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PHOSPHOROUS ADDITIVE-LEAD EXTENDER FORMULATION WITH POSITIVE SYNERGISTIC OCTANE APPRECIATION

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Int. Cl. C10l 1/22, 1/26
U.S. Cl. 44—69 9 Claims

ABSTRACT OF THE DISCLOSURE

It was found in accordance with the present invention that an additive for gasoline containing tetraethyl lead consisting of phosphorous sesquisulfide in combination with an organo-ammonium carboxylate had a positive synergistic effect on octane appreciation.

BACKGROUND OF THE INVENTION

A highly important problem that has been with the motor industry for over thirty years is the need for a fuel that has a high anti-knock value, synonymous with a high octane number. Too low an antiknock value produces an irritating sound as well as improper detonation of the gaseous fuel mixture, which results in loss of power and possible damage to the engine.

The problem was temporarily solved by adding a lead alkyl compound such as tetraethyl lead or tetramethyl lead, or a combination thereof. It seems that tetraethyl lead during the combustion process breaks down into lead oxide, which interferes with the chemical reaction causing knocking. However, with the advent of higher performance engines, there was a demand for higher octane fuels. The effectiveness of tetraethyl lead was found to decrease as the octane number of the base gasoline increased due to the increased aromatic and the simultaneous decrease of paraffinic nature of said base gasoline. In particular, it was found that concentrations of tetraethyl lead greater than about 3.00 cc./gal. of gasoline had progressively less effect upon octane number as desired. Thus a new problem existed.

Tetra methyl lead (TML) had the antiknock quality needed for ordinary high octane fuels to solve the problem but is at the same time expensive in comparison with tetra ethyl lead (TEL). Different additives or extenders of TEL were developed that enhanced the antiknock quality of the TEL fuel mixture sufficiently beyond that of TEL. Examples of such extenders are carboxylic acids, derivatives of carboxylic acids, and esters of alcohols. Since only a small amount of extender was required to raise the octane number to the desired level, the development proved to be economically satisfying.

However, the alkyl lead compounds leave deposits in th combustion chamber and must be removed. So-called "scavengers": such as ethyl dichloride and ethyl dibromide, or combinations thereof, have traditionally been used for this purpose. While the scavengers remove most of the lead residue from the chamber, some lead does remain, building up deposits on the surface of the combustion chamber, on the valves, and on the spark plugs. These deposits create added problems of spark plug fouling and pre-ignition, caused by the effect of the lead on any carbonaceous material present in the chamber while at high engine temperatures. This problem was solved when it was found that the addition of phosphorous compounds to the gasoline suppressed the adverse effects of the lead deposits. The phosphorous compounds actually raised the electrical resistance of the lead deposits, preventing the deposits to short-out or "foul" the spark plugs and also raised the glowing temperature of the

lead deposits so as to prevent pre-ignition. However, it is known in the literature that these phosphorous deposit modifiers have a deleterious effect upon the anti-knocking characteristics of the TEL.

U.S. Pat. No. 2,794,717 claims a phosphorous compound additive such as P_4S_3 which act as a lead protector, reducing storage and engine deposits. It teaches that this phosphorous sesquisulfide has little or no deleterious effect upon the antiknock agent utilized in the fuel. In contrast, the additive of the instant invention will overcome these depreciative effects on the antiknock quality of the alkyl lead compound known to the art and demonstrate a positive octane appreciation.

SUMMARY OF THE INVENTION

This invention solves the problem of octane depreciation in phosphorous compound-lead alkyl additives that exists in conventional fuels. Specifically, it was found that a P_4S_3 additive to an organo-ammonium carboxylate extender such as N-methyl anilinum acetate (hereinafter denoted by NMAA) gives the TEL-containing additive improved antiknock characteristics, as well as excellent deposit modifying ability, preventing plug fouling and precombustion. The literature has taught the use of phosphorous compounds as deposit modifiers, but at the expense of obviating the antiknocking ability of the TEL or TEL and extender composition. This invention overcomes the disadvantages existent in the prior art.

This invention provides an additive to an aromatic-containing high octane gasoline that improves the deposit modifying characteristics of the fuel, while retaining the antiknock quality of the TEL additive.

The invention also provides an additive to an aromatic-containing high octane gasoline that improves the deposit modifying characteristics of the fuel, while substantially improving the antiknock quality of the TEL additive.

What is surprising and unexpected about the invention is that adding a phosphorous compound deposit modifier such as P_4S_3 to the TEL and extender-containing additive increases, or has a synergistic effect upon, the antiknock quality of the additive as measured by the fuel's octane number. We have found that this phenomenon is maximized when the TEL-extender is an organo-ammonium carboxylate.

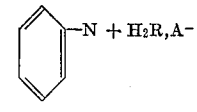
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The organo-lead compound used as an antiknocking agent in this specification is preferably a lead-alkyl compound, and more preferably TEL or TML or a combination thereof.

The aromatic-rich high octane base gasoline employed in the instant invention will have a reseach octane number (RON) of from 90 to 105 and a corresponding motor octane number (MON) of from 80 to 95.

The phosphorous deposit modifier of this invention will preferably be P_4S_3, phosphorous sesquisulfide, the structure of which is given on page 298 of Phosphorous and Its Compounds, vol. 1, 1958, by John R. Van Wazer.

The lead extender, or promoter, utilized in this invention will be an organo-ammonium carboxylate of the form



where R is an alkyl group preferably containing from 1 to about 20 and more preferably 1 to about 5 carbon atoms, and A is an anion selected from the group consisting preferably of carboxylates containing at least 2 carbon atoms, more preferably of mono carboxylates, and

most preferably of acetate, propionates, butyrates, and pentanoates. Preferably, the aspects of this invention can best be carried out when the extender is NMAA. The preferred weight ratio of lead extender plus phosphorous additive to gasoline is from about 0.01 to 2.5%, but ratios outside this range are operative.

An additive for gasoline made in accordance with this invention is not to be restricted to the components herein before listed, but can be supplemented by additional components to meet the desired characteristics of the particular fuel. Thus, a scavenger agent, rust inhibitor, carburetor anti-icer, antioxidant or a component, or the like could be easily incorporated with the above listed components. A specific embodiment of this invention is illustrated by the following three-step process:

(1) The extender N-methyl anilinium acetate is prepared by adding theoretical amounts of N-methyl aniline and acetic acid in a 1:1 stoichiometric ratio dropwise, then stirring the mixture until it has cooled and become a clear solution. One "theory" of N-methyl aniline, for example in this case, is that amount of N-methyl aniline needed to react completely with acetic acid to form N-methyl anilinium acetate.

(2) To this clear solution is added finely pulverized P_4S_3 with stirring and/or slight warming to effect complete solution. This additive solution is then filtered if any insoluble impurities remain.

(3) The pure additive solution is then added to a gasoline containing 3 cc. of TEL per gallon of gasoline with a research octane number of from 90 to 105 in an amount to give a 0.15 theory ratio of phosphorous needed to react completely with lead to form $Pb_3(PO_4)_2$.

The following table illustrates the results of an additive prepared by the aforementioned process:

TABLE I.—EXTENDER—P_4S_3 SYNERGISM IN AROMATIC GASOLINE
(0.15 Theories P:TEL)

Example		ΔRON	ΔMON	G./l.
I	P_4S_3, Alone	0.0	−0.9	0.020
II	NMAA, Alone	+0.6	+0.5	2.22
	Calculated Combined Effect (from Examples I and II).	+0.6	−0.4	
III	P_4S_3/NMAA Effect	+1.25	+1.5	2.22
	Synergistic Effect	+0.65	+1.9	

The research and motor octane numbers were obtained by employing the ASTM research and motor method for octane determination using the compression ratio test on single cylinder octane evaluation engines, as described by The Ethyl Corporation's pamphlet, "Octane Numbers by Push Button," of Oct. 3, 1963.

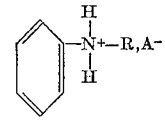
The results in the table show the octane-appreciation synergistic effect of the P_4S_3/NMAA additive to TEL aromatic-rich high octane gasoline. These results are diametrically opposed to the expected decrease in octane number as taught in the prior art (see "Effect of Phosphorous Deposit Modifiers on Gasoline Octane Quality," by F. C. Gunderloy, Jr., and R. F. Neblett, Journal of Chemical and Engineering Data, vol. 7, No. 1, January 1962).

Although not narrowly critical, the percent by weight of P_4S_3-lead extender (based on the weight of the gasoline) is preferably 0.01 to 5.0 and more preferably 0.05 to 2.5 and most preferably 0.1 to 1.0. The amount of P_4S_3 to TEL or TML, or mixture thereof, should preferably lie in the range of from 0.01 to about 2.0 theories and more preferably in the range of from 0.05 to 0.50 theories. The most preferred amount of P_4S_3 to TEL in the present invention is about 0.15 theories.

The invention should not be limited except to the spirit of the appended claims.

What is claimed is:

1. An additive for aromatic-rich gasoline having a research octane number of from 90 to 105, said gasoline containing a lead alkyl antiknocking agent, said additive comprising in combination, a deposit modifier having the molecular formula P_4S_3, and a lead extender having the structure



where R is an alkyl group containing 1 to about 20 carbon atoms or a hydrogen atom, and A is a carboxylate anion, containing at least 2 carbon atoms, said additive producing a positive synergistic antiknock effect when added to said aromatic-rich gasoline.

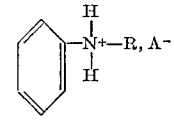
2. The additive of claim **1** wherein A is a monocarboxylate anion.

3. The additive of claim **1** wherein A is selected from the group consisting of acetate, propionates, butyrates, and pentanoates.

4. The additive of claim **1** wherein the lead extender is N-methyl anilinium acetate.

5. An additive for aromatic-rich gasoline of research octane rating of from 90 to 105 containing tetra ethyl lead as an antiknock agent which comprises, in combination, a P_4S_3 deposit modifier, and N-methyl anilinium acetate as a lead extender, said additive producing a positive synergistic antiknock effect when added to said aromatic-rich gasoline.

6. A composition comprising tetra ethyl lead and an aromatic-rich gasoline base of research octane number of from 90 to 105 in combination with a deposit modifier having the molecular formula P_4S_3, and a lead extender, having the structure



where R is an alkyl group containing from 1 to 20 carbon atoms or a hydrogen atom, and A is a carboxylate anion, in a ratio of 0.01% to 5.0% by weight of P_4S_3-lead extender to gasoline.

7. The composition of claim **6** wherein A is a monocarboxylate anion.

8. The composition of claim **6** wherein A is selected from the group consisting of acetate, propionates, butyrates, and pentanoates.

9. The composition of claim **6** wherein the lead extender is N-methyl anilinium acetate.

References Cited

UNITED STATES PATENTS

2,794,717 6/1957 Gilbert.

FOREIGN PATENTS

880,457 10/1961 Great Britain.

DANIEL E. WYMAN, Primary Examiner

Y. H. SMITH, Assistant Examiner

U.S. Cl. X.R.

44—71, 76; 252—386

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,522,023 Dated September 13, 1967

Inventor(s) C. J. Norton

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1	line 56	th	should read	-- the --
Col. 2	line 6	act	should read	-- acts --
Col. 2	line 20	anilinum	should read	-- anilinium --

SIGNED AND
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Attest:

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