An improved motor fuel which comprises hydrocarbons boiling in the motor fuel boiling range, an added alkyl lead antiknock compound, a scavenging agent and a sulfur compound boiling in the range from about 340° F. to 390° F. and which is selected from the class of alkyl thiophenes.

2. An improved aviation fuel which comprises hydrocarbon constituents boiling in the range from about 80° F. to 325° F., an added alkyl lead antiknock compound, a scavenging agent and a sulfur compound which is characterized by boiling above about 325° F. and which is selected from the class of alkyl thiophenes.

3. Process as defined by claim 2, wherein said sulfur compound boils in the range from about 340° F. to 390° F.

4. Composition as defined by claim 2, wherein the amount of lead present in said fuel is in the range from about 1 to 5 cc. per gallon and wherein the sulfur concentration is from about 0.2 to 5.0 atoms of sulfur per atom of lead.

5. An improved aviation fuel comprising hydrocarbons boiling in the motor fuel boiling range, from 1 to 5 cc. of tetra ethyl lead per gallon, an organic halide scavenging agent and added sulfur compounds boiling in the range from about 340° F. to 390° F. selected from the class of alkyl thiophenes, wherein said sulfur compounds are present in concentration of from 0.2 to 5.0 atoms of sulfur per atom of lead.

6. Composition defined by claim 5 wherein said added sulfur compound comprises tetramethyl thiophene.

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