United States Patent Office 2,922,707 Patented Jan. 26, 1960

2,922,707

AMINO AMIDE SALTS OF ORGANIC MONOCARBOXYLIC ACIDS AS ADDITIVES FOR REDUCING CARBURETOR DEPOSITS

Eddie G. Lindstrom, Martinez, and Maurice R. Barusch, Richmond, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Application February 26, 1958
Serial No. 717,571

11 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, especially, 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.

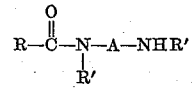
It has been established that the primary source of these deposits is the contaminants in the intake air of the engine when operating at idle. The greatest source of these intake air contaminants is engine blowby, which accounts for approximately one-half of the deposits. Exhaust from other vehicles, 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 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.

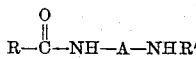
It has been discovered and claimed in the copending application Serial No. 424,243 of the applicants, that the incorporation in a hydrocarbon base fuel, boiling within the gasoline boiling range, of a small amount of an oil-soluble aliphatic-substituted amino alkylene amide, and preferably an acyclic amino alkylene amide containing an aliphatic radical, such as an alkyl radical of less than 5 carbon atoms, and preferably of 2 to 4 carbon atoms, attached to the amino group, 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:



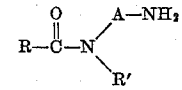
(I)

in which R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is 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 4 and fewer carbon atoms, such as an alkyl, a hydroxyalkyl, or an aminoalkyl radical. 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 4 and fewer carbon atoms, such as an alkyl, a hydroxyalkyl, or an aminoalkyl radical.

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 the condensation of a higher fatty acid, a salt or an ester thereof with N-aliphatic-substituted alkylene polyamines under conditions of reaction such as to control the condensation to the elimination of one mol 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 polyamine reactant may be a polyalkylene polyamine or an N-(alkylene oxide) derivative 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 improving 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 is directed to the free amino amide compounds, certain modifications in composition of the agents may be employed to advantage. Thus, the salts 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.

Among the various classes of organic acid salts of the amino alkylene amides which may be used as additives to gasoline in accordance with the present invention, an eminently suitable class of salts is that of salts of organic monocarboxylic acids (aliphatic, cycloaliphatic and aromatic). A particularly effective class, because of the case of preparation and effectiveness in reducing deposits, is formed by salts of saturated C_1–C_{20} aliphatic monocarboxylic acids and salts of unsaturated C_1–C_{20} aliphatic monocarboxylic acids having one double carbon-to-carbon bond in the hydrocarbon portion of their molecule. Among the salts of these latter, salts of monoalkenoic (mono-olefinic) monocarboxylic acids containing 4 or more carbon atoms are preferred, whereas among salts of saturated aliphatic (alkanoic) acids, those containing 1 to 4 carbon atoms are particularly suitable for practical applications. Formates are particularly effective and desirable as additives to gasoline according to the invention.

As illustrative examples of suitable salts, there may be mentioned the amide salts of formic, acetic, butyric, isobutyric, valeric, caproic, pelargonic, lauric, myristic, myristoleic, palmitoleic, stearic, oleic, palmitic, isovaleric, arachidic acid, and the like. Certain advantages may furthermore be gained, in appropriate cases, by using amino amide salts of mixtures of the aliphatic monocarboxylic acids and aromatic monocarboxylic acids and/or hydroxy-substituted aliphatic monocarboxylic acids. When the improving agents are employed in the form of their salts and particularly as a multi-functional agent, the concentration 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. Amounts in the range from 0.01 to 1.0 percent by weight are preferred in ordinary practical applications.

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 deposit-reducing characteristics of representative improving agents of the invention.

Example I

This example illustrates the general procedure for the preparation of the aminoalkylene amide addition to gasoline. 100 grams (0.96 mol) of aminoethylethanolamine, 100 grams (0.34 mol) of methyl oleate, and 75 ml. 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.

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 that the product was substantially amino alkylene amide.

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. The product was chosen as a typical amino amide material of the invention for the preparation of salts of organic monocarboxylic acids.

By subsequent conventional purification techniques (repeated recrystallizations), pure "linear amino amide" may be recovered from this crude amide mixture. Suitable modifications of the reaction conditions permits of varying the ratio of "linear amino amide" to "tertiary amino amide" in the crude amide mixture.

Example II

The amide propionate was prepared in a straightforward manner by intimately mixing a solution containing about 53% of mono-oleoyl amide of N-2-hydroxyethyl-1,2-ethylenediamine, 35% of an aromatic hydrocarbon thinner (boiling from 316° to 330° F.), 4% of n-butanol and 5% by weight of water, with an equivalent amount of propionic acid (based on the amide content in the concentrate). The mixture was thoroughly stirred to assure uniform reaction.

Other amide salts of aliphatic monocarboxylic acids were prepared and recovered in a similar fashion as liquid to soft wax-like products, and then tested for their deposit-reducing ability in accordance with the procedure described in the next example.

Example III

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 3,000 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.

Several representative amino amide carboxylate salts were tested as described hereinabove, and the results of the following tabulation illustrate the beneficial deposit-reducing action of these salts in accordance with the invention.

Fuel	Deposit Rating [1]
Base Fuel	(6.0)
Base fuel +30 p.p.m. of the formate of mono-oleoyl amide of N-2-hydroxyethyl-1,2-ethylenediamine (average of 4 runs)	2.9
Base fuel +50 p.p.m. of the oleate of the same amide (average 2 runs)	4.2
Base fuel +100 p.p.m. of the propionate of the same amide (average of 2 runs)	4.7
Base fuel +100 p.p.m. of the laurate of the same amide (average of 2 runs)	3.1

[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.

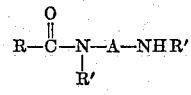
In addition to the foregoing test data, a gasoline composition compounded in accordance with the present inventoin was field tested in representative fleet service and private automobile operation over an extended period of time with periodic inspection of the air-fuel induction systems of the engines 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.

This application is a continuation-in-part of our copending application Serial No. 424,243, filed on April 19, 1954, and issued as U.S. Patent No. 2,839,372 on June 17, 1958.

We claim:

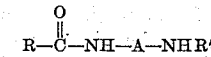
1. An improved gasoline composition which comprises a major portion of a hydrocarbon base fuel boiling within the gasoline boiling range, having incorporated therein from about 0.0003 to about 1.5% by weight of a salt of a C_1–C_{20} aliphatic monocarboxylic acid and an acyclic amino alkylene amide of the following formula:



(I)

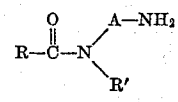
wherein R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is an alkylene radical containing 2 to 4 carbon atoms, and in the two occurrences of R′ one is hydrogen and the other is an aliphatic radical containing 4 and fewer carbon atoms and selected from the group consisting of alkyl, hydroxyalkyl and aminoalkyl radicals.

2. An improved gasoline composition which comprises a major portion of a hydrocarbon base fuel boiling within the gasoline boiling range, having incorporated therein from about 0.0003 to about 1.5% by weight of a salt of a C_1–C_{20} aliphatic monocarboxylic acid and a mixture of amides of the following formulas:



(II)

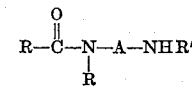
and



(III)

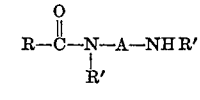
wherein R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is an alkylene radical containing 2 to 4 carbon atoms, and R′ is an aliphatic radical containing 4 and fewer carbon atoms and selected from the group consisting of alkyl, hydroxyalkyl and aminoalkyl radicals.

3. An improved gasoline composition which comprises a hydrocarbon base fuel boiling within the gasoline boiling range, having incorporated therein about 0.0003 to about 1.5 percent by weight of a salt of a saturated C_1–C_{20} aliphatic monocarboxylic acid and an acyclic 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 2 to 4 carbon atoms, and in the two occurrences of R′ one is hydrogen and the other is an aliphatic radical containing 4 and fewer carbon atoms and selected from the group consisting of alkyl, hydroxyalkyl and aminoalkyl radicals.

4. An improved gasoline composition which comprises a hydrocarbon base fuel boiling within the gasoline boiling range, having incorporated therein about 0.0003 to about 1.5 percent by weight of a salt of a C_4–C_{20} monoalkenoic monocarboxylic acid and an acyclic oil-soluble aliphatic-substituted amino alkylene amide of the following formula:

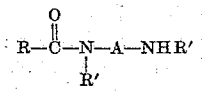


wherein R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is an alkylene radical containing 2 to 4 carbon atoms, and in the two occurrences of R′ one is hydrogen and the other is an aliphatic radical containing 4 and fewer carbon atoms and selected from the group consisting of alkyl, hydroxyalkyl and aminoalkyl radicals.

5. The gasoline composition of claim 1 containing, in addition, 0.05 to 0.5 percent by volume of a nonvolatile oil.

6. An additive concentrate capable of incorporation into a gasoline, which consists essentially of a hydrocar-

bon solvent boiling substantially within the gasoline boiling range and having dissolved therein an amount ranging from about 10 to about 70% by weight of a salt of a C_1–C_{20} aliphatic monocarboxylic acid and an oil-soluble acyclic amino alkylene amide of the formula



wherein R is an acyclic hydrocarbon radical containing 11 to 17 carbon atoms, A is 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 4 and fewer carbon atoms and selected from the group consisting of alkyl, hydroxyalkyl and aminoalkyl radicals.

7. An additive concentrate as defined in claim 6, wherein the salt of a C_1–C_{20} aliphatic monocarboxylic acid is a salt of a saturated C_1–C_{20} aliphatic monocarboxylic acid.

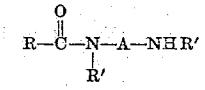
8. An additive concentrate as defined in claim 6, wherein the salt of a C_1–C_{20} aliphatic monocarboxylic acid is a salt of a C_4–C_{20} monoalkenoic monocarboxylic acid.

9. An improved gasoline composition as defined in claim 3, wherein the salt of saturated aliphatic monocarboxylic acid is a salt of a saturated C_1–C_4 aliphatic monocarboxylic acid.

10. An additive concentrate as defined in claim 6, wherein the salt of saturated monocarboxylic acid is a salt of a saturated C_1–C_4 aliphatic monocarboxylic acid.

11. An improved gasoline composition which comprises

a major portion of a hydrocarbon base fuel boiling within the gasoline boiling range, having incorporated therein from about 0.0003 to about 1.5% by weight of a salt of an unsubstituted saturated aliphatic monocarboxylic acid selected from the group of C_1–C_{20} saturated aliphatic monocarboxylic acids, the lowest member of which is formic acid and the highest is arachidic acid, and an acyclic 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 2 to 4 carbon atoms, and in the two occurrences of R′ one is hydrogen and the other is an aliphatic radical containing 4 and fewer carbon atoms and selected from the group consisting of alkyl, hydroxyalkyl and aminoalkyl radicals.

References Cited in the file of this patent

UNITED STATES PATENTS

2,014,924	Benedict	Sept. 17, 1935
2,312,082	Dietrich	Feb. 23, 1943
2,340,881	Kelley et al.	Feb. 8, 1944
2,387,501	Dietrich	Oct. 23, 1945
2,508,924	Mertens et al.	May 23, 1950
2,568,876	White et al.	Sept. 25, 1951