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FUEL COMPOSITIONS FOR SPARK IGNITION ENGINES

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This invention relates to novel fuel compositions which substantially reduce the problem of spark plug fouling in spark ignition internal combustion engines. The fuel compositions of the invention contain novel additives which have been found to be particularly effective spark plug anti-fouling agents.

The fouling of spark plugs in spark ignition engines is a well known and serious problem when commercially available hydrocarbon fuel compositions are employed. The problem is aggravated by the presence, in such fuel compositions, of commonly used organo-metallic additives such as tetraethyl lead. During combustion, organo-metallic additives are decomposed and form deposits which remain in the engine. Thus, tetraethyl lead decomposes to form deposits which are known to remain in the combustion chamber as deposits on the walls and on the spark plug ceramic. Such deposits either conduct electricity, or are converted under combustion chamber conditions to products which conduct electricity. A build-up of such deposits on spark plugs provides an alternate path for the flow of electrical current. The resulting current leakage between spark plug terminals reduces the spark potential and eventually causes the plug to misfire. This phenomenon is known in the art as spark plug fouling. Many materials have been tested to determine their effectiveness, as fuel additives, in reducing spark plug fouling, but only limited success has been obtained.

An object of this invention is to provide novel fuel compositions for spark ignition engines. A specific object is to provide novel fuel compositions which, when employed in a spark ignition internal combustion engine, effectively and substantially reduce the fouling of spark plugs. Another object of the invention is to provide a process for operating an engine in which the tendency toward fouling of the spark plugs is substantially reduced.

It has now been discovered that spark plug fouling can be substantially reduced by incorporating in fuel for a spark ignition engine a minor amount of an ester formed by reacting naphthenic acids with certain monohydric alcohols. Monohydric alcohols which can be used to prepare the naphthenate esters in the fuel compositions of the present invention are cyclopentanols, cyclohexanols, phenylcarbinols, phenylethyl alcohols, phenylpropyl alcohols and thienylcarbinol.

The novel gasoline compositions of the present invention comprise mainly mixtures of petroleum hydrocarbons boiling in the range of from about 80° F. to 440° F., and usually from about 90° F. to 400° F. The gasoline compositions of the invention also contain, in addition to the additives of this invention, an anti-knock amount of an organo-metallic anti-knock agent such as tetraethyl lead, iron carbonyl, bis-cyclopentadienyl iron, and the like. Tetraethyl lead is the most commonly used organo-lead anti-knock additive, although other lead compounds such as tetramethyl lead, tetraphenyl lead, triethylmethyl lead, and the like have been described as

useful. These lead anti-knock agents are used in amounts in the range of from about 0.1 to 6.0 cc./gallon of gasoline. Other commonly used gasoline additives can be present, such as scavengers for the organo-metallic compound, anti-icing agents, detergents, other anti-knock agents, and the like.

In practicing the present invention, the spark plug anti-fouling additive is incorporated in the gasoline in a minor amount sufficient to substantially reduce spark plug fouling in a spark ignition internal combustion engine. The addition of from about 0.1 to 5.0 cc./gallon of gasoline, and preferably from about 0.5 to 1.0 cc./gallon of gasoline, of the additive gives good results. On occasion, however, amounts of the additive outside of the above cited ranges can advantageously be used.

The spark plug anti-fouling additives of the present invention are naphthenate esters of a monohydric alcohol. The monohydric alcohol can be cyclopentanol, a cyclohexanol, a phenylcarbinol, a phenylethyl alcohol, a phenylpropyl alcohol or thienyl carbinol. The esters can be derived from any of the well known alcohols within the defined group. With the exception of thienyl carbinol, the alcohol can have alkyl substituents attached to nuclear carbon atoms. Preferably not more than 3 such substituents, each containing from 1 to about 4 carbon atoms, are present. Cyclopentanol, cyclohexanol, phenylcarbinols, phenylethyl alcohols and phenylpropyl alcohols are well known and are preferably used. Thienyl carbinol (thienyl methyl alcohol), which can be prepared in accordance with a method given in "Berichte," volume 19, page 636, also gives good results.

The naphthenic acids used in preparing the naphthenate esters of the present invention are normally obtained from petroleum. Petroleum naphthenic acids are complex mixtures of alkyl-substituted, cycloparaffinic, monocarboxylic acids which occur in small amounts as natural constituents of crude petroleum and fractions thereof. The naphthenic acids from which the additives of the present invention are derived are preferably those recovered from the lubricating oil and gas oil fractions of petroleum which boil within the range of from about 500° F. to about 1000° F. at atmospheric pressure. The acids from a fraction boiling within this range normally contain from about 8 to about 30 carbon atoms per molecule, and distill in the range of from about 250° F. to about 600° F. at 2 mm. of mercury absolute pressure. Such acids can range in saponification value from about 50 to about 300 mgs. of KOH/gram on an unsaponifiables-free basis. In the practice of this invention, esters derived from mixtures of such acids having an average saponification value of 175–185 mgs. of KOH/gram are preferred, since excellent results are obtained therewith.

Methods of recovering naphthenic acids from petroleum fractions are well known in the art. Generally, such methods comprise saponifying the desired fraction of petroleum to obtain a mixture consisting essentially of a major proportion of unsaponifiable material and a minor proportion of naphthenate soaps, effecting at least a partial separation between the soaps and unsaponifiable material, and then acidifying the separated soaps to obtain the desired naphthenic acids fractions in relatively concentrated form.

Specific examples of naphthenate esters of monohydric alcohols which may be employed in practicing the present invention are: cyclopentyl naphthenates, butyl cyclopentyl naphthenates, dipropyl cyclopentyl naphthenates, trimethyl cyclopentyl naphthenates; cyclohexyl naphthenates, propyl cyclohexyl naphthenates, dimethyl cyclohexyl naphthenates, triethyl cyclohexyl naphthenates; butylbenzyl naphthenates, trimethylbenzyl naphthenates, dipropylbenzyl naphthenates; diphenylmethyl

naphthenates, triphenylmethyl naphthenates; alpha-phenylethyl naphthenates, beta-phenylethyl naphthenates; gamma-phenylpropyl naphthenates; thienyl methyl naphthenates; and homologues and isomers thereof.

The naphthenate esters constituting the anti-fouling additives of this invention can be prepared from the acids and monohydric alcohol by any of the methods commonly known in the art. Generally, the esterification of naphthenic acids with an alcohol can be carried out by heating and stirring the acids with excess alcohol in the presence of a catalyst such as para-toluene sulfonic acid, concentrated sulfuric acid or dry hydrogen chloride. It is not essential to esterification that the naphthenic acids be substantially free from unsaponifiable material, and acids containing up to about 20% by weight of unsaponifiable material can advantageously be employed. A lower unsaponifiables content is preferred, however, such as below 10% by weight, quantities of from about 3% to 8% by weight giving excellent results.

In order to illustrate the spark plug anti-fouling effectiveness of the novel compositions of the present invention, methyl cyclohexyl naphthenates were prepared by esterification of methyl cyclohexanol with a petroleum naphthenic acid fraction. The alcohol employed was a commercially available mixture of the ortho, meta and para isomers having a boiling range of from 155° F. to 180° F., a refractive index ($n_D^{20°\ C.}$) of 1.461 and a specific gravity (15° C./15° C.) of 0.924. The naphthenic acids used, also commercially available, were recovered from a gas oil-lubricating oil fraction of petroleum. The acids contained 5.6 weight percent of unsaponifiable matter and had a distillation range, at 2 mm. of mercury absolute pressure, of from 315° F. to 485° F. Their average saponification value was 183 mgs. of KOH/gram which corresponds to an average molecular weight of naphthenic acids of 297, and to an average of about 19 carbon atoms per molecule. The above described acids were mixed with an excess of the alcohol in the presence of a small amount of para-toluene sulfonic acid as catalyst, and refluxed with stirring for about 3 hours at approximately 165–170° F. The resulting reaction products were washed with water containing dissolved Na_2CO_3 to remove the catalyst, and diluted with a low boiling organic solvent. Methyl cyclohexyl naphthenates were recovered in relatively concentrated form by flashing off the water and organic solvent. Physical properties of the ester were as follows:

Specific gravity (15° C./15° C.)	0.9567.
Viscosity @ 100° F	200.4 SSU.
Viscosity @ 210° F	43.36 SSU.
Refractive index ($n_D^{20°\ C.}$)	1.4885∓0.0005.
Acid number	7.46 mgs. KOH per gm.
Saponification value	110.9 mgs. KOH per gm.

The spark plug anti-fouling effectiveness of the above prepared ester was demonstrated in a single-cylinder engine having a hemispherical combustion chamber, an overhead valve and a compression ratio of 11:1. This engine was operated on a highly aromatic, high octane, leaded gasoline fuel and a 10W30 mineral oil lubricant. The engine was designed to stop when the spark plug misfires or shorts. The time of operation before such an engine stops is therefore a measure of the severity of spark plug fouling. The engine when employing the above fuel without the anti-fouling additive stopped after 110 hours of operation. When the engine was operated on the same fuel containing 1 ml./gallon of the methyl cyclohexyl naphthenate additive prepared as above described, it operated for 180 hours before stopping. This increase in time of operation is indicative of a significant and substantial reduction in spark plug fouling.

When the above procedure is repeated using cyclopentyl naphthenates, benzyl naphthenates, thienyl methyl naphthenates, other esters as above described, or mixtures of such esters, as the spark plug anti-fouling fuel additive, substantially equivalent results are obtained.

The exact mechanism by which the novel fuel compositions of this invention reduce the tendency toward fouling of the spark plugs is not definitely known. It is known, as above described, that the incorporation of small amounts of naphthenate esters of certain monohydric alcohols in a fuel for a spark ignition engine reduces spark plug fouling to a remarkable extent.

The invention claimed is:

1. A spark ignition internal combustion engine fuel composition consisting essentially of a major proportion of a mixture of petroleum hydrocarbons boiling in the gasoline range, an anti-knock amount of an organo-lead anti-knock additive and a minor amount, sufficient to substantially reduce spark plug fouling, of a petroleum naphthenate ester of a monohydric alcohol, said monohydric alcohol being selected from the group consisting of cyclopentanol, cyclohexanol, phenylcarbinol, phenylethyl alcohol, phenylpropyl alcohol and thienyl carbinol.

2. Composition according to claim 1 wherein the monohydric alcohol is cyclopentanol.

3. Composition according to claim 1 wherein the monohydric alcohol is cyclohexanol.

4. Composition according to claim 1 wherein the monohydric alcohol is phenylcarbinol.

5. Composition according to claim 1 wherein the monohydric alcohol is phenylethyl alcohol.

6. Composition according to claim 1 wherein the monohydric alcohol is thienyl carbinol.

7. Composition according to claim 1 wherein said organo-lead anti-knock additive is tetraethyl lead.

8. A spark ignition internal combustion engine fuel composition consisting essentially of a major proportion of gasoline, an anti-knock amount of an organo-lead anti-knock additive and from about 0.1 ml. to 5.0 mls. per gallon of gasoline of petroleum naphthenate esters of a monohydric alcohol selected from the group consisting of cyclopentanol, cyclohexanol, phenylcarbinol, phenylethyl alcohol, phenylpropyl alcohol, and thienyl carbinol.

References Cited in the file of this patent

UNITED STATES PATENTS

1,841,254	Rosenbaum	Jan. 12, 1932
2,316,754	Backoff et al.	Apr. 20, 1943
2,765,220	Yust	Oct. 2, 1956