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GASOLINE COMPOSITION

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9 Claims. (Cl. 44—66)

This invention relates to an improved hydrocarbon fuel composition suitable for operation in a spark-ignition internal combustion engine, and particularly to a gasoline composition containing a unique addition agent which functions to reduce deposits in the induction system of spark-ignition engines.

In certain types of automotive engine service, rough idling and engine stalling has long been a consistent problem and has required frequent carburetor adjustments and reconditioning in order to maintain satisfactory operation. This problem of poor idling operation has been accentuated and expanded with the increased traffic density in metropolitan areas and the use of multi-throat carburetors in private automobiles. It has been determined that a primary factor in poor idling operation is an accumulation of deposits in the throttle body section of the carburetor which causes an over-rich mixture at idle and a reduction in idle speed. The accumulation of deposits in the induction system of the engine and particularly in the throttle section of the carburetor is particularly pronounced in services requiring considerable idling, such as taxicab and door-to-door delivery service. In private automobile operation, this problem is particularly emphasized in the metropolitan areas where heavy city traffic is encountered with appreciable stop-and-go driving.

The critical accumulation point for these deposits is adjacent to the throttle plate, whose position controls the air-fuel ratio. As these deposits accumulate, the air flow at idle is restricted with no change in fuel flow and a rich mixture results causing erratic idling and engine stalling. In order to compensate for the presence of these deposits, the throttle must be opened slightly by increasing the idle speed adjustment which, although allowing more air flow, automatically supplies more fuel. This requires a fuel correction by changing the idle mixture adjustment screw a compensating amount. The amount of idle adjustment required to maintain satisfactory idle performance is an indication of the deposit build-up. Furthermore, deposits will often form in the idle air passageway causing restriction which allows the manifold vacuum to draw more gasoline into the engine, again causing rich idle and engine stalling.

It has been established that the primary source of these deposits is the contaminants in the intake air of the engine when operating at idle. The greatest source of these intake air contaminants is engine blowby, which accounts for approximately one half of the deposits. Exhaust from other vehicles, dust, and other components classed as normal air pollutants contribute to the formation of deposits.

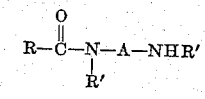
The hydrocarbon components of the gasoline fuel bear no direct relation to the formation of these deposits. Tests have been indicated that unstable or aged gasolines having a high ASTM gum or high potential gum values produce no greater deposits than stable, low-gum gasolines under comparable operating conditions.

In contrast to the periodic mechanical adjustments and engine reconditioning necessary to compensate for the presence of the carburetor and induction system deposits,

it has now been found possible to provide a fuel composition which is capable of preventing an accumulation or build-up of these deposits and will also function to reduce the existing deposits. Thus, by operating a spark-ignition engine with a fuel composition compounded in accordance with the present invention, it is possible to materially improve the idling operation of the engine and sustain this improved operation even under adverse conditions of intake air pollution.

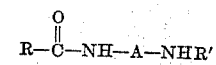
It has been discovered that the incorporation in a hydrocarbon base fuel, boiling within the gasoline boiling range, of a small amount of an oil-soluble aliphatic-substituted amino alkylene amide of a higher fatty acid containing a terminal hydroxyl group in the aliphatic substituent will provide a fuel composition which will effectively inhibit the build-up of deposits in the carburetor of an engine operated thereon. In addition, a gasoline composition containing this improving agent will substantially reduce and prevent the formation of deposits throughout the area of the air-fuel induction system of the engine.

A particular class of compounds which function as the above unique improving agents may be represented by the following general formula:



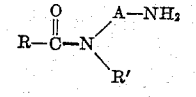
I

in which R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A in an alkylene radical and preferably an alkylene radical containing 2 to 4 carbon atoms and, in the two occurrences of R′, one is hydrogen and the other is an aliphatic radical containing 2 to 4 carbon atoms and containing a terminal hydroxyl group. It will be noted that the alternate positions of the aliphatic radical R′ in Formula I are representative of the isomeric forms of the compound, both of which are normally present to a greater or lesser extent, depending upon the reaction employed in the preparation of these compounds. These isomeric forms may be conveniently referred to as a "linear amino amide" with reference to the form:



II

and as an "amino tertiary amide" with respect to the following form:



III

wherein the symbols R and A follow the definitions given for formula I and R′ is an aliphatic radical containing from 2 to 4 carbon atoms and a terminal hydroxyl group.

The improving agents of the invention may be prepared in accordance with conventional reactions involving the formation of amides. Thus, these compounds may be prepared by condensation of a higher fatty acid, a salt or an ester thereof with N-aliphatic-substituted alkylene diamines under conditions of reaction such as to control the condensation to the elimination of one mole of water. The higher fatty acid component of the reaction may be an acid such as lauric, myristic, palmitic, stearic, linoleic or oleic acid, while the diamine reactant is preferably the N-(alkylene oxide) derivatives of an alkylene diamine. In all instances, the alkylene group is preferably an ethylene, propylene or butylene group. Other methods of preparing the amides of the invention may also be employed.

It is usually desirable to prepare or formulate the im-

proving agents of the invention in the form of a concentrate to facilitate handling problems and permit a simple blending operation in the incorporation of the additive in the fuel. In the preparation of the concentrate, the improving agent is dissolved in a hydrocarbon solvent, and particularly an aromatic solvent, in a concentration range of at least 10 percent by weight and up to about 70 percent by weight.

The improving agents of the invention, by reason of their unique effectiveness, are incorporated in the hydrocarbon base fuel in relatively small amounts and preferably within the range of about 0.0003 to 0.1 percent by weight. Although larger concentrations may be employed, their effectiveness insofar as the reduction of carburetor deposit build-up does not materially improve with additional concentration of the additive.

While the foregoing description of the improving agents of the invention are directed to the free amino amide compounds, certain modifications in composition of the agents may be employed to advantage. Thus, the salts or soaps of the amino amide with organic and inorganic acids may be used to provide added improving characteristics to the agents and to the gasoline compounded therewith. The bicarbonate salts and the salts of a substituted or unsubstituted acid of phosphorus are particularly desirable, whereas certain advantages may be gained by the use of salts of representative organic acids such as benzoic acid, acetic acid, and lauryl acid succinate, etc. When the improving agents are employed in the form of their salts and particularly as a multi-functional agent, the incorporation of the additives in the gasoline may vary over a wider range such as, for example, from 0.0003 to 1.5 percent by weight.

In addition to the subject improving agents in the fuel composition, other conventional fuel additives may be incorporated. An added factor in the reduction of deposits within the air-fuel induction system of the engine may be obtained by the incorporation, in combination with the subject improving agents, of a nonvolatile oil, such as a light mineral lubricating oil or a petroleum spray oil, which functions as a carrier for the deposits dispersed by the amino amide improving agents. Satisfactory results have been obtained by incorporating a nonvolatile oil in the range of between 0.05 to 0.5 percent by volume and have shown effectiveness in the reduction of deposits in the area of the intake ports of the engine.

The following examples are presented to illustrate the preparation and unique characteristics of representative improving agents of the invention.

Example I

100 grams (0.96 mole) of aminoethylethanolamine, 100 grams (0.34 mole) of methyl oleate, and 75 milliliters of benzene were charged to a reaction flask fitted with a 12-inch fractionating column packed with glass helices. The reaction temperature was held at 110 to 120° C. while methanol was removed through the column as a benzene azeotrope distilling at 59° C. The reaction was continued until methanol formation was complete, which required about 10 hours. A small amount of water was formed in the reaction and removed as the benzene azeotrope indicating cyclization of the product.

The reaction product was dissolved in 3 volumes of equal parts of benzene and "mixed hexanes." The solution was washed four times with 10 percent aqueous sodium chloride solution to remove excess diamine. The solvents were removed on the steam plate and a solid waxy product resulted on cooling.

Titration of a product sample with hydrochloric acid using a Beckman glass electrode pH meter indicated a mid pH of 7.7. The pH curve indicated the presence of about 10 percent of a stronger base which presumably was the cyclization product or imidazoline derivative.

The reaction product was dissolved in benzene, filtered, and solvent removed to a 115° C. pot temperature at 2 millimeters pressure. 116 grams of product having an equivalent weight of 479 were recovered. This indicates that the total amino amide content was 77 percent based on a calculated equivalent weight of 369. The neutral impurity is probably methyl oleate. A Van Slyke nitrogen determination indicated the presence of 0.26 percent primary amino nitrogen which corresponds to approximately 7 percent of the isomeric amino tertiary amide with the residual amide consisting of the linear amino amide. This product will be designated in the subsequent tests as "mixed amino amide A."

Example II

This crude amino amide product was purified by two recrystallizations from "mixed hexanes" and a final crystallization from acetone. The white, micro-crystalline product had a melting point of 68 to 76° C. The following analyses were obtained:

	Found	Calculated for the Linear Amide, $C_{22}H_{44}N_2O_2$
Percent carbon	71.38, 71.64	71.68
Percent hydrogen	12.39, 12.56	12.03
Percent nitrogen	7.76, 7.84	7.60
Equivalent weight	368	369
Tertiary amine content	0.0	0.0

This pure linear amino amide will be designated in the subsequent tests as "linear amino amide A."

Example III

For comparative purposes, the aminoethylethanolamine oleate was prepared by mixing molecular amounts of the diamine (37 grams) and oleic acid (100 grams). The salt was a sticky solid, and a 60 percent solution in toluene was prepared to facilitate handling.

Example IV

The amide bicarbonates were prepared by saturating a 25 percent solution of the amide in toluene with carbon dioxide. Three theories of water were added at the start of the carbon dioxide bubbling. A carbon dioxide stream was passed through the solution for an hour, and three additional theories of water were added three times to replace water lost by evaporation and to insure maximum carbonation. Analysis of these products follows:

	Concentration, percent	Percent CO_2
Mixed amino amide A bicarbonate	26.8	1.58, 1.49
Linear amino amide bicarbonate	28.6	1.80, 1.79

Example V

As an example of the variation in the ratio of linear amino amide to tertiary amino amide in a mixed amino amide product, 1-(hydroxyethyl)-2-heptadecenyl-2-imidazoline was hydrolyzed at room temperature to obtain a mixed amino amide product containing about 53 percent by weight of the corresponding amino tertiary amide, the remainder being the linear isomer. This product is identified in subsequent tests as "mixed amino amide B."

Example VI

An additional improving agent of the invention was the amide product obtained by hydrolyzing 1-(hydroxyethyl)-2-heptadecyl-2-imidazoline to form a mixture of the isomeric amino amides which are identified in the subsequent tests as "mixed amino amide S."

Example VII

A laboratory test was developed to correlate the formation of carburetor deposits with field experience. In this test, a glass throttle body is inserted between the float section and the cast iron throttle body of a conventional carburetor. This glass throttle body is a section of glass tubing ¼-inch thick, approximately 1¼ inches inside diameter, and about 2 inches long. About ¾-inch down from the upper edge, holes are drilled diametrically to receive a conventional metal throttle plate and shaft. The carburetor and engine employed in the test are those of a 1952 Plymouth.

The engine is started with the throttle plate in the cast iron body controlling the speed, and the throttle plate in the glass body wide open. When the engine is warmed up so that no danger of backfiring exists, the throttle in the glass body is made to assume the throttling function, and the plate in the iron body is opened wide. Two small tubes carry the idle mixture from the float section to appropriate passageways in the cast iron throttle body.

The engine is operated a total of two hours on the test gasoline at about 500 R. P. M. idle, with five full-throttle, no-load accelerations, up to a speed of about 3000 R. P. M. every 15 minutes during the test period. During each run, all of the engine blowby is piped to the engine's air cleaner atop the carburetor. At the end of the test run, the engine is shut down and the glass throttle body removed and rated in accordance with the degree of deposits on a scale ranging from 1 to 7. A rating of "1" indicates a complete lack of deposits with the throttle body clean, and a rating of "7" indicates substantially complete coverage with black, opaque deposits. This test procedure and the rating of compounded gasolines obtained thereby have found excellent correlation with actual test operations in the field.

In accordance with the foregoing test procedure, the following representative data were obtained:

Fuel	Deposit Rating [1]
Base fuel	(6.0)
Base fuel + 30 p. p. m. linear amino amide A	3.0
Base fuel + 30 p. p. m. mixed amino amide A	2.3
	2.3
	2.9
Base fuel + 30 p. p. m. mixed amino amide B	3.3
Base fuel + 30 p. p. m. mixed amino amide A bicarbonate	4.3
Base fuel + 30 p. p. m. linear amino amide A bicarbonate	4.3
Base fuel + 30 p. p. m. mixed amino amide S	3.3
Base fuel + 30 p. p. m. mixed amino amide S bicarbonate	3.0
Base fuel + 30 p. p. m. aminoethylethanolamine oleate	6.4

[1] All deposit ratings corrected to a base fuel rating of 6.0.

The base fuel employed was a commercial leaded regular gasoline which is representative of nationally-available commercial gasolines. As was previously mentioned, the hydrocarbon composition of the base fuel has a negligible effect upon the formation of carburetor deposits except as it influences the composition of the blowby, and the test results given above on the base fuel will be approximately the same, irrespective of the stability, gum content, or other characteristics of the hydrocarbon components of the fuel.

In addition to the foregoing test data, a gasoline composition compounded in accordance with the present invention was field tested in representative fleet service and private automobile operation over an extended period of time with periodic inspection of the air-fuel induction systems of the engines and in particular the carburetors. In all instances, the test fuel not only inhibited the formation of carburetor deposits, but also was effective in removing existing deposits within the carburetor and the intake manifold, and permitted continuous satisfactory operation extending beyond periods where, normally, carburetor overhauling was to be expected.

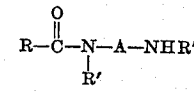
Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A gasoline composition capable of reducing deposits normally formed in the induction system of a spark-ignition engine which comprises a major proportion of a hydrocarbon base fuel boiling within the gasoline boiling range having incorporated therein a small amount, sufficient to reduce said deposits, of an oil-soluble N-aliphatic-substituted amino alkylene amide of a higher fatty acid containing a terminal hydroxyl group in the aliphatic substituent, said alkylene and said aliphatic radicals containing from 2 to 4 carbon atoms.

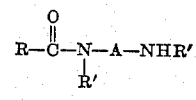
2. An improved gasoline composition which comprises a major proportion of a hydrocarbon base fuel boiling within the gasoline boiling range having incorporated therein about 0.0003 to 1.5 percent by weight of an oil-soluble N-aliphatic-substituted amino alkylene amide of a higher fatty acid containing a terminal hydroxyl group in the aliphatic substituent, said alkylene and said aliphatic radicals containing from 2 to 4 carbon atoms.

3. A gasoline composition capable of reducing deposits normally formed in the induction system of a spark-ignition engine which comprises a major proportion of a hydrocarbon base fuel boiling within the gasoline boiling range having incorporated therein a small amount, sufficient to reduce said deposits, of an oil-soluble aliphatic-substituted amino alkylene amide of the following formula:



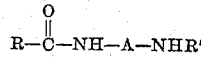
wherein R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is an alkylene radical containing from 2 to 4 carbon atoms and, in the two occurrences of R', one is hydrogen and the other is C_2–C_4 aliphatic radical containing a terminal hydroxyl group.

4. An improved gasoline composition which comprises a major proportion of a hydrocarbon base fuel boiling within the gasoline boiling range having incorporated therein about 0.0003 to 1.5 percent by weight of an oil-soluble aliphatic-substituted amino alkylene amide of the following formula:

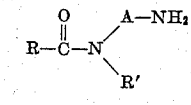


wherein R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is an alkylene radical containing from 2 to 4 carbon atoms and, in the two occurrences of R', one is hydrogen and the other is C_2–C_4 aliphatic radical containing a terminal hydroxyl group.

5. An improved gasoline composition which comprises a major proportion of a hydrocarbon base fuel boiling within the gasoline boiling range having incorporated therein about 0.0003 to 1.5 percent by weight of a mixture of amides of the following formulas:



and



wherein R is an acylic hydrocarbon radical containing 11 to 17 carbon atoms, A is C_2–C_4 alkylene radical, and R' is C_2–C_4 aliphatic radical containing a terminal hydroxyl group.

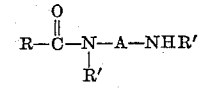
6. A gasoline composition capable of reducing deposits normally formed in the induction system of a spark-ignition engine, which comprises a major proportion of a hydrocarbon base fuel boiling within the gasoline boiling range and containing a small amount, sufficient to reduce said deposits, of bicarbonate salts of the aliphatic-substituted amino alkylene amides of claim 3.

7. A gasoline composition containing as an improving agent bicarbonate salts of the amides of claim 5.

8. The gasoline composition of claim 5 containing, in addition, 0.05 to 0.5 percent by volume of a nonvolatile oil.

9. An additive concentrate capable of incorporation into a gasoline, which comprises a hydrocarbon solvent boiling substantially within the gasoline boiling range, having dissolved therein an amount from about 10 to

about 70% by weight of an oil-soluble acyclic amino alkylene amide of the formula



wherein R is an acyclic C_{11}–C_{17} hydrocarbon radical, A is a C_2–C_4 alkylene radical, and in the two occurrences of R′ one is hydrogen and the other is a C_2–C_4 aliphatic radical containing a terminal hydroxyl group.

References Cited in the file of this patent

UNITED STATES PATENTS

2,553,183	Caron et al.	May 15, 1951
2,622,018	White et al.	Dec. 16, 1952
2,638,450	White et al.	May 12, 1953