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3,139,330

MOTOR FUEL

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12 Claims. (Cl. 44—63)

The present invention relates to an improved motor fuel composition for spark-ignition internal combustion engines, and more particularly to such motor fuel compositions containing an additive which functions to inhibit or to reduce deposits in the induction system of spark-ignition internal combustion engines.

Rough idling and engine stalling requiring frequent carburetor adjustments and reconditioning have been problems in certain kinds of automotive engine service. These problems have been accentuated with increased traffic in congested areas and the use of multi-throat carburetors in private passenger cars. 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 rate of deposit build-up. Furthermore, deposits will often form in the idle air passageway causing restriction which allows manifold vacuum to draw more gasoline into the engine, again causing rich idle and engine stalling.

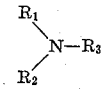
It has been established that the primary sources of these deposits is the contaminants in the intake air of the engine when operating at idle. The greatest source of these intake air contaminants is engine blow-by, which accounts for approximately one-half of the deposits. Exhaust from other vehicles,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

It is accordingly an object of the present invention to provide a motor fuel composition for spark-ignition internal combustion engines which will inhibit or alleviate deposits in the induction system of such engines. Another object of the invention is to provide a motor fuel composition for spark-ignition internal combustion engine which will prevent rough idling and stalling of such engines due to the accumulation of deposits in the induction system of such engines. Still another object of the invention is to provide a motor fuel composition which will remove deposits from the induction system of spark-ignition internal combustion engines. A further object of this invention is to provide an additive concentrate, which when added in small amounts to a motor fuel for spark-ignition internal combustion engines will inhibit or reduce deposits in the induction system of such engines. It is also an object of this invention to provide a method of removing blow-by deposits accumulated in the induction system of spark-ignition internal combustion engines. Further, objects and advantages of the herein described invention will become apparent from the following description thereof.

I have previously proposed mixtures of ingredients comprising a substituted cyclic propylene urea and a hydroxyalkyl 3-(N-alkylaminopropylcarbamate or hydroxyalkyl 3-(N-alkenylamine)-propylcarbamate for use in the inhibition or reduction of deposits in the induction systems of spark-ignition internal combustion engines. The mixture is more completely described in U.S. Patent No. 2,991,162, filed May 11, 1960, issued July 4, 1961.

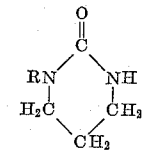
In accordance with the present invention I have provided a new mixture of ingredients and in the present invention the foregoing objects are attained by incorporating in a motor fuel for spark-ignition internal combustion engines, particularly in a hydrocarbon fuel in the gasoline distillation range, a small amount, sufficient to inhibit or reduce deposits in the induction system of such engines, from about 0.0005% to about 0.5% preferably from about 0.001% to about 0.01%, based on the hydrocarbon fuel, of a mixture consisting essentially of (1) a secondary or tertiary aliphatic amine as hereinafter defined and (2) an N-alkyl or N-alkenyl substituted propylene urea.

Suitable aliphatic amines are those secondary or tertiary aliphatic amines having the formula



wherein R_1 and R_2 are each acylic aliphatic radicals, i.e., alkyl or alkylene radicals, having from about 8 to about 24 carbon atoms and R_3 is selected from the class consisting of hydrogen and an acyclic aliphatic radical having from 1 to 24 carbon atoms. R_1 and R_2 are preferably C_{10} to C_{20} alkyl radicals and R_3 is preferably hydrogen or a C_{10} to C_{20} alkyl radical.

Suitable ureas are those having the general formula



in which R is an acyclic aliphatic radical having from about 8 to about 32 carbon atoms, and is preferably an alkyl group of from about 10 to about 20 carbon atoms derived from a fatty acid or mixed fatty acids.

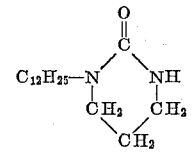
Although either the amine or urea may be used in excess in the mixture, e.g., in weight ratios of from 1:10 to 10:1, the two ingredients or agents may more advantageously be used in weight ratios of from 2:1 to 1:2, either ingredient based on the other. The preferred use is in the ratio of about 1:1.

Illustrative of suitable secondary and tertiary amines are: trilauryl amine, dicoco amine, diisooctyl amine, dicapryl amine, tricaprylyl amine, methyl di (hydrogenated tallow) amine, methyl dilauryl amine, tri (hydrogenated tallow) amine, dioleyl amine, methyl dilinoleyl amine, disoybean amine, dieicosyl amine, tripentadecyl amine, didecadienyl amine, tridocosyl amine, lauryl dilinolenyl amine, butyl dilauryl amine, tricapryl amine, octadecyl dicaprylyl amine, tricoco amine, tristearyl amine, and the like. As used herein, the terms "tallow," "coco," "soybean" and the like represent hydrocarbon groups, usually alkyl groups, derived from sources indicated by the nomenclature of the groups. For example, the "tallow," "coco" and "soybean" groups are derived from tallow

fatty acids, coco fatty acids, and soybean fatty acids, respectively, and are groups which may correspond to R_1 and R_2 in the above structural formula. The coco groups are derived from mixtures of capric, lauric, palmitic, myristic, oleic and linoleic acids predominating in palmitic, lauric and myristic acids. The coco groups, thus include alkyl and alkenyl groups in the C_{10} to C_{18} range and predominate in C_{12} to C_{16} alkyl groups. The tallow groups are derived from mixtures of myristic, palmitic, stearic and oleic acids, i.e., tallow fatty acids, predominating in stearic and palmitic acids. Thus, the tallow groups are mixtures of alkyl and alkenyl groups in the C_{14} to C_{18} range and predominating in C_{16} and C_{18} alkyl groups. The soybean groups are derived from soybean fatty acids including acids ranging in the same approximate carbon atom ranges as the above-described mixtures of acids.

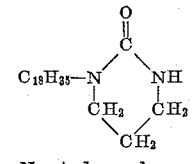
Suitable cyclic ureas are illustrated by the following examples:

(1)



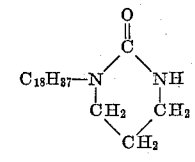
N-dodecylpropylene urea

(2)



N-oleyl or N-octadecenylpropylene urea

(3)

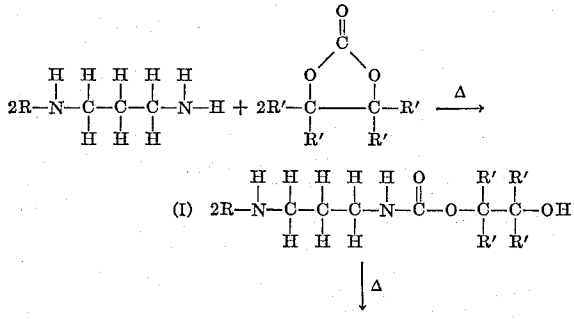


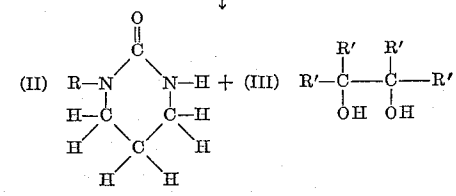
N-stearyl or N-octadecylpropylene urea

While combinations of the described amines and cyclic ureas in the defined ratios are effective, they are not all necessarily equivalent in their effectiveness, since the specific activity of such mixtures may vary to some extent depending upon the severity of conditions during use and other factors.

In the preparation of the motor fuel composition, the amine and the urea can be added to the fuel individually in the defined amounts and proportions, the amine and the urea can be pre-admixed in the desired ratio and the mixture added to the fuel, or the mixture of carbamate and urea prepared in situ can be added to the fuel.

The cyclic urea can be conveniently prepared in situ by reacting molar proportions of an N-alkyl or N-alkenyl-1,3-propylene diamine and an alkylene carbonate at a temperature of from about 100° C. or 150° C. to about 250° C. for a time sufficient to give the cyclic urea as the reaction product. The reaction is represented by the equation





wherein R is as above described and R′ represents hydrogen or the same or different alkyl radicals, e.g., having 1 to 4 carbon atoms.

The formation of the cyclic urea (II) a tetrahydropyrimidone, is a condensation reaction involving the splitting out from the 3-amino carbamate (I) a molecule of a glycol (III) corresponding to the starting carbonate ester. The secondary reaction forming the cyclic urea is much slower than the initial reaction forming the carbamate. Increasing the reaction time and temperature favor formation of cyclic urea and the completion of the reaction. The cyclic urea is readily determinable by infra-red spectroscopy.

As a typical illustration of formation of the cyclic propylene urea, to 144 g. of N-coco-1,3-propylene diamine was added 39.6 g. (0.45 mole) of ethylene carbonate with stirring over a 5-hour period at 200° C. The intermediate product weighed 179 g. To 135 g. of this material was added 100 ml. of mixed xylenes. The mixture was refluxed for 30 hours, during which time 16 ml. of ethylene glycol was removed as a xylene azeotrope. The final product, after removal of the solvent, weighed 113 g. The product was essentially pure N-coco-propylene urea. The N-coco-1,3-propylene diamine used in the above illustration was a commercial product marketed as "Diam 21–D." Diam 21–D is a fatty propylene diamine having both a primary and secondary amine group of the general formula $RNHCH_2CH_2OH_2NH_2$ where R is derived from a mixture of fatty acids, obtained from the hydrolysis of coconut oil, having 6–18 carbon atoms, which are predominately fatty acids of 10, 12 and 14 carbon atoms.

The following mixtures of ingredients were used to further exemplify and illustrate this invention and embodiments thereof.

Example 1: A 50:50 weight ratio mixture of di(coco) amine and N-coco propylene urea.

Example 2: A 50:50 weight ratio mixture of tri(lauryl) amine and N-coco propylene urea.

Additional examples of useable compositions are the various weight ratio mixtures of the secondary and tertiary amines and cyclic ureas as described hereinabove.

The effectiveness of the described amine and cyclic urea in preventing stalling due to carburetor deposits is demonstrated by the data in Table 1. These data were obtained in a so-called "Pontiac Carburetor Gum Test" conducted in the following manner: A 1957 Pontiac engine provided with a 4-barrel Rochester carburetor is used in making the test. A vacuum part for distributor spark advance is provided in the carburetor throat area, and is normally located in the atmospheric pressure area during idling. As deposits build upon the throttle bore, it is necessary to open the throttle valve more to provide the same air flow for the same r.p.m. When this is done, the vacuum port then is partially in the manifold vacuum area. At the start of the test the vacuum on the port is about 2 to 3 inches of mercury. The failure point of the test is considered reached when this vacuum increases about 8 inches of mercury, i.e., when the port vacuum reaches 10 to 11 inches of mercury. To increase the severity of the test, all of the crankcase blow-by and some of the exhaust are admitted to the carburetor. The time required for the base fuel (Control) to fail is about 20 hours, i.e., the time required for the vacuum to increase 8

inches of mercury when using the control fuel. During the test the engine is operated on a three (3) minute cycle of 2.75 minutes at 500 r.p.m. idle and 0.25 minute at 1600 r.p.m. with no load. Throttle opening and mixture adjustments are made every hour, if necessary, to maintain a 500 r.p.m. idle speed.

The improvement factor is calculated by:

$$\frac{\text{Time required for failure on fuel containing the additive}}{\text{Time required for failure on base fuel}} = \text{Improvement Factor}$$

The results of the test are expressed in terms of the "Improvement Factor" as above defined. The base motor fuel employed was a commercial premium gasoline containing the usual additives, i.e., tetraethyllead, scavengers, anti-oxidant, metal deactivator, etc.

Table I.—Pontiac Carburetor Gum Test Results

Sample No.	Fuel	Improvement Factor
1	Base Fuel	1.0
2	Sample 1 containing 24 p.p.m. N-coco propylene urea.	2.0
3	Sample 1 containing 24 p.p.m. of Example 1.	4.3

In addition to the above test data, gasoline compositions of the present invention were subjected to the Super Rotogum Test. The Super Rotogum Test is a test for detergency activity, i.e., the ability of a formulated gasoline to remove the deposits formed and is especially adaptable for testing detergency at high engine operation temperatures. The test employs a test apparatus which includes a rotating inclined glass tube through which a 100 ml. sample is flowed by gravity flow in the presence of air during a 42-minute test period. The apparatus used and an acceptable test procedure are described by Mickel in U.S. Serial No. 25,577, filed April 29, 1960. The glass tube is maintained at a temperature of 485° F. during the test and the sample and air flow are maintained constant. After the test period, the glass tube is cooled to the touch, removed and washed with heptane while rotating until deposits cease to be removed. The remaining deposits are then removed by a strong triple solvent mixture and the solvent is evaporated therefrom by regular ASTM D-381 gum procedures yielding the "insoluble gum," i.e., those deposits which would not be removed by the hydrocarbon components of gasoline. The insoluble gum is reported in mg./100 ml.

Table II.—Super Rotogum Test Results

Sample No.	Fuel	Heptane Insol. Gum, mg./100 ml.
4	Base Fuel	2.4
5	Sample 4 containing 25 PTB [1] di(coco) amine.	2.1
6	Sample 4 containing 25 PTB tri(lauryl) amine.	1.8
7	Sample 4 containing 25 PTB N-coco propylene urea.	2.2
8	Sample 4 containing 25 PTB of Example 1	1.3
9	Sample 4 containing 25 PTB of Example 2	1.0
10	Sample 4 containing 12.5 PTB di(hexyl) amine and 12.5 PTB N-coco propylene urea.	2.9

[1] PTB=lbs. per 1000 bbls.

Samples 8 and 9 including the combination of ingredients of this invention demonstrate marked superiority over the base fuel (Sample 4), either ingredient alone (Samples 5–7) and a combination not falling within this invention (Sample 10). The Super Rotogum Test correlates well with actual engine tests. The results demonstrate excellent carburetor throat detergency properties of the present addition agents.

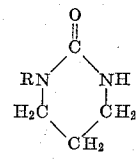
Gasoline compositions of this invention containing the addition agent mixtures of this invention may be used as fuels for internal combustion engines even over extended periods without expectation of accumulating undesirable induction system deposits. Existing deposits in the induction system may be effectively removed by using the present fuel compositions and the present fuel compositions may be used to give continuous satisfactory service extending beyond periods when normally carburetor adjustments or overhauling is to be expected.

Motor fuels containing the amine-urea mixture herein described can contain in addition thereto well known antioxidants, stabilizers, anti-icing agents, anti-knock agents, scavenging agents and/or other additives which are commonly employed in motor fuels for spark-ignition internal combustion engines.

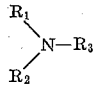
Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

I claim:

1. A motor fuel composition comprising a major proportion of a hydrocarbon base fuel distilling within the gasoline distillation range and from about 0.0005% to about 0.5% of a mixture of (1) a substituted propylene urea having the general formula



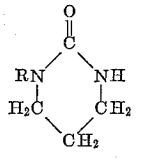
in which R is an acyclic aliphatic hydrocarbon radical having from about 8 to about 32 carbon atoms, and (2) an aliphatic amine having the general formula



in which R_1 and R_2 are each acyclic aliphatic hydrocarbon radicals having from about 8 to about 24 carbon atoms and R_3 is selected from the class consisting of hydrogen and an acyclic aliphatic hydrocarbon radical having from 1 to about 24 carbon atoms, said urea and amine being present in a weight ratio within the range of about 2:1 to about 1:2.

2. A motor fuel composition as described in claim 1 wherein R is an alkyl radical of from about 10 to about 20 carbon atoms derived from mixed fatty acids, R_1 and R_2 are C_{10} to C_{20} alkyls and R_3 is hydrogen.

3. A motor fuel composition to spark-ignition internal combustion engines comprising a major amount of a hydrocarbon base fuel distilling within the gasoline distillation range, a tetraalkyl lead anti-knock agent and from about 0.0005% to about 0.05% of a mixture of (1) a substituted propylene urea having the general formula



where R is an alkyl group of from about 8 to about 32 carbon atoms, and (2) an acyclic aliphatic amine selected from the class consisting of secondary acyclic aliphatic hydrocarbon amines and tertiary acyclic aliphatic hydrocarbon amines having from 8 to 24 carbon atoms in at least two of the acyclic aliphatic hydrocarbon groups and having in the third of the acyclic aliphatic hydrocarbon groups 1 to 24 carbon atoms, said amine and said urea being present in said mixture in the weight ratio of from about 2:1 to about 1:2.

4. A motor fuel composition as described in claim 3 in which R is an alkyl group of from 10 to about 20 carbon atoms derived from coconut fatty acids, in which the acyclic aliphatic hydrocarbon group is an alkyl group

of from 10 to about 18 carbon atoms derived from coconut fatty acids, and in which said amine and said urea are present in said mixture in the weight ratio of about 1:1.

5. A motor fuel composition as described in claim 3 in which R is an alkyl group of from 10 to about 18 carbon atoms derived from coconut fatty acids and in which the acyclic aliphatic amine is trilauryl amine.

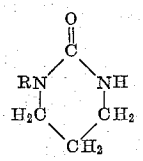
6. A motor fuel composition as described in claim 3 in which the tetraalkyl lead anti-knock agent is tetraethyl lead.

7. A motor fuel composition as described in claim 3 in which R is an oleyl radical.

8. As a composition of matter, a mixture capable of use in small amounts in leaded gasoline for spark-ignition internal combustion engines to maintain the induction system of such engines essentially free of deposits, said mixture consisting essentially of (1) the N-substituted cyclic propylene urea wherein the N-substituent is an acyclic aliphatic hydrocarbon having from about 8 to about 32 carbon atoms and (2) an acyclic aliphatic amine selected from the class consisting of secondary acyclic aliphatic hydrocarbon amines and tertiary acyclic C_1 to C_{24} aliphatic hydrocarbon amines having from 8 to 24 carbon atoms in at least two of the acyclic aliphatic hydrocarbon groups, said amine and said cyclic urea being present in said mixture in a weight ratio of from about 2:1 to about 1:2.

9. A composition as described in claim 8 in which the N-substituent is an alkyl group of from 10 to about 18 carbon atoms derived from coconut fatty acids, and in which said amine and said urea are present in said mixture in the weight ratio of about 1:1.

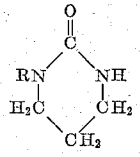
10. An additive for use in small amounts in leaded gasoline for spark-ignition internal combustion engines to maintain the induction system of such engines essentially free of deposits, said additive consisting essentially of a mixture consisting of (1) dicoco amine and (2) a substituted propylene urea having the general formula



where R is an alkyl group of from about 8 to about 32 carbon atoms, said amine and said urea being present in said mixture in the weight ratio of from about 2:1 to about 1:2.

11. An additive as described in claim 10 in which R is an alkyl group of from 10 to about 18 carbon atoms derived from coconut fatty acids, and in which said amine and said urea are present in said mixture in the weight ratio of about 1:1.

12. An additive for use in small amounts in hydrocarbon fuels of the gasoline boiling range adapted for use in spark-ignition internal combustion enignes to maintain the induction system of such engines essentially free of deposits, said additive consisting essentially of (1) trilauryl amine and (2) a substituted propylene urea having the general formula



in which R is an acyclic aliphatic hydrocarbon radical having from about 8 to about 32 carbon atoms, said amine and said cyclic urea being present in said mixture in the weight ratio of from about 2:1 to about 1:2.

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