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3,399,982

DETERGENT GASOLINE CONTAINING STRAIGHT-CHAIN TERTIARY ALKYL ATTACHED PRIMARY AMINES

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3 Claims. (Cl. 44-69)

ABSTRACT OF THE DISCLOSURE

Leaded detergent gasoline composition containing straight-chain tertiary alkyl attached primary amines and alkyl orthophosphates thereof in which the tertiary alkyl group contains 12 to 30 carbon atoms.

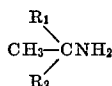
This invention relates to detergent gasolines. More particularly, the invention is concerned with gasolines containing detergent additives which substantially reduce carburetor deposits in spark ignition internal combustion engines.

In the operation of spark ignition internal combustion engines there have been problems of rough idling and engine stalling, and carburetor adjustments and reconditioning are often necessary to provide satisfactory service. It is found, particularly in the case of stop-and-go driving in metropolitan areas, that such stalling and idling problems are more frequent, especially in the case of multithroat carburetors of the type employed in many present-day automobiles. It has been determined that the rough idling and engine stalling are primarily due to the accumulation of deposits in the throttle body section of the carburetors. As the deposits build up, the amount of air for given amount of fuel is impeded and greatly reduced, and the air-fuel mixture is overly rich for satisfactory engine operation. Frequent adjustments of the carburetor are needed to overcome the effect of this deposit buildup, and finally it becomes necessary to replace the carburetor or give it a complete overhaul.

Various additives have been suggested for use in gasoline to cut down on the buildup of carburetor deposits. However, such additives have usually suffered certain disadvantages as to overall effectiveness, and the search has continued for more suitable compositions.

It has now been found that deposits in the carburetors of spark ignition internal combustion engines are substantially reduced by an improved detergent gasoline composition comprising a major proportion of a hydrocarbon base fuel boiling in the gasoline boiling range and from about 0.0001 to 1.5% by weight of straight-chain tertiary alkyl primary amine having from about 12 to 30 carbon atoms in the alkyl group.

The straight-chain tertiary alkyl primary amines of the gasoline compositions of the invention are characterized by the formula



in which one of the branches, R_1 , is a straight-chain alkyl group of from 1 to 4 carbon atoms and the other branch, R_2 , is a straight-chain alkyl group of 6 to 28 carbon atoms. Such amines may also be described as aminoalkanes, that is, 2-methyl-2-aminoalkane, 3-methyl-3-aminoalkane or 4-methyl-4-aminoalkane in which the alkane is straight-chain and contains 11 to 29 carbon atoms.

The straight-chain tertiary alkyl primary amines of the

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gasoline compositions may also be present in the form of their alkyl orthophosphoric acid salts. In such salts, the alkyl groups of the orthophosphoric acid contain from 8 to 18 carbon atoms and are preferably derived from branched-chain primary alkyl acid esters, also known as acid mono- and dialkyl esters of orthophosphoric acid or alkyl mono- and dihydrogen phosphates. In these phosphorus compounds, one or two of the three available acidic hydrogens or orthophosphoric acid have been replaced by alkyl groups of 8 to 18 carbon atoms, the remaining acidic hydrogens thus being reactive to form the salts of the straight-chain tertiary alkyl primary amines.

The alkyl orthophosphoric acids and mixtures of them are conveniently obtained by reacting an alcohol having the desired alkyl group with phosphorus pentoxide. Ordinarily at least 2 moles of the alcohol will be used for each mole of the phosphorus pentoxide, but preferably from about 3 to 4 moles of alcohol per mole of phosphorus pentoxide is employed. In a particularly suitable mixture, alcohol and phosphorus pentoxide are reacted in a molar ratio of about 3:1 to give monoalkyl esters and dialkyl esters in proportions of about 40 to about 60 mole percent of each. Mixtures of alcohols are also desirable. A particular class of suitable alcohols includes those obtained by the Oxo process from branched-chain olefins, carbon monoxide and hydrogen, the branched-chain olefins themselves being suitably derived from polymerization of low molecular weight unsaturated hydrocarbons, such as propylene and butylene.

The salts of the amines and the alkyl orthophosphoric acids are prepared by reacting the amine and acid using conventional procedures. One equivalent of amine is ordinarily reacted with one equivalent of the acid phosphate to produce the substantially neutral salt. Ordinarily, the mole ratio of amine to alkyl orthophosphoric acid will range from about 1:0.9 to about 1:0.4. Illustrative alkyl groups include the octyl, nonyl, decyl, dodecyl, tridecyl, pentadecyl, heptadecyl and octadecyl groups, particularly effective examples of which are the salts of the straight-chain tertiary alkyl amines and 56.7/43.3 weight percent mixtures of mono- and di(tridecyl)orthophosphoric acid.

Although the straight-chain tertiary alkyl primary amine is satisfactorily employed in any amounts sufficient to impart detergency to the gasoline composition, it is preferred that it be present in the gasoline in amounts from about 0.0001 to 1.5% by weight. For present purposes, amounts in the range from about 0.003 to about 0.03% by weight are most satisfactory from the standpoint of effectiveness and cost.

To facilitate handling, it is customary to formulate the improved detergent additives of this invention as concentrates. Since the additives are unusually stable and possess good solubility characteristics, these concentrates represent a particular embodiment of the invention. In the preparation of the concentrate, the detergent additive is dissolved in a suitable hydrocarbon or alcohol solvent boiling in the range from about 150° to 400° F., preferably an aromatic hydrocarbon solvent such as benzene, toluene, xylene, or higher boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, as well as mutually compatible mixtures of such alcohols and hydrocarbon solvents, are also suitable for use with the detergent additive. The amounts of detergent additive in the concentrate are ordinarily at least 10% by weight, and may vary up to about 70% by weight.

In addition to the detergent additive, other fuel additives may be used in the gasoline compositions of the

invention. The deposit-reducing benefits are obtained in combination with lead alkyl antiknock agents, such as tetramethyl lead or tetraethyl lead. Such antiknock agents are ordinarily employed in amounts sufficient to enhance the octane number, usually from about 0.5 to 4 ml./gal.

A nonvolatile light mineral lubricating oil, such as petroleum spray oil, is also a suitable additive for the gasoline compositions of the invention. These oils are believed to act as a carrier for dispersed deposits. They are employed in amounts from about 0.05 to 0.5% by volume based on the final gasoline composition.

The straight-chain tertiary alkyl primary amine detergent additives are available from a number of sources. For example, they may be derived from the telomers of ethylene and a secondary alkyl amine, such as isopropyl amine. When prepared in this way, they are mixtures of homologous compounds. Such straight-chain tertiary alkyl amines and their method of preparation are more fully described in copending application Ser. No. 373,517, filed June 8, 1964, by Donald J. Anderson. Suitable straight-chain tertiary alkyl amines in general are also available from unsaturated aliphatic hydrocarbons by the so-called "Ritter" reaction as set forth in Ritter U.S. Patent No. 2,573,673, issued Oct. 30, 1951.

The preferred telomer amines have a methyl group as R_1 in the above structural formula as already mentioned. Such amines are termed 2-methyl-2-aminoalkanes, in which the alkane is a straight-chain preferably containing 11 to 29 carbon atoms.

Other suitable telomer straight-chain tertiary alkyl primary amines are obtained by reacting a secondary alkyl primary amine having from about 3 to about 20 carbon atoms in the alkyl group with an olefin, such as ethylene, propylene, isobutylene, etc., ethylene being preferred. Suitable secondary alkyl primary amines are characterized by an alpha hydrogen and are generally available in the art, including isopropyl amine, 2-aminobutane, 3-aminooctane, 2-aminopentadecane, mixtures of 2-, 3- and 4-aminoalkanes containing from 15 to 20 carbon atoms as obtained by amination of thermally cracked wax olefin mixtures and the like, as well as secondary cycloalkyl primary amines, such as cyclohexyl amine. The straight-chain tertiary alkyl primary amines derived from these secondary alkyl primary amines have the general formula



in which R_2 is as described above, and R_1 and R_3 are alkyl groups or cycloalkyl groups characteristic of the aforementioned secondary amines.

The improved gasoline compositions containing the straight-chain tertiary alkyl primary amines in accordance with the invention provide excellent detergent performance compared to gasoline compositions containing other alkyl amines. Such detergent properties are determined by the generally accepted method of appraising the gasoline compositions in the "glass throttle body" engine test, which has been especially developed to observe and to evaluate deposits in the carburetors of typical gasoline induction systems.

In the Glass Throttle Body Test, a 6-cylinder Plymouth automobile engine is set up in the laboratory and is provided with a conventional carburetor by the introduction of a removable glass throttle body section between the carburetor body and the original cast iron throttle body. This glass throttle body is a section of glass tubing $\frac{1}{4}$ " thick, of approximately $1\frac{3}{4}$ " outside diameter and about $1\frac{3}{4}$ " long. An automatic cycler or timer, which consists of a constant-speed electric motor and a magnetic clutch, is provided for insuring cyclic operation of the engine with 7.5 min. idle periods followed by five accelerations to 2000 r.p.m. Crankcase fumes are vented to the carburetor air inlet, since these fumes are now

known to be responsible for the larger portion of the deposits. The engine is started up, using leaded gasoline containing a conventional amount of tetraethyl lead (1.5 ml./gal.), but no surface-active additives of any kind. It is run for 4 hours with the blowby fumes being drawn in at the air intake. The engine is then stopped, the glass body is removed, and both sides of its are photographed. Thereupon the dirty glass body is again installed on the engine and run for one hour on the same leaded base gasoline compounded with the detergent-action additive. This time the blowby fumes are not piped to the carburetor. After the run is completed, the glass throttle body is again photographed, and the effectiveness of the detergent-containing gasoline (the percentage of cleanup of deposits) is visually estimated.

In these tests, representative straight-chain tertiary alkyl primary amines, namely, the 2-methyl-2-aminoalkanes as described above, were evaluated in the gasoline composition at a concentration of 0.003% by weight. The results are given in the following table.

TABLE

Amine, average composition:	Cleanup, percent
(A) 2-methyl-2-aminohexadecane	74
(B) 2-methyl-2-aminononadecane	62
(C) 2-methyl-2-aminooctadecane	67

Substance A is the telomer of ethylene and isopropyl amine containing an average of 17 carbon atoms. It has a molecular weight of 244 and boils from 100° to 150° C. at 2 mm. Hg pressure.

Substance B is the telomer of ethylene and isopropyl amine containing an average of 20 carbon atoms. It has a molecular weight of 301 and boils from 150° to 175° C. at 2 mm. Hg pressure.

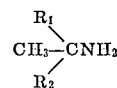
Substance C is the telomer of ethylene and isopropyl amine containing an average of 29 carbon atoms. It has a molecular weight of 406 and boils from 190° to 295° C. at 1 mm. Hg pressure.

From the above tests, it will be noted that the 2-methyl-2-aminoalkanes give excellent carburetor throttle body cleanups of as high as 74%. By comparison, a commercial detergent-action aminoalkylene amide prepared from oleic acid and hydroxyethyl ethylenediamine at the same concentration gave 55% cleanup.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

I claim:

1. An improved detergent gasoline composition comprising a major proportion of a hydrocarbon base fuel boiling in the gasoline boiling range, lead alkyl antiknock agent in amount sufficient to enhance the octane number and from about 0.0001 to 1.5 percent by weight of a straight-chain tertiary alkyl attached primary amine having from about 12 to 30 carbon atoms in the alkyl group of the formula:



in which one of the branches, R_1 , is methyl and the other branch, R_2 , is a straight-chain n-alkyl group of 6 to 28 carbon atoms.

2. The composition of claim 1 in which the amine is derived by telomerization of ethylene and isopropyl amine and contains 15 to 20 carbon atoms per molecule.

3. An improved detergent gasoline concentrate consisting essentially of a hydrocarbon solvent and from 10 to

75 percent by weight of the straight-chain tertiary alkyl
primary amine of the gasoline composition of claim 1.

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