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AMINE-PHOSPHORUS-CONTAINING ADDUCTS AND MOTOR FUEL CONTAINING SAME

Frederic C. McCoy, Beacon, George W. Eckert, Wappingers Falls, and Edwin C. Knowles, Poughkeepsie, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

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This invention relates to novel amine-phosphorus-containing adducts and to a hydrocarbon fuel composition containing same having excellent surface ignition properties. More particularly, the fuel is a leaded gasoline containing a combustion chamber deposit modifier which reduces surface ignition and other harmful effects brought about by the formation and laydown of deposits in the combustion chamber of a gasoline engine.

Most conventional gasolines contain an alkyl lead compound, such as tetraethyl lead and tetramethyl lead, as an anti-knock compound to improve the octane level of the gasoline. During combustion, the alkyl lead compounds break down to lead oxide and lead salts and form deposits in the combustion chamber of the engine. These deposits interfere with proper engine operation. Specifically, the lead deposits which are characterized by a low ignition temperature become incandescent at engine operating temperatures. These glowing or incandescent deposits cause premature firing of the fuel-air mixture during the compression stroke of the combustion cycle resulting in uneven firing in the engine with concomitant loss of power and an audible rumble noise. This phenomenon is known as surface ignition. Combustion chamber deposits also seriously reduce the efficiency of the sparkplugs even to the point of causing them to misfire completely. This is a serious or critical defect particularly in the case of leaded gasoline for aircraft operation.

The formation of lead deposits in gasoline engines has been greatly reduced by employing scavenger agents in conventional leaded gasolines. Scavenger agents are compounds capable of reacting with the tetraalkyl lead compounds during combustion to produce volatile lead compounds. The principal scavengers in use are alkylene dihalides, such as ethylene dichloride, ethylene dibromide and their mixtures. These compounds bring about the formation of lead chloride and lead bromide which, being volatile, are substantially removed from the engine during the exhaust cycle. Unfortunately, minor amounts of the lead compounds remain deposited in the engine creating a surface ignition problem which is particularly serious for modern high compression engines.

Considerable research has been conducted to reduce or overcome the surface ignition problem caused by combustion chamber deposits. This has led to the discovery of certain phosphate esters which are effective in reducing surface ignition. Indeed, certain amyl phosphate esters have achieved some degree of commercial acceptance. The known phosphate esters, however, have harmful side effects on gasoline. The principal objectionable feature of these phosphate esters is that they lower the octane value of gasoline, a particularly serious drawback where one's object is to produce the highest quality gasoline on a competitive basis.

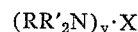
The present invention provides a novel class of amine-phosphorus-containing adducts and a leaded gasoline con-

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taining said adducts which exhibits an outstanding reduction in surface ignition. The amine-phosphorus-containing adducts are also useful for imparting anti-wear properties to mineral lubricating oils.

An unexpected feature of the invention is that the adducts have no harmful or deleterious effect on the overall octane quality of the gasoline. Another surprising feature is that the adducts are more effective for inhibiting surface ignition than the commercially available aryl phosphate esters.

The amine-phosphorus-containing adduct of the invention is represented by the formula:



in which R is an aliphatic radical having from 8 to 30 carbon atoms, R' is either hydrogen or an aliphatic radical having from 1 to 30 carbon atoms, X is a metal salt from the group consisting of zinc and aluminum mono- and di-hydrogen phosphate and zinc and aluminum mono- and di-hydrogen phosphite, y is an integer from 1 to 12 and the total number of carbon atoms in said adduct is at least 24. The motor fuel of the invention is a leaded gasoline containing a minor deposit-modifying amount of the above described adduct. More particularly, the leaded gasoline will contain from about 0.01 to 1 theories of the adduct, as described later in more detail.

Amines which can be employed to prepare the adduct of the invention are amines having one or more aliphatic radicals in which at least one aliphatic radical has at least 8 carbon atoms. This requirement together with the requirement of at least 24 carbon atoms in the adduct is critical to insure the solubility of the adduct in a leaded gasoline. The effective amines correspond to the formula:



wherein R is an aliphatic radical having from 8 to 30 carbon atoms and R' is hydrogen or an aliphatic radical having from 1 to 30 carbon atoms. R is generally a branched chain alkyl radical because of the ready availability of these materials. Preferably, R is a tertiary alkyl radical having from 12 to 30 carbon atoms.

Examples of specific effective amines include laurylamine, 2-ethylhexylamine, tri-n-octylamine, tridecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, tricosylamine, nonacosylamine, methyldecylamine, dimethyldodecylamine, methyloctadecylamine, dimethyloctadecylamine. Particularly preferred amines are certain commercially available mixtures of tertiary alkyl primary amines. For example, a mixture of tertiary alkyl primary amines in which the alkyl radical comprises a mixture of alkyl groups having from 11 to 14 carbon atoms is available under the name Primene 81-R. Another commercially available amine is the mixture of tertiary alkyl primary amines in which the alkyl radical comprises a mixture of alkyl groups having 18 to 24 carbon atoms sold under the name Primene JM-T.

The adducts of the invention are prepared by mixing from 1 to 12 moles of an aliphatic amine with a mole of a zinc or aluminum salt of an acid phosphate or phosphite defined above. The reactants are generally heated at a moderate temperature from about 75 to 125° C. to effect formation of the adduct. The reaction is usually accomplished by refluxing the reactants in a solvent, such

as benzene or toluene, the solvent being finally stripped off using conventional methods to recover the adduct.

Examples of adducts of the invention and the mole ratio of their component parts, i.e., of the amine and metal salt are given below:

Primene JM-T: Zn(H ₂ PO ₄) ₂ -----	4:1
Primene JM-T: ZnHPO ₄ -----	4:1
Primene 81-R: Zn(H ₂ PO ₄) ₂ -----	4:1
Primene JM-T: Zn(H ₂ PO ₃) ₂ -----	4:1
Primene JM-T: ZnHPO ₃ -----	2:1
Primene JM-T: ZnHPO ₃ -----	1:1
Primene 81-R: ZnHPO ₃ -----	2:1
Primene JM-T: Al(H ₂ PO ₄) ₃ -----	12:1
Primene 81-R: Al(H ₂ PO ₄) ₃ -----	12:1
Primene JM-T: Al ₂ (HPO ₄) ₃ -----	12:1
Primene JM-T: Al ₂ (HPO ₃) ₃ -----	4:1
Primene JM-T: Al(H ₂ PO ₃) ₃ -----	12:1

The amine-phosphorus-containing adduct of the invention is added to a motor fuel in the gasoline boiling range containing an anti-knock amount of a tetra-alkyl lead compound. The motor fuel may consist of any hydrocarbon fuel including paraffinic, naphthenic, and aromatic hydrocarbons or mixtures thereof suitable for use in an internal-combustion, spark-ignition engine. These fuels are derived by the distillation of crude oil, by the catalytic or thermal cracking of gas oils, by the alkylation of isoparaffins with olefins, or by the polymerization of olefins. The boiling point of the motor fuel or gasoline will generally be in the range from about 100° F. to about 450° F. The motor fuel of the invention will contain a tetra-alkyl lead compound, such as tetraethyl lead, in a concentration from about 0.5 ml. to about 5 ml. or more per gallon of fuel. The motor fuel may also contain a number of additives conventionally employed in a gasoline, such as scavengers, anti-oxidants, stabilizers, dyes, and metal suppressors.

The amount of the phosphorus-containing adduct employed in the gasoline of the invention is expressed in terms of theories. One theory of the phosphorus-containing adduct is defined as the amount of the adduct which will provide sufficient phosphorus to react stoichiometrically with the lead atoms in the tetra-alkyl lead anti-knock compound present to form the compound Pb₃(PO₄)₂. The adduct is blended into the leaded gasoline in a concentration ranging from about 0.01 theory to about 1 theory in accordance with the foregoing definition based on the lead content of the fuel. Concentrations between about 0.05 and 0.5 theory are in the preferred range for the suppression of surface ignition.

Gasoline containing the adduct of the invention was tested for effectiveness in a single cylinder CFR L-head engine with an 11.3/1 compression ratio. The engine was continuously run on the test fuel over a 20-hour test period during which time engine operation was alternated between a 50-second idle cycle (600 r.p.m.) and a 150-second full throttle cycle (900 r.p.m.). The surface ignition count rate was obtained using an ionization gap (spark-plug) as the surface ignition pickup coupled to a recording counter device. The surface ignition rate is expressed as the number of counts per hour, the lower the count value the better the quality and performance of the fuel.

Tests were conducted using a high octane blended gasoline as the motor fuel. This gasoline containing 40 percent aromatic hydrocarbons boiled in the range of 97 to 373° F., had a research octane number of 101.9 and contained 3 ml. of TEL per gallon. The adduct of the invention was blended into the leaded gasoline to provide phosphorus in the amounts indicated as theories of phosphorus according to the foregoing definition.

Example I

The adduct formed from Primene JM-T and zinc di-hydrogen phosphate in the mole ratio of 4:1 respectively was blended into the above-described base fuel. In this test, the base fuel had a surface ignition count of 455.

When 0.3 theory of the foregoing adduct was employed, the surface ignition count dropped to 185. At a concentration of 0.6 theory, the surface ignition count was 65.

Example II

The adduct formed from Primene JM-T and aluminum di-hydrogen phosphate in the mole ratio of 12:1 respectively was blended in the base fuel having a surface ignition count level of 455. At a concentration of 0.3 theory for this adduct, the surface ignition count dropped to 95. At a concentration of 0.6 theory, the surface ignition count dropped to 46.

Example III

The adduct formed from Primene JM-T and zinc monohydrogen phosphite in a mole ratio of 2:1 respectively was blended into the base fuel having a surface ignition count level of 315. At a concentration of 0.2 theory for the adduct the surface ignition count level dropped to 120. This adduct also gave a substantial improvement in surface ignition when employed in a concentration of 0.15 theories.

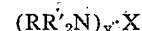
The adduct of Primene 81-R and zinc monohydrogen phosphite in molar ratio of 2:1 respectively gave a substantial reduction in surface ignition when employed in a concentration of 0.05 theory.

The adducts of the invention have given outstanding improvements in the surface ignition of leaded gasoline. This improvement was obtained without any loss or reduction in the octane value of the fuels tested. In contrast to the foregoing improvements, Primene JM-T and tricaprilylamine adducts of phosphoric acid in mole ratios of 3:1 respectively did not suppress the surface ignition of the base fuel.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. An amine-phosphorus-containing adduct represented by the formula:



in which R is an aliphatic hydrocarbon radical having from 8 to 30 carbon atoms, R' is selected from the group consisting of hydrogen and an aliphatic hydrocarbon radical having from 1 to 30 carbon atoms, X is a metal salt selected from the group consisting of zinc and aluminum mono- and di-hydrogen phosphate, y is an integer from 1 to 12 and the total number of carbon atoms in said adduct is at least 24.

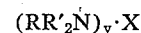
2. An adduct according to claim 1 consisting of a primary amine and zinc di-hydrogen phosphate.

3. An adduct according to claim 1 consisting of a primary amine and aluminum di-hydrogen phosphate.

4. An adduct according to claim 1 consisting of a C₁₈₋₂₄ tertiary alkyl primary amine and zinc di-hydrogen phosphate in a 4:1 mole ratio respectively.

5. An adduct according to claim 1 consisting of a C₁₈₋₂₄ tertiary alkyl primary amine and aluminum di-hydrogen phosphate in a 12:1 mole ratio respectively.

6. A motor fuel in the gasoline boiling range containing a minor amount of an organo-lead anti-detonant and from about 0.01 to 1.0 theory of an amine-phosphorus-containing adduct represented by the formula:



in which R is an aliphatic hydrocarbon radical having from 8 to 30 carbon atoms, R' is selected from the group consisting of hydrogen and an aliphatic hydrocarbon radical having from 1 to 30 carbon atoms, X is a metal salt selected from the group consisting of zinc and aluminum mono- and di-hydrogen phosphate and zinc and aluminum mono- and di-hydrogen phosphite, y is an integer from 1

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to 12 and the total number of carbon atoms in said adduct is at least 24.

7. A motor fuel according to claim 6 in which said adduct consists of a primary amine and zinc di-hydrogen phosphate.

8. A motor fuel according to claim 6 consisting of a primary amine and aluminum di-hydrogen phosphate.

9. A motor fuel according to claim 6 in which said adduct consists of a primary amine and zinc mono-hydrogen phosphite.

10. A motor fuel according to claim 6 in which said adduct consists of a C₁₈₋₂₄ tertiary alkyl primary amine and zinc di-hydrogen phosphate in a 4:1 mole ratio respectively.

11. A motor fuel according to claim 6 in which said adduct consists of a C₁₈₋₂₄ tertiary alkyl primary amine and aluminum di-hydrogen phosphate in a 12:1 mole ratio respectively.

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12. A motor fuel according to claim 6 in which said adduct consists of a C₁₈₋₂₄ tertiary alkyl primary amine and zinc mono-hydrogen phosphite in a 2:1 mole ratio respectively.

13. A motor fuel according to claim 6 containing 0.5 to 5 ml. of an organo-lead anti-detonant.

14. A motor fuel according to claim 6 in which said organo-lead anti-detonant is tetraethyl lead.

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