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NONSTALLING GASOLINE COMPOSITION

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This invention relates to gasoline fuel compositions, and more particularly to gasoline fuel compositions that have reduced engine stalling tendencies at cool, humid atmospheric conditions.

When an internal combustion engine is operated at cool, humid atmospheric conditions, using a gasoline fuel having a relatively low 50 percent ASTM distillation point, i.e., below about 235° F., excessive engine stalling is apt to be encountered at idling speeds during the warm-up period, especially where engine idling occurs following a period of light load operation. Engine stalling under such conditions has been attributed to the partial or complete blocking of the narrow air passage that exists between the carburetor throat and the carburetor throttle valve during engine idling, by ice particles and/or solid hydrocarbon hydrates that deposit upon and adhere to the metal surfaces of the carburetor parts. Such icing of carburetor parts occurs as a result of the condensation of moisture from the air drawn into the carburetor and as a result of the solidification of such condensed moisture. The aforesaid condensation and solidification of moisture are caused by the refrigerating effect of rapidly evaporating gasoline. Accordingly, excessive engine stalling due to carburetor icing occurs as a practical matter only in the instance of gasolines containing a large proportion of relatively highly volatile components. In practice, the problem of engine stalling due to carburetor icing has been found to be serious, under cool, humid atmospheric conditions, in connection with gasolines having a 50 percent ASTM distillation point below about 220° F.

Excessive engine stalling is, of course, a source of annoyance owing to the resulting increased fuel consumption, battery wear and inconvenience of frequent restarting. It is therefore important that the inherent engine stalling characteristics of gasoline fuel be reduced substantially, where the 50 percent ASTM distillation point of such gasoline fuels is sufficiently low to cause a problem in this respect.

The present invention relates to gasoline fuel compositions that comprise hydrocarbon mixtures boiling in the gasoline range and that normally tend to promote engine stalling by carburetor icing, which fuel compositions exhibit reduced engine stalling tendencies, and which are thereby rendered more suitable for use as fuels in spark-ignition, reciprocating internal combustion engines. We have found that such improved gasoline compositions can be obtained by incorporating therein a small amount of an addition salt of a stabilized rosin amine and an oil-soluble hydrocarbon sulfonic acid, or by incorporating therein a small amount of a polyoxyalkylene derivative of a stabilized rosin amine containing per molecule about 4 to 20, preferably 5 to 15, oxyalkylene groups that contain 2 to 3 carbon atoms each. Salts of dehydroabietylamine and oil-soluble petroleum sulfonic acids are examples of preferred salts whose use is included by this invention. The polyoxyethylene derivative of dehydroabietylamine that contains about 11 oxyethylene groups per molecule is an example of another especially effective material for the purposes of this invention. The above-indicated addition agents are normally employed in proportions between about 0.001 and 0.01 percent by weight, but other proportions can be used. The invention is important in connection with gasolines having a 50 percent ASTM distillation point not greater than about 220° F., as such gasolines normally involve a severe engine stalling problem.

The amine salts and polyoxyalkylene derivatives of stabilized rosin amines whose use is included by this invention are polar, surface active materials. While the invention is not limited to any theory of operation, it might appear that the addition agents disclosed herein, by virtue of their polarity, tend to orient themselves upon the metal surfaces of the throttle valve and other critical carburetor parts contacted by the gasoline compositions, thus forming a moisture-displacing residual coating upon said carburetor parts which tend to prevent the adherence to said metal surfaces of accumulations of ice of such magnitude as to block the narrow air passages that exist in carburetor throats at engine idling conditions. It is also considered possible that the addition agents disclosed herein may tend to orient themselves about small, ice particles, thus tending to prevent the formation of macrocrystals of ice of a size sufficient to block carburetor air passages at engine idling conditions. Although the effectiveness of the herein disclosed addition agents is believed to be attributable in some way to the particular polar, surface active characteristics thereof, this general explanation is somewhat negatived by the fact that many other surface active agents, including, for example, other salts and oxyalkylene derivatives of stabilized rosin amines, as well as salts of other amines than rosin amines, have little or no effect upon the carburetor icing tendencies of gasolines.

The antistalling addition agents disclosed herein are useful when incorporated in gasoline compositions of the type disclosed in any amount sufficient to reduce the engine stalling characteristics thereof. For example, an improvement in the stalling characteristics of gasolines of the type disclosed herein will normally be obtained by addition thereto of the herein disclosed addition agents in amounts of at least 0.001 percent by weight of the composition (approximately 2.5 to 2.6 lbs./1000 bbls. of gasoline). Preferably the antistalling addition agents disclosed herein will be employed in proportions of at least 0.006 percent by weight of the composition (approximately 15 lbs./1000 bbls. of gasoline). Thus, a marked improvement in the stalling characteristics of gasolines has been obtained by incorporation therein of addition agents of the kind disclosed herein in proportions of about 15 to 25 pounds per thousand barrels of gasoline. Normally, we prefer to employ the addition agents disclosed herein in proportions of about 15 to 50 pounds per thousand barrels of gasoline. Although in some instances, it may be desired to employ the antistalling addition agents disclosed herein in amounts in excess of 250 pounds per thousand barrels of gasoline, that is 0.1 percent by weight or higher, such proportions are not necessary and normally produce no significant additional improvement in the stalling characteristics of the gasoline. In no instance sohuld the antistalling addition agents disclosed herein be added to gasoline in amounts such as to produce an undue adverse effect on the volatility, combustibility, antiknock or gum-forming characteristics of the gasoline.

It will be appreciated that the optimum proportion of the antistalling addition agents disclosed herein can vary within the range indicated above in accordance with the particular gasoline employed, inasmuch as the problem of engine stalling due to carburetor icing is a function of the 50 percent ASTM distillation point of the gasoline. Thus, greater concentrations of the antistalling addition agents are normally desirable with decreasing 50 percent ASTM distillation points. The optimum concentration of the antistalling addition agents disclosed herein may also vary somewhat in accordance with the particular make and model of engine in which the gasoline is used, as

well as in accordance with the severity of the atmospheric conditions encountered. With regard to this last-mentioned factor, the problem of engine stalling due to carburetor icing resulting from the refrigerating effect of evaporating gasoline upon moisture condensed from the atmosphere has been found to be serious at low temperatures, e.g., 35°, 40°, 45°, 50°, and when the relative humidity is in excess of about 55 percent, e.g., 75 percent, 99 percent. The optimum proportion of the antistalling addition agents disclosed herein in any given case will be sufficient to effect substantial reduction in the stalling tendencies of the fuel at the particular atmospheric conditions of temperature and humidity which are likely to be encountered in service.

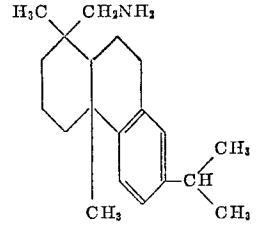
Practically speaking, the problem of engine stalling due to carburetor icing caused by rapid evaporation of gasoline occurs only in connection with gasolines having a 50 percent ASTM distillation point less than 235° F. While occasional engine stalling may occur as a result of carburetor icing at severe atmospheric conditions of temperature and humidity with gasolines having somewhat higher 50 percent ASTM distillation points, experience has indicated that the problem does not assume major importance except with gasolines of the character indicated. As indicated, the problem of engine stalling due to carburetor icing is especially severe in connection with gasolines having a 50 percent ASTM distillation point of less than about 220° F. The invention is particularly useful in connection with such gasolines. The term "gasoline" is used herein in its conventional sense to include hydrocarbon mixtures having a 90 percent ASTM distillation point of not more than about 392° F. and a 10 percent ASTM distillation point of not greater than 149° F.

The antistalling addition agents whose use is included by this invention can be incorporated in the base gasoline fuel compositions in any suitable manner. Thus, they can be added as such to gasoline or in the form of dispersions or solutions in solvents such as butanol, isopropanol, ethanol, methanol, benzene, toluene, heptane, kerosene, gasoline, mineral lubricating oil, or the like, which solvents may or may not themselves contribute to the antistalling characteristics of the gasoline motor fuel composition. If desired, the herein disclosed antistalling addition agents can be incorporated in gasoline fuel compositions in admixture with other materials designed to improve one or more properties of the gasoline, such as antioxidants, antigumming agents, e.g., 2,6-ditertiarybutyl, 4-methylphenol, antiknock agents, e.g., tetraethyl lead, lead scavenging agents, e.g., ethylene dibromide, ethylene dichloride, corrosion inhibitors, e.g., oil-soluble amine phosphates, dyes, and the like.

The gasoline fuel compositions of this invention can be further illustrated by reference to the following specific examples:

EXAMPLE I

(*a*) To a base gasoline, there was added a polyoxyethylene derivative of a stabilized rosin amine (Rosin Amine D) containing eleven oxyethylene groups per molecule, in the proportion of 25 pounds per thousand barrels of gasoline. The stabilized rosin amine referred to in this example was a dehydroabietylamine having the formula:



The base gasoline of this example had the following inspections.

Inspections:	
Vapor pressure, Reid, lb	8.5
ASTM, distillation, gasoline—	
Over pt. ° F	100
End pt. ° F	357
10% evaporated at ° F	136
50% evaporated at ° F	200
90% evaporated at ° F	277
Recovery, percent	98.3
Residue, percent	1.4

(*b*) The addition agent of Example I(*a*) was incorporated in the base gasoline of Example I(*a*) in proportion of 15 pounds per thousand barrels of gasoline.

EXAMPLE II

(*a*) The addition agent of Example I(*a*) was incorporated in a base gasoline in the proportion of 250 pounds per thousand barrels of gasoline. In this composition the base gasoline had the following inspections.

Inspections:	
Gravity, ° API	62.6
Existent gum, mg./100 ml	3
Oxidation stability, minutes	557
Knock rating—	
Motor Method, octane number	84.4
Research Method, octane number	95.4
TEL, ml./Gal	3.19
Vapor pressure, Reid, lb	8.4
ASTM distillation, gasoline—	
Over point, ° F	100
End point, ° F	394
10% evaporated at ° F	135
50% evaporated at ° F	210
90% evaporated at ° F	316
Recovery, percent	97.6
Residue, percent	0.9

EXAMPLE III

(*a*) A polyoxyethylene derivative of the stabilized rosin amine of Example I(*a*) containing about 5 oxyethylene groups per molecule was blended with the base gasoline of Example I(*a*) in the proportion of 25 pounds per thousand barrels of gasoline. The addition agent of this example contained approximately 15 percent free rosin amine which had no significant effect on the stalling characteristics of the gasoline.

(*b*) The addition agent of Example III(*a*) was incorporated in the base gasoline of Example II in the proportion of 250 pounds per thousand barrels of gasoline.

EXAMPLE IV

(*a*) The salt of the stabilized rosin amine of Example I(*a*) and oil-soluble petroleum sulfonic acids having an average molecular weight of 392 was incorporated in a base gasoline containing 88 percent L-4 test fuel and 12 percent light thermally cracked gasoline distillate in the proportion of 25 pounds per thousand barrels of gasoline. The stabilized rosin amine sulfonate of this example had the following analysis:

Rosin amine sulfonate	52.0
Mineral oil	47.5
Inorganic salts	Trace
Water	0.5
Ash	0
Molecular weight	709

The base gasoline of this example had the following inspections.

Inspections:	
Gravity, ° API	65.2
Existent gum, mg./100 ml	2.4
Oxidation stability, minutes	220
TEL, ml./gal	2.52
Vapor pressure, Reid, lbs	7.7

Inspections—Continued

ASTM distillation, gasoline—

Over point, ° F	1.01
End point, ° F	380
10% evaporated at ° F	134
50% evaporated at ° F	200
90% evaporated at ° F	283
Recovery, percent	97.9
Residue, percent	1.0

(*b*) The addition agent of Example IV(*a*) was incorporated in a base gasoline in the proportion of 250 pounds per thousand barrels of gasoline. The base fuel of this example had the following inspections.

Inspections:

Gravity, ° API	63.3
Existent gum, mg./100 ml	1.6
Oxidation stability, minutes	560
Knock rating, octane number—	
Motor Method	84.4
Research Method	95.6
TEL, ml./gal	3.03
Vapor pressure, Reid, lbs	7.7
ASTM distillation gasoline—	
Over point, ° F	103
End point, ° F	392
10% evaporated at ° F	139
50% evaporated at ° F	211
90% evaporated at ° F	316
Recovery, percent	97.7
Residue, percent	1.1

(*c*) The addition of agent of Example IV(*b*) was incorporated in the base gasoline of Example II in the proportion of 250 pounds per thousand barrels of gasoline.

The utility of the gasoline motor fuel compositions of this invention has been demonstrated by two different test procedures. In the one test, referred to hereinafter as the Mock Fuel System Test, test fuel at about 50° F. and air at about 60° F. and 75 percent relative humidity are supplied at controlled rates to a glass vaporizer chamber maintained at an absolute pressure of 12 inches of Hg and having an initial temperature of 45° F. The time for icing to occur and/or the amount of ice formed on a movable brass throttle plate in the glass vaporizer chamber are observed and recorded.

According to the other test procedure employed, hereinafter referred to as the Engine Test, a 216 cubic inch Chevrolet engine employing a standard, Carter downdraft carburetor is operated at no load on a test stand under cycling conditions in a cold room maintained at 40° F. for a warm-up period of 20 cycles. Each cycle comprises 40 seconds at 2000 r.p.m. followed by an idle for 20 seconds at 450 r.p.m. Air is supplied to the carburetor at 40° F. and 80 to 90 percent relative humidity. The number of engine stalls is observed and reported as stalls per 20 cycles. The results obtained in the testing of the motor fuel compositions of the above-indicated examples are presented in the following tables:

Table A

Fuel composition	Mock fuel system test	
	Extent of ice formation on throttle plate	Time to icing, minutes
Base fuel	Very heavy	1.5
Example II	Light	18.3
Example III(*b*)		7
Example IV(*c*)		15.2
Base fuel	Heavy	
Example IV(*b*)	Light	

Table B

Fuel composition	Engine test; avg. number stalls per 20 cycles
Base fuel	10.2
Example I(*a*)	3.7
Example I(*b*)	4.7
Example III(*a*)	6.7
Base fuel	11.8
Example IV(*a*)	5.5

From the results set forth in Tables A and B, it will be seen that addition agents of the class described herein effect a marked reduction in the carburetor icing and/or engine stalling tendencies of gasoline compositions in which they have been incorporated. While the addition agents employed in the above-indicated specific embodiments are especially effective for the purposes of this invention, it is to be understood that the invention is not limited to the use of these materials. Other addition agents of the class described herein can be substituted for those indicated in the preceding examples in the same or equivalent proportions with good results. For example, there can be substituted in the above-indicated gasoline motor fuel compositions polyoxyethylene and polyoxypropylene derivatives of stabilized rosin amine that contain, respectively, 20 and 7 oxyalkylene groups per molecule.

The oil-soluble petroleum sulfonic acids whose stabilized rosin amine salts are employed in the gasoline motor fuel compositions of this invention are preferably the sulfonic acids known as the mahogany acids. These acids, together with the water-soluble green acids, are produced during the sulfuric acid refining of petroleum lubricating oil distillates. Methods of recovering these acids, as well as methods of making amine salts thereof, are well known and form no part of the present invention.

The term "stabilized rosin amine" as used herein is employed in its normal sense to mean a rosin amine having the ring structure of a stabilized rosin acid, such as dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, or a mixture of such rosin amines, unless specifically indicated to the contrary.

To the gasoline fuel compositions of the present invention there can be added one or more additional agents designed to improve one or more characteristics of the gasoline fuel. For example, antioxidants, antiknock agents, ignition control additives, other de-icing agents, antirust agents, dyes, lead scavenging agents and the like can be added to the gasoline compositions of this invention, and the invention specifically includes gasoline compositions containing such additives.

Numerous additional embodiments of the invention will readily suggest themselves to those skilled in the art. Accordingly, only such limitations should be imposed on the invention as are indicated in the claims appended hereto.

We claim:

1. A gasoline motor fuel composition comprising a major amount of a hydrocarbon mixture boiling in the gasoline range and that normally tends to promote stalling of internal combustion engines, and a small amount, sufficient to reduce the engine stalling characteristics of the composition of a member selected from the group consisting of addition salts of stabilized rosin amine and an oil-soluble hydrocarbon sulfonic acid, and polyoxyalkylene derivatives of stabilized rosin amine containing about 4 to 20 oxyyalkylene groups per molecule, where said oxyalkylene groups contain two to three carbon atoms each.

2. The fuel composition of claim 1 where the hydrocarbon mixture has a 50 percent ASTM distillation point not greater than 220° F.

3. The fuel composition of claim 1 wherein said small amount is 0.001 to 0.1 percent by weight of the composition.

4. The fuel composition of claim 1 where said small acount is about 15 to 50 pounds of said member per thousand barrels of said hydrocarbon mixture.

5. The fuel composition of claim 1 where said member is a salt of oil-soluble petroleum sulfonic acids and stabilized rosin amine.

6. The fuel composition of claim 1 where said member is a polyoxyethylene derivative of stabilized rosin amine containing about 11 oxyethylene groups per molecule.

7. The fuel composition of claim 1 where said member is a polyoxyethylene derivative of stabilized rosin amine containing about 5 oxyethylene groups per molecule.

8. The fuel composition of claim 1 where said member is a polyoxyalkylene derivative of stabilized rosin amine containing about 4 to 20 oxyalkylene groups per molecule, and where said oxyalkylene groups contain 2 to 3 carbon atoms each.

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