United States Patent Office 3,284,177
Patented Nov. 8, 1966

3,284,177

GASOLINE COMPOSITION

Eddie G. Lindstrom, Martinez, and Maurice R. Barusch, Richmond, Calif., assignors to Chevron Research Company, a corporation of Delaware

No Drawing. Filed June 19, 1963, Ser. No. 289,445
5 Claims. (Cl. 44—56)

This invention relates to improved hydrocarbon motor fuels suitable for operating internal combustion engines. Specifically it relates to gasoline compositions whose performance in spark-ignition engines is remarkably improved by addition of a comparatively small amount of a particular kind of oil-soluble aminoalkylene amide.

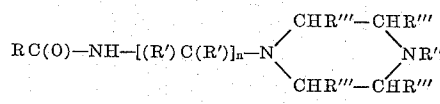
In the past a number of materials have been proposed, tried and used as additives to gasoline for the purpose of substantially reducing, if not entirely preventing, formation of deposits in the induction system of spark-ignition engines, and particularly in the throttle body section of the carburetor, in the intake manifold, in the ports, and on the underside of the valves. Some of these materials have been applied with success, others not only brought about new difficulties in engine operation, but in fact were found to be impractical.

A typical instance of such difficulties is observed in the use of many aminoalkylene amides proposed as additives to gasoline. Thus, the mono-oleoyl amide of N-2-hydroxyethyl-1,2-ethylene diamine, a very effective additive indeed with respect to the removal of carburetor deposits and induction system deposits in general, has been observed, while being introduced into gasoline by conventional blending techniques in the presence of water, to produce haze due to emulsification. At higher concentrations, in particular, on blending the aforementioned amide into gasoline in the presence of water, a stable emulsion is formed, and considerable time is required for its disappearance on standing. To illustrate, at 60 p.p.m. of the amide, the gasoline becomes bright again within a time ranging from several minutes to several hours, depending on the kind of gasoline, the nature of the water present, and the degree of agitation or stirring. At higher concentrations the prospect of a rapid disappearance of haze and breakdown of the emulsion wanes considerably; so that, for instance, at 250 p.p.m. concentration of the amide in gasoline, a stable emulsion persists, taking an unduly long time—a matter of several days in many instances—to separate into two distinct phases: an upper bright gasoline phase and a lower clear aqueous phase at the bottom of the blending or storage tank.

This extended time to settle the gasoline to brightness is a troublesome disadvantage in the blending and transportation of gasoline under conditions where water is present as is frequently the case in such operations. Because of the outstanding ability of amino-amides to remove and prevent intake system deposits, to prevent stalling due to carburetor icing, and to protect against corrosion, the search has continued for aminoamides that would be free of the tendency to promote emulsification and haze, and still would possess the high degree of detergency, anti-stalling activity and anti-rust protection, characteristic of most aminoamides.

A new class of oil-soluble aminoalkylene amides has now been found, the members of which not only act as effective deposit-reducing additives to gasoline, but at the same time are practically free of emulsion-forming tendencies of other known oil-soluble amides. In all events, even though an emulsion may be formed with the particular amides contemplated by the present invention for use in gasoline to reduce engine deposit formation, the time of phase separation of such an emulsion is short.

These particular oil-soluble aminoamides may be represented by the following general formula:



In this formula R is an acylic hydrocarbon radical of 11 to 21 carbons, R′ is selected among hydrogen, methyl and ethyl radicals, *n* is an integer from 2 to 4, R″ is a radical selected among hydrogen, C_1–C_4-alkyl, C_1–C_4-hydroxyalkyl and C_1–C_4-aminoalkyl radicals, and R‴ is selected among hydrogen, methyl and ethyl radicals.

When the aminoamides having the aforeshown structure are dissolved in gasoline in amounts ranging from about 0.0002 to about 1.5% by weight, and preferably from about 0.001 to about 1.0% by weight, deposit-forming tendencies of the so-treated gasoline are substantially reduced if not completely eliminated. At the same time, problems due to emulsion formation are avoided. Any emulsion that may form as a consequence of the presence of water in the gasoline blending tank rapidly breaks, with water separating at the bottom of the tank. In actual practice, the concentrations of the aminoamide additive of this invention, effective in reducing substantially deposit formation in the intake system, are usually chosen in the range of from about 0.001 up to about 0.1% by weight. This corresponds to from about 10 to about 1000 parts of the amide per one million parts by weight (abbreviated as p.p.m.) of the gasoline. At these use concentrations, phase separation, with water dropping out to the bottom of the tank and the upper gasoline phase resuming a clear appearance, ordinarily occurs in less than an hour, often even in a few minutes.

The exact reason why the particular oil-soluble aminoamides of the structure shown hereinbefore display desirable good water reaction properties is not completely understood, but it is believed that this improvement is in some way due to the replacement, either of all or at least of most of the aminohydrogens in the molecule of these amides with monovalent and divalent hydrocarbon radicals, i.e., with alkyl or alkylene groups.

The aforementioned aminoalkylene amides may be prepared as follows: an excess of a suitable alkylene diamine or triamine is reacted with an aliphatic monocarboxylic acid, e.g., oleic acid, at 185–200° C., for some 5 to 6 hours, removing the water of reaction continuously by azeotropic distillation, e.g., with a small amount of toluene in the system, and a suitable colmun and water separator. Titration of small samples of the reaction mixture with a base serves to indicate the amount of amine oleate still present. In some cases more than 6 hours may be required to convert completely the aliphatic acid to the amide. On completing the reaction, the excess amine reactant and the reflux medium, such as toluene, are removed by vacuum stripping, and the product is analyzed, infra-red absorption analysis additionally confirming the exact nature of the final amide.

The relative freedom of the gasoline containing the aminoamide additives from the formation of stable, persisting emulsions and haze in the presence of water has been demonstrated in the "Water Reaction" or "Water Tolerance" test (a modification of ASTM D–1094 Test), a simple but effective and persuasive procedure. It consists in shaking vigorously for one minute 80 milliliters of gasoline with 20 milliliters of distilled water in a 100-milliliter graduate and noting the time required for the separation of the shaken mixture into two distinct bright phases.

Example I

In the test series of this example 1-(2-oleamidoethyl) piperazine, i.e., the mono-oleoylamide of N-aminoethyl piperazine, was added to commercial leaded motor gasolines of both regular and premium grades, so as to provide a concentration of 250 p.p.m. of the amide in the gasolines.

The resulting amide-containing fuels were tested in accordance with the aforedescribed water reaction test technique. In all instances the emulsion was found to disappear, and two substantially haze-free phases—an upper gasoline phase and a lower water phase—became separated in about 30 minutes.

Example II

In this case a batch of similar commercial leaded motor gasolines, again of both regular and premium grades, were treated with an oil-soluble aminoamide in which the amino hydrogens have been replaced with alkylene (ethylene and hydroxyethyl) groups. This was 1-(2-hydroxyethyl)-4-oleamidopiperazine, i.e. the mono-oleoyl amide of hydroxyethylpiperazine. In one series of tests a concentration of 60 p.p.m. of the amide was provided. In the other series a concentration of 250 p.p.m. of the oleic acid amide of hydroxyethylpiperazine was introduced into the fuel to be tested for water tolerance. At 60 p.p.m. of the amide the gasoline phase brightened in 30 seconds with some water droplets still clinging on the sides of the graduate. At 250 p.p.m. the emulsion disappeared completely and the gasoline became bright in as little as two minutes in each of the 6 tests in the series.

Many other results of the water tolerance test of gasoline containing the amides the of the general structure shown hereinabove can be adduced; however, it is believed that the aforegiven examples illustrate the improvement achieved according to the invention.

Gasolines treated with the aminoamides of the present invention have also been tested in the procedure known as the "Glass Throttle Body Test" to demonstrate their effectiveness in removing and preventing engine deposits, and, in particular, those deposits occurring in the throttle body section of a carburetor. In this test, a glass throttle body is inserted between the float section and the cast iron throttle body of a conventional carburetor. The throttle plate and shaft are removed from the cast iron throttle body and the shaft holes are brazed shut. The glass body is a section of glass tubing ¼" thick, about 1¼" in diameter and about 2" long. At a distance of about ¾" from the upper edge, holes are drilled diametrically in this glass tubing to receive a conventional metal throttle plate and shaft. The carburetor and engine in this instance were those of a 1954 Plymouth automobile engine. Two small tubes carry the idle fuel mixture from the float section to appropriate passages in the cast iron throttle body.

The engine is operated a total of one hour on a base fuel (gasoline), without any detergent additive, at about 500 r.p.m. idle with full-throttle, no-load accelerations up to a speed of about 3000 r.p.m. every fifteen minutes, the engine blowby being piped to the engine's air cleaner above the carburetor. After one hour the engine is changed to operation on the same base fuel but with a specified amount of the deposit-removing additives. Before starting this second phase of the test, the glass throttle body is photographed to record the deposit appearance after the first hour. The glass is then reinstalled with deposits in place. The engine is then run for four hours, without returning blowby to the air cleaner. At the end of the run, the engine is shut down, the glass throttle body is removed, and the percentage of deposits removed is determined. This two-stage procedure is called the "clean-up" procedure.

A variation of the glass throttle body test is the so-called "dirty-up" procedure; here the test begins with a clean glass throttle body (rating of 1) and is continued for four hours on gasoline containing the test additive, and the extent of deposits is rated from 1 to 6. A rating of 6 corresponds to the deposits equivalent to those obtained in a test lasting the same number of hours (4) on a base gasoline containing no amide or detergent. In this procedure the engine blowby is piped to the engine's air cleaner above the carburetor during the entire test.

In the following illustrative example the "clean-up" procedure was used.

Example III

The engine was run on a regular grade currently available commercial leaded automotive gasoline. The glass throttle body was first "dirted-up" by running the engine as described on the base gasoline, whereupon it was run for four hours on the same gasoline containing 30 p.p.m. of the oleamidoethyl piperazine of Example I. At the completion of the test, the glass throttle body was removed and the extent of "clean-up" rated. It was observed that as much as 50% of the initially present deposits had been removed.

These laboratory results have been further confirmed in actual driving tests on the road.

Another advantage of the amide additives of the present invention resides in that they tend to reduce the occurrence of engine stalling due to ice formation in the carburetor. Consequently, when present in gasoline in the amounts from 2 to 1500 p.p.m., and preferably from 10 to 10000 p.p.m., they assure improved operation of the engine under cool and humid ambient conditions.

Confirmation of this valuable property of the particular aminoalkylene amides of the invention has been obtained in several series of tests carried out as follows:

Example IV

A Plymouth L-head 6-cylinder engine was set up and operated without load in the laboratory, with the carburetor thermally insulated from the engine. In each series, the intake air was maintained at 40° F. and 100% relative humidity. The engine was operated at fast idle (2200 r.p.m.) for 30 seconds and then was returned to slow idle conditions for 15 seconds.

The base gasoline was a premium grade commercial gasoline with the mid-point of 185° F. It received 280 p.p.m. of 1-(2-oleamidoethyl) piperazine before the beginning of test runs. The behavior of the engine during the slow idle period was used as a measure of the effectiveness of the amide additive in preventing carburetor icing.

The average number of engine revolutions during slow idle with the amide additive in the fuel was compared with the number of revolutions with the base gasoline alone under identical icing conditions and also under non-icing conditions. The number of idle revolutions was used as a criterion, because this number depends on both the length of time the engine was able to continue idling and how well it idled during this time. An anti-icing rating was calculated, rating "0" denoting no improvement in idling over the base gasoline alone under icing conditions and rating "100" denoting idling performance equal to that of the base gasoline under non-icing conditions. The average "anti-icing" rating was 70, the extremes ranging from 64 to 76.

Also effective in reducing the engine stalling due to carburetor icing are salts of the particular aminoalkylene amides of the invention with mono- and dialkylphosphoric acids containing from 8 to 20 carbon atoms in each of their alkyl radicals.

Thus, salts of the same 1-(2-oleamidoethyl) piperazine of the preceding example with monotridecyl phosphoric acid and with an equimolar mixture of mono and ditri-

decylphosphoric acids, when tested in the above-described procedure at 16 p.p.m. (parts per one million parts of base gasoline), respectively, were found to be effective anti-icing agents.

Likewise, the aminoamides of the invention exercise desirable action in minimizing ferrous corrosion which takes place upon contact of metal parts of the engine with gasoline in the presence of moisture or water. This corrosion protection is also available in fuel distribution systems, i.e., in preventing rusting of tanks, pipelines and tankers.

Examples of other operative aminoalkylene amides of the present invention are

1-(2-dodecanamidoethyl)piperazine;
1-methyl-4-(2-octadecanamidoethyl)piperazine;
1-(3-linoleamidopropyl)piperazine;
1-(2-hydroxyethyl)-4-(2-tetradecanamidoethyl)piperazine;
1-(2-aminoethyl)-4-[2-(9-methyl)octadecanamidopropyl]piperazine;
1-(2-docosanamidoethyl)-4-(2-hydroxypropyl)piperazine;
2,6-dimethyl-1-(2-oleamidoethyl)piperazine;
1-(2-oleamidopropyl)piperazine.

While the foregoing description of the gasoline compositions of the present invention is directed to the action of the free aminoamides of the structure hereinabove specified, certain modifications of this structure may be employed to advantage. Accordingly, salts of these amides with organic and inorganic acids may be effectively employed as deposit-reducing additives, anti-stall (anti-carburetor icing) additives and corrosion inhibitors. Among these salts particularly suitable are salts of organic hydrocarbon monocarboxylic acids, most desirably salts of saturated C_1–C_{20} aliphatic monocarboxylic acids. Likewise, various salts of phosphorus-containing acids, in particular, oxyphosphorus acids and acids having one or two organic (hydrocarbon) radicals bound to the central phosphorus atom, such as phosphoric acids, phosphonic acids, alkyl phosphoric acids and alkyl phosphonic acids, may be effectively employed to reduce engine deposits and to minimize stalling in cool, moist weather.

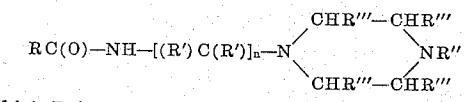
Commonly it is desirable to prepare and distribute the amides of the present invention and/or their corresponding salts in the form of concentrates to facilitate handling and to permit a simple mixing operation when introducing the additive into gasoline. To form these concentrates, gasoline-compatible organic solvents boiling substantially in the gasoline range, such as a hydrocarbon solvent or an alcohol, may be used. Particularly effective hydrocarbon solvents are aromatic solvents, whereas among the alcohols there may be mentioned, in particular, C_3–C_6 aliphatic alcohols, such as isopropanol, n-butyl alcohol, methylisobutylcarbinol, and the like. The additive may be dissolved in the corresponding solvents within a wide range of concentrations from at least 10 up to about 70% by weight.

In addition to the amides or their salts the gasoline compositions of the present invention can contain conventional additives in equally conventional minor amounts, provided these additives do not interfere with and detract from the advantages imparted by the presence of the amides. These commonly used additives are lead alkyl anti-knock agents, e.g., tetraethyl lead, lead scavengers, dyes, sparkplug-fouling inhibitors, oxidation inhibitors, etc. Quite often an added improvement is obtained by incorporating into such gasolines a non-volatile oil, such as a light mineral lubricating oil or a petroleum spray oil, to function as a carrier for the engine deposits removed by the amides in accordance with this invention. These carrier oils may be incorporated in amounts ranging from about 0.05 to about 0.5% by volume.

In concluding this description, it is emphasized that the invention is not limited by the particular examples and/or by the recitals of the illustrative materials, and that many modifications which come within the spirit and scope of the invention, as defined in the following claims, are intended to be included therein.

We claim:

1. A hydrocarbon motor fuel for use in spark-ignition internal combustion engines, which comprises a major proportion of gasoline and in combination therewith, as an additive effective in reducing the deposits normally formed in the induction system of spark-ignition engines, a small amount of from about 0.0002 to about 1.5% by weight of an oil-soluble aminoalkylene amide having the general formula

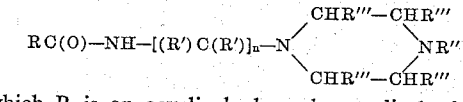


in which R is an acyclic hydrocarbon radical of 11 to 21 carbon atoms, R′ is selected from the group consisting of hydrogen, methyl and ethyl radicals, *n* is an integer from 2 to 4 and R″ is a radical selected from the group consisting of hydrogen, C_1–C_4-alkyl, C_1–C_4-hydroxyalkyl and C_1–C_4-aminoalkyl radicals, and R‴ is selected among hydrogen, methyl and ethyl radicals.

2. A hydrocarbon motor fuel as defined in claim 1, wherein said aminoalkylene amide is present in the amount from about 0.001 to about 1.0% by weight.

3. A hydrocarbon motor fuel as defined in claim 1, wherein said additive effective in reducing engine deposits is present in the form of a salt of said aminoalkylene amide selected from the group consisting of salts of phosphorus-containing acids and hydrocarbon monocarboxylic acids.

4. An additive concentrate intended for incorporation into a gasoline, consisting essentially of an organic, gasoline-compatible solvent boiling substantially in the gasoline range and selected from the group consisting of hydrocarbon solvents and C_3–C_6 aliphatic alcohols, and, dissolved in said organic solvent, from about 10 to about 70% by weight of an oil-soluble aminoalkylene amide having the general formula



in which R is an acyclic hydrocarbon radical of 11 to 17 carbon atoms, R′ is selected from the group consisting of hydrogen, methyl and ethyl radicals, *n* is an integer from 2 to 4, and R″ is a radical selected from the group consisting of hydrogen, C_1–C_4-alkyl, C_1–C_4-hydroxyalkyl and C_1–C_4-aminoalkyl radicals and R‴ is selected among hydrogen, methyl and ethyl radicals.

5. An additive concentrate as defined in claim 4 wherein said aminoalkylene amide is 1-(2-oleamidoethyl) piperazine.

References Cited by the Examiner

UNITED STATES PATENTS

2,922,708 1/1960 Lindstrom et al. ------ 44—58

DANIEL E. WYMAN, *Primary Examiner.*

W. J. SHINE, *Assistant Examiner.*