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FUEL AND LUBRICANT ADDITIVES FOR REDUCING COMBUSTION CHAMBER DEPOSITS

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9 Claims. (Cl. 252—25)

This invention relates to a new method for reducing combustion chamber deposits in spark ignition internal combustion engines by the use of a novel combination of additives in either the fuel or lubricant of such engines, and to the novel fuel or lubricant compositions so produced.

The deleterious effects on engine performance resulting from the presence of a substantial amount of such deposits in the combustion chamber of a spark ignition engine are well known. Such deposits are known to promote preignition due to the presence of glowing particles of deposits. Also, poor thermal efficiency of the engine results from the reduced rate of heat transfer through the combustion chamber walls due to the insulating effect of such deposits.

There is a long and unsuccessful history of attempts to develop a deposit removal or preventative additive which could be directly incorporated in the fuel or lubricant for spark ignition engines. Only very limited success has been achieved although numerous additives have been tried.

It is an object of this invention to provide a method for substantially removing or preventing the accumulation, in the combustion chambers of spark ignition engines, of deposits resulting from the decomposition of hydrocarbon fuels, lubricants and/or common additives therein such as organo-metallic compounds including tetraethyl lead, and the like. It is also an object of this invention to provide novel fuel and lubricant compositions for use in such engines which will achieve the above-mentioned objectives.

It has now been discovered that the accumulation of combustion chamber deposits in spark ignition internal combustion engines can be substantially removed or prevented by incorporating in the fuel or lubricant used in such engine, a minor amount of the combination of a compound selected from the group consisting of pyridine, picoline or a picoline isomer, piperidine, quinoline, isoquinoline, quinaldine, and mixtures thereof, together with an anhydrous copper salt. Certain of the individual compounds specified in the foregoing group, when incorporated in gasoline or spark engine lubricants, may reduce combustion chamber deposits to a minor extent. However, in accordance with the present invention, the combination of the heterocyclic organic compound with an anhydrous copper salt, when used in spark ignition engine fuels or lubricants, exhibits synergism in that the beneficial effect achieved from using the combination unexpectedly far surpasses the sum of the effects of the individual components.

In order to illustrate the synergism obtained through the use of the above-described combination of additives, a clean spark ignition internal combustion engine was operated on commercially available leaded gasoline and S.A.E. No. 10W30 lubricating oil for a period of time sufficient to accumulate a substantial amount of deposit in the combustion chambers. A portion of this deposit

was removed from the chambers by scraping and was divided into four 1000 mg. samples. The first sample was used, as described below, without any pretreatment. To the second sample was added 50 mgs. of anhydrous copper chromite; to the third sample was added 0.5 ml. of quinoline; and to the fourth sample was added 50 mgs. of anhydrous copper chromite and 0.5 ml. of quinoline. The four resulting samples were then placed in individual glass tubes and heated externally while being swept with a stream of nitrogen. The cumulative weights lost in heating up to and including a temperature of 400° F., over and above that lost by the sample containing no additives, are shown in the following table.

Table I

	Cumulative weight lost in heating to 400° F., over and above that lost by deposit containing no additive
	Mgs.
Deposit+copper chromite	2.2
Deposit+quinoline	5.7
Deposit+quinoline and copper chromite	16.2

The above procedure was performed again under identical conditions except that pyridine was substituted for quinoline. The results were substantially equivalent. The above procedure was repeated using copper sulfate as the anhydrous copper salt, in combination with pyridine and again in combination with quinoline. In all of these cases, the results were substantially equivalent in that the combination of the heterocyclic organic compound with an anhydrous copper salt effectively decomposed the combustion chamber deposit to a degree far superior than would be expected from the sum of the independent effects of the additives. It can thus be seen that the combination disclosed herein of a heterocyclic organic compound with an anhydrous copper salt will result in a substantial reduction of combustion chamber deposits in a spark ignition engine when such a combination is introduced into the combustion chamber as an additive in the fuel, the lubricant, or both the fuel and the lubricant.

In carrying out the invention, the novel additive combination is incorporated in either gasoline or spark engine lubricating oil in minor amount sufficient to substantially lessen the accumulation of deposits in the engine combustion chambers. Normally the addition of about 0.05% to 5.0% by weight, and preferably about 0.1% to 2.0%, of the additive combination is adequate. The anhydrous copper salt is present in said additive combination in an amount such that there will be no more than one mole of such copper salt for every four moles of said heterocyclic organic compound in the resulting additive combination. The copper salt may constitute as little as 5 mole percent of the additive combination but 20 mole percent is preferred. On occasion, however, amounts of either additive constituent outside of the above cited ranges can advantageously be used.

The anhydrous copper salt employed in this invention can be any organic or inorganic cuprous or cupric salt that is not a hydrate and does not contain free moisture. Preferably, it should be soluble in the liquid hydrocarbons commonly used in spark ignition internal combustion engines as fuels and lubricants. Water of hydration and free moisture, if either or both are present, should be removed by heating prior to use. Salts of divalent copper are preferred, but the known corresponding salts of monovalent copper can be used. Inorganic salts are also preferred, but low molecular weight organic salts are also effective. Examples of inorganic copper salts are copper

meta borate, copper phosphate, copper cyanide, copper chromite and copper sulfate. Copper chromite and copper sulfate have been found to be particularly effective. Examples of organic copper salts are copper formate, copper tartrate, copper oxalate, copper acetylacetonate and copper acetate. Copper acetate and copper acetylacetonate are preferred organic copper salts to employ in the composition of the invention.

The lubricating oil to which the above combination of additives in incorporated can be any of the known petroleum lubricating oils normally used in spark ignition internal combustion engines. The lubricating oils may contain, in addition to the additives of this invention, any of various additives such as extreme pressure agents, detergent additives, and the like, which are known in the art.

The gasoline in which the present combination of additives is incorporated comprises mixtures of petroleum hydrocarbons boiling in the range of about 80° F. to 440° F., and usually about 90° F. to 400° F. The gasoline compositions can contain, in addition to the additives of this invention, any of the gasoline additives commonly used in the art. Organo-metallic anti-knock additives such as tetraethyl lead, iron carbonyl, bis-cyclopentadienyl iron and the like can be included in the compositions of this invention. These organo-metallic additives are commonly used in amounts in the range of 5 to 8 cc. per gallon of fuel. Other gasoline additives such as scavengers, anti-icing agents, detergents, and the like, can be used.

In order to illustrate a specific embodiment of this invention, an additive combination composed of 80 mole percent of quinoline and 20 mole percent of anhydrous copper chromite is incorporated in a commercially available leaded gasoline in an amount sufficient to constitute 1% by weight of the resulting composition. A spark ignition internal combustion engine containing appreciable combustion chamber deposits is operated using the resulting gasoline composition and a commercially available lubricant. A substantial reduction in the amount of existing deposits is observed, and with continued engine operation, accumulation of such deposits is substantially prevented.

In another specific embodiment of this invention, an additive combination composed of 80 mole percent of quinoline and 20 mole percent of anhydrous copper chromite is incorporated in a commercially available spark ignition engine lubricating oil from petroleum in an amount sufficient to constitute 3% by weight of the resulting composition. A spark ignition internal combustion engine containing appreciable combustion chamber deposits is operated using the resulting lubricant composition and a commercially available leaded gasoline. A substantial reduction in the amount of existing deposits is observed, and with continued engine operation accumulation of such deposits is substantially prevented.

The exact mechanism by which the fuel or lubricant additives of this invention reduce the accumulation of combustion chamber deposits is not definitely known. However, the fact that the heterocyclic organic compounds of the present invention in the presence of an

anhydrous copper salt do reduce the quantity of combustion chamber deposits to a remarkable and wholly unanticipated degree, is clearly evident.

I claim:

1. A composition consisting essentially of a liquid petroleum fraction for use in spark ignition internal combustion engines selected from the group consisting of gasoline and lubricating oil, and a small amount, sufficient to reduce the accumulation of combustion chamber deposits in each engines, of a mixture composed of at least 80 mole percent of a compound selected from the group consisting of pyridine, quinoline, and mixtures thereof, and up to and including 20 mole percent of an anhydrous copper salt selected from the group consisting of copper chromite and copper acetate.

2. A composition according to claim 1 wherein said liquid petroleum fraction is gasoline.

3. A composition according to claim 1 wherein said liquid petroleum fraction is lubricating oil.

4. A composition consisting essentially of gasoline and from about 0.05% to about 5.0% by weight of a mixture composed of at least 80 mole percent of a compound selected from the group consisting of pyridine, quinoline, and mixtures thereof, and up to and including 20 mole percent of an anhydrous copper salt selected from the group consisting of copper chromite and copper acetate.

5. A composition according to claim 4 wherein the said mixture is composed of pyridine and copper chromite.

6. A composition according to claim 4 wherein the said mixture is composed of pyridine and copper acetate.

7. A composition according to claim 4 wherein the said mixture is composed of quinoline and copper chromite.

8. A composition according to claim 4 wherein said mixture is composed of quinoline and copper acetate.

9. A composition consisting essentially of a petroleum lubricating oil for spark ignition internal combustion engines and from about 0.05% to about 5.0% by weight of a mixture composed of at least 80 mole percent of a compound selected from the group consisting of pyridine, quinoline, and mixtures thereof, and up to and including 20 mole percent of an anhydrous copper salt selected from the group consisting of copper chromite and copper acetate.

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