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3,167,410

COMBINATION ADDITIVE FOR GASOLINE

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5 Claims. (Cl. 44—69)

This invention relates in general to improved motor fuels, and particularly to leaded gasolines containing a multifunctional additive which enhances the octane quality of the gasoline.

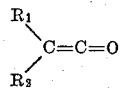
It is well known that organolead compounds are added to most modern gasolines in order to improve the antiknock characteristics of the fuels. However, the octane increment obtained by the use of increasing amounts of lead antiknock additive has diminished as the amounts of aromatic and olefinic components employed in modern gasolines have increased.

It is also well known that various phosphorus compounds are utilized in gasoline to serve as deposit modifiers. However, the compounds commonly employed often seriously degrade the octane quality of the gasoline. Thus, more lead antiknock additive must be added in order to counterbalance the octane degradation caused by the phosphorus compound. However, since it takes a large amount of the lead compound to enhance the octane quality of modern fuels, and since there are health limitations on the amount of lead compounds that can be utilized in gasoline, a problem exists in the industry.

Thus, it is an object of this invention to provide multifunctional additives which enhance the octane quality of leaded gasoline.

The additives of this invention serve as deposit modifiers to control surface ignition and spark plug fouling. More importantly, these additives enhance rather than degrade the octane quality of the leaded fuel.

The additives of this invention are obtained by reacting acids of phosphorus with highly reactive compounds referred to as ketenes wherein the carbon atom of the carbonyl group is directly attached to an adjacent ethylenically bonded carbon atom. These ketenes may be represented by the formula:



wherein R_1 and R_2 are organic radicals selected from the group consisting of aromatic, aliphatic and alicyclic radicals and hydrogen.

Suitable ketenes of this invention included aliphatic aldo- and ketoketenes wherein R_1 and R_2 are selected from the group consisting of alkyl radicals of from 1 to 6 carbon atoms and hydrogen. Such ketenes included dimethyl ketene, diethyl ketene, dicyclohexyl ketene, methyl cyclohexyl ketene, ethyl phenyl ketene, and the like.

Ketenes can be prepared by well-known methods, e.g., from α halogen acyl halides by the action of zinc, as set forth in "Die Ketene" by H. Staudinger, Stuttgart, 1912.

Ketene, the preferred agent of this invention, can be prepared by the pyrolysis of acetone or acetic acid vapor at about 600° to 750° C. The thermal decomposition of 1 mol of acetic acid yields 1 mol of ketene and 1 mol of water. The pyrolysis of 1 mol of acetone yields 1 mol of ketene and 1 mol of methane. The latter method is generally preferred since the methane acts as an inert carrier for the ketene.

The anhydrous acids of phosphorus which are suitable for this invention include the monobasic hypophosphorus acid, H_3PO_2, phosphorus acid, H_3PO_3, which usually exists in the dibasic form but may exist in the tribasic form,

the tribasic orthophosphoric acid, H_3PO_4, and the tetrabasic hypophosphoric acid, $H_4P_2O_6$, and pyrophosphoric acid, $H_4P_2O_7$.

The preferred acid is anhydrous orthophosphoric acid, H_3PO_4. The commercial preparations of this acid are well known.

The amount of ketene to be utilized in this invention will depend upon whether the acid of phosphorus is monobasic, dibasic, tribasic or tetrabasic. In general, the agent should be employed within the range of from 0.8 to 1.1 mols of ketene for each mol of hydroxyl in the acid of phosphorus. A range of 0.95 to 1.05 mols is preferred. The reaction temperature is not critical, but is generally within a range of from 40° to 100° F.

In preparing the preferred additive of this invention, gaseous ketene is bubbled by means of a sparger into dry H_3PO_4. It is desirable to continue the reaction until about three mols of ketene have reacted with each mol of H_3PO_4. The reaction can also be accomplished by contacting the gaseous ketene and the anhydrous H_3PO_4 in a packed tower.

The fuels in which the additives of this invention are useful are conventional leaded gasolines used in internal combustion engines. Such gasolines generally boil between 80° and 450° F. Their octane numbers, as determined by ASTM Method D-908, range from about 83 to 105 or higher. The additives are particularly useful in gasolines having an octane number above 95. Lead compounds, such as tetraethyl lead, tetramethyl lead, and tetravinyl lead, are generally employed in concentrations of from about 0.5 to 7 cc./gal.

The additives of this invention are advantageously employed in minor amounts sufficient to enhance the octane quality of a leaded gasoline. Said minor amounts are generally in the range of from about 0.05 to 2% by volume based on the gasoline blend, and preferably in the range of from about 0.1 to 1% by volume.

The following examples illustrate the efficacy and unobvious nature of this invention.

EXAMPLE 1

Ketene, prepared by the pyrolysis of acetone, was bubbled by means of a sparger into a reactor containing 340 g. of anhydrous H_3PO_4. The temperature of the reaction was maintained at about 80° F. by means of a water bath. An analysis of the product showed that approximately 3.1 mols of the ketene reacted with each mol of H_3PO_4, or approximately 1.03 mols of ketene reacted per mol of hydroxyl originally present in the H_3PO_4.

The product was added to a gasoline having the following characteristics:

Reid vapor pressure	7.3
Saturates, volume percentage	67.3
Olefins, volume percentage	11.7
Aromatics, volume percentage	21.0
Percentage evaporated:	
158° F.	23.5
212° F.	45.9
257° F.	77.0
302° F.	97.3
Tetraethyl lead, cc./gal.	1.96
Research Octane Number	102.7
Motor Octane Number	94.1

Laboratory octane ratings of the Research Octane Number and the Motor Octane Number were obtained using the Direct Match Method.

The RON of the gasoline was determined by the Standard ASTM Research Method Test Procedure D-908-51, which is described in the 1952 edition of "ASTM Manual of Engine Test Methods for Rating Fuels." The MON was determined by the Standard ASTM Motor

Method Test Procedure D–357, which is explained in the 1953 edition of "ASTM Manual of Engine Test Methods for Rating Fuels."

The improved octane quality of the fuel can be ascertained by reference to the data in Table I.

Table I

Volume Percent Additive	RON	Δ RON	MON	Δ MON
0	102.7		94.1	
0.1	103.65	+0.95	94.0	−0.1
0.25	104.5	+1.8	94.85	+0.75
0.5	105.6	+2.9	95.75	+1.65
1.0	103.3	+0.6	94.05	−0.05

The above data clearly demonstrate the beneficial effect obtained by adding small amounts of the instant additives to a leaded gasoline.

EXAMPLE 2

Other tests proved that compounds closely related to the ketene treated acids of phosphorus do not enhance the octane quality of leaded gasolines. 1.65 g. of a mixture of monoalkyl and dialkyl phosphates were added to 1840 cc. of a leaded gasoline in order to determine the effect of the mixture on the octane quality of the gasoline. A similar mixture was then treated with ketene. 1.85 g. of the reaction products were added to 1840 cc. of the same gasoline and tests were performed in order to determine the effect of the ketene treated phosphates on the octane quality of the fuel. The results appear in Table II.

Table II

	Δ RON [2]	Δ MON [2]
Monoalkyl and dialkyl phosphate [1]	−0.2	−0.75
Ketene treated monoalkyl and dialkyl phosphate [1]	0	−0.65

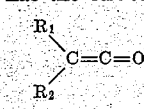
[1] Alkyl groups are C_8 Oxo.
[2] Average of 4 direct match determinations.

These data show that the phosphates degraded the octane quality of the fuel. Moreover, treating the phosphates with ketene had little effect on the octane quality of the fuel. Most importantly, these data show that the ketene treated phosphates did not enhance the octane quality of the leaded gasoline.

In summary, it is seen that the instant invention is limited to products obtained by reacting various ketenes with acids of phosphorus, and that closely related products are not effective.

What is claimed is:

1. A leaded gasoline containing a minor amount sufficient to enhance the octane quality of the gasoline of the reaction products obtained by reacting with an organic ketene which has the structural formula:



wherein R_1 and R_2 are organic radicals selected from the group consisting of hydrogen and alkyl radicals of from 1 to 6 carbon atoms.

2. A leaded motor fuel according to claim 1 wherein said organic ketene is ketene.

3. A leaded motor fuel according to claim 1 wherein said minor amount of reaction products is from 0.05 to 2% by volume, and the ratio of mols of organic ketene per mol of hydroxyl in the acid of phosphorus being within the range of from 0.8 to 1.1.

4. A leaded motor fuel boiling in the gasoline boiling range containing from 0.05 to 2% by volume of the products obtained by reacting H_3PO_4 with ketene in a ratio of from 0.8 to 1.1 mols of ketene per mol of hydroxyl in the H_3PO_4.

5. A leaded motor fuel according to claim 4 wherein said ratio is from 0.95 to 1.05.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,167,410 January 26, 1965

Robert W. Malone

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 10, after "reacting" insert -- H_3PO_4 --.

Signed and sealed this 6th day of July 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents