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NONSTALLING GASOLINE MOTOR FUEL

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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 at-
mospheric 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 com-
plete blocking of the narrow air passage that exists be-
tween 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 evaporat-
ing 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 rela-
tively highly volatile components. In practice, the prob-
lem of engine stalling due to carburetor icing has been
found to be serious, under cool, humid atmospheric con-
ditions, in connection with gasolines having a 50 percent
ASTM distillation point below about 220° F.

Excessive engine stalling is, of course, a source of an-
noyance owing to the resulting increased fuel consump-
tion, battery wear and inconvenience of frequent restart-
ing. It is therefore important that the inherent engine
stalling characteristics of gasoline fuels be reduced sub-
stantially 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 com-
positions that comprise hydrocarbon mixtures boiling in
the gasoline range and that normally tend to promote en-
gine stalling by carburetor icing, which fuel compositions
exhibit reduced engine stalling tendencies, and which are
thereby rendered more suitable for use as motor fuels.
We have found that such improved gasoline compositions
can be obtained by incorporating therein a small amount
of a quaternary ammonium salt wherein two of the
covalent N-bonds are attached to aliphatic hydrocarbon
substituents containing 8 to 22 carbon atoms and the re-
maining covalent N-bonds are attached to saturated
aliphatic hydrocarbon radicals containing 1 to 4 carbon
atoms, and wherein the ionic N-bond is attached to an
anionic salt-forming radical derived from a member se-
lected from the group consisting of (a) oil-soluble organic
mono-carboxylic acids containing 7 to 30 carbon atoms
per molecule, (b) oil-soluble monohydric phenols having
attached to the aromatic nucleus 1 to 3 hydrocarbon sub-
stituents containing at least four carbon atoms, and hav-
ing not more than one substituent in the ortho position
that contains more than one carbon atom, (c) oil-soluble
mono- and di-acid esters of o-phosphoric acid having as

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one phosphato substituent an aliphatic hydrocarbon radical
containing 8 to 22 carbon atoms, and as another a
member selected from the class consisting of hydrogen
and aliphatic hydrocarbon radicals containing 2 to 22
carbon atoms, and (d) oil-soluble hydrocarbon sulfonic
acids. Especially good results are obtained from di-C₁₂₋₁₈
alkyl, di-C₁₋₂ alkylammonium dialkyl o-phosphates and
alkyl phenates, such as dioctadecyldimethylammonium di
Oxo octyl o-phosphate, bis(dioctadecyldimethylammoni-
um isooctyl o-phosphate, dioctadecyldimethylammonium
p-tert-octyl phenate. However, good results are also ob-
tained with other quaternary ammonium salts of the class
disclosed, for example, dioctyldecyldimethylammonium
naphthenate, dioctadecyldimethylammonium oil-soluble
petroleum sulfonate, and others. The invention is im-
portant 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 due to carburetor icing.

The quaternary ammonium salts whose use is included
by this invention are polar, surface active materials.
While the invention is not limited to any theory of opera-
tion, it might appear that the addition agents disclosed
herein, by virtue of their polarity, tend to orient them-
selves 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 tends 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 a carburetor throat at engine idling con-
ditions. 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 more or less negated by the
fact that many other surface active agents, including for
example, other quaternary ammonium salts, have little
or no effect upon the carburetor icing tendencies of gaso-
lines.

The quaternary ammonium salts disclosed herein can
be prepared in any suitable manner. Inasmuch as the
method of preparing the quaternary ammonium salts dis-
closed herein does not as such constitute any part of this
invention, such preparation need not be described in de-
tail. However, in the interest of clarity it may be men-
tioned that according to a preferred procedure the quater-
nary ammonium salts disclosed herein are formed by
neutralizing an appropriate quaternary ammonium hydroxide
with an oil-soluble acid of the kind disclosed
herein. This reaction proceeds spontaneously at ambient
atmospheric conditions with evolution of heat. The quater-
nary ammonium hydroxide is conveniently prepared
by reacting a suitable quaternary ammonium halide with
an alkali metal hydroxide, e.g., potassium hydroxide in
an alcoholic solution, thus forming a precipitate of an
alkali metal halide and an alcoholic solution of a quater-
nary ammonium hydroxide. Several quaternary ammoni-
um halides suitable for use in preparing the quaternary
ammonium salts disclosed herein can be obtained commer-
cially. When this is not the case, the desired quaternary
ammonium halide can be prepared in conventional fash-
ion, i.e., by reacting an appropriate tertiary amine with
an appropriate alkyl halide. The detailed preparations of
several quaternary ammonium salts of the kind disclosed

herein are described in the present assignee's copending application Ser. No. 538,799, filed in the name of Earl E. Myers, on October 5, 1955.

Any quaternary ammonium hydroxide having two of its covalent N-bonds attached to aliphatic hydrocarbon substituents containing 8 to 22 carbon atoms and the remaining covalent N-bonds attached to aliphatic hydrocarbon atoms containing 1 to 4 carbon atoms can be utilized to form quaternary ammonium salts useful for the purposes of this invention. It is important that two of the covalent N-bonds be attached to long-chain aliphatic hydrocarbon substituents as the presence of two such substituents imparts especially desirable gasoline solubility and water insolubility characteristics to the quaternary ammonium salts. Such characteristics are important to avoid any reduction in antistalling properties on account of a reduction in the effective concentration of the addition agent due to separation from solution or water leaching. The long-chain aliphatic hydrocarbon radicals can be, for example, alkyl, alkenyl or alkadienyl radicals containing 8 to 22 carbon atoms. Quaternary ammonium hydroxides wherein the two long-chain aliphatic hydrocarbon substituents are alkyl groups containing 12 to 18 carbon atoms form especially effective quaternary ammonium salts for the purposes of this invention. The two long-chain aliphatic hydrocarbon N-substituents can be derived from natural fats and oils, for example, coconut oil, soybean oil, animal tallow and the like. In such instances the long-chain aliphatic hydrocarbon radicals will consist essentially of mixed alkyl and alkenyl groups containing 8 to 22 carbon atoms. The two short-chain aliphatic hydrocarbon N-substituents can be any lower alkyl group, although methyl and ethyl substituents are preferred for the reason that they tend to minimize hindrance to addition of the long-chain substituents to the nitrogen atom. These substituents can comprise, for example, isopropyl, propyl, or butyl radicals. Examples of preferred quaternary ammonium hydroxides are didodecyldimethylammonium hydroxide, ditetradecyldimethylammonium hydroxide, dihexadecyldimethylammonium hydroxide, and dioctadecyldimethylammonium hydroxide. Examples of other quaternary ammonium hydroxides that can be used are dioctyldiethylammonium hydroxide, didodecenyldibutylammonium hydroxide, dioctadecenyldimethylammonium hydroxide and dioctadecadienyldiethylammonium hydroxide.

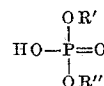
The nature of the acidic component of the quaternary ammonium salts disclosed herein is of great importance to the present invention, inasmuch as the acidic components contribute significantly to the antistalling properties of the quaternary ammonium salts. Nevertheless, various oil-soluble acids of the class disclosed above can be used to form quaternary ammonium salts that are useful for the purposes of this invention. Oil-soluble organic monocarboxylic acids that can be used to form salts of this invention will normally contain 7 to 30 carbon atoms. Quaternary ammonium salts wherein the anionic substituent is a salt-forming radical derived from petroleum naphthenic acids constitute a preferred class of carboxylic acid salts. As is known, such naphthenic acids are mixed alicyclic monocarboxylic acids recovered by alkali washing of petroleum such as kerosene, naphtha, gas, oil, and lubricating distillates. The acids derived from these distillates are mixtures of alicyclic monocarboxylic acids containing about 7 to 30 carbon atoms per molecule, which mixtures have average molecular weights in the range of about 200 to 450. Within the general class of petroleum naphthenic acids, the higher molecular weight acids derived from higher boiling distillates and containing 14 to 30 carbon atoms per molecule and having molecular weights of about 250 to 450 are considered to form especially effective quaternary ammonium salts for the purposes of this invention. Examples of other monocarboxylic acids that can be used to form quaternary ammonium salts whose use is included by this invention

are: oil-soluble synthetic naphthenic acids such as cyclohexylacetic, cyclohexylpropionic, and cyclohexylstearic acids, and oil-soluble saturated or unsaturated fatty acids, such as caprylic, lauric, myristic, palmitic, stearic, oleic, and linoleic acids. Mixtures of long-chain fatty acids such as those derived from the saponification of natural fats and oils also can be used to form quaternary ammonium salts within the scope of this invention. Examples of such mixed fatty acids are coconut, soya, and tallow fatty acids. In such instances the acids will consist essentially of mixtures of oil-soluble, straight-chain, unsubstituted monocarboxylic acids containing 8 to 22 carbon atoms.

As previously indicated, phenols that form salts whose use is included by this invention are oil-soluble monohydric phenols having attached to the aromatic nucleus at least one hydrocarbon substituent containing at least four carbon atoms and having not more than one substituent in the ortho position that contains more than one carbon atom. Although mono-substituted phenols are preferred, phenols containing 2 or 3 nuclear hydrocarbon substituents can be used. The hydrocarbon substituent or substituents can be straight or branched chain and saturated or unsaturated. The hydrocarbon substituent or substituents and even the aromatic nucleus itself may contain substituents containing halogen, oxygen, phosphorous, nitrogen or sulfur, e.g., chloro, nitro, amino, aryl, keto, or mercapto groups which do not affect the oil-solubility of the phenol and which do not react preferentially with the quaternary ammonium hydroxide. Phenols of the preferred class possess particularly advantageous solubilizing and salt-forming characteristics.

Oil-soluble, monohydric phenols containing one aliphatic hydrocarbon substituent, having 4 to 15 carbon atoms, in the meta or para position to the hydroxyl group are considered to form especially effective quaternary ammonium salts within the scope of this invention. For example, outstanding results have been obtained with quaternary ammonium salts of p-tert-octylphenol. Examples of other phenols that form suitable quaternary ammonium salts are p-tert-butylphenol, p-tert-amylphenol, p-sec-amylphenol, o-sec-amylphenol, o-tert-amylphenol, p-nonylphenol, cardanol, which consists essentially (approx. 90%) of a mixture of C₁₅ straight chain meta-substituted phenols with different degrees of unsaturation in the side chains, hydrocarbanol, i.e., m-pentadecylphenol, 2,6-dimethyl-4-tert-butylphenol, 2-tert-amyl-4-methylphenol, 3-methyl-6-tert-butylphenol, 2-methyl-4,6-di-tert-butylphenol, and 2,4-di-tert-butylphenol.

As suggested above, oil-soluble acid esters of o-phosphoric acid that form salts whose use is included by this invention are those having the general formula:



wherein R' is an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms and R'' is a member selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms. Acid esters of o-phosphoric acid that form a preferred class of quaternary ammonium salts according to this invention are those wherein R' is an aliphatic hydrocarbon radical containing 8 to 18, and preferably 8 to 12 carbon atoms and wherein R'' is an aliphatic hydrocarbon radical containing 2 to 8 carbon atoms. Specific examples of acid esters of o-phosphoric acid capable of forming preferred quaternary ammonium salts according to this invention are diisooctyl acid o-phosphate, isoamyl octyl acid o-phosphate, ethyl lauryl acid o-phosphate, and ethyl oleyl acid o-phosphate. Other acid esters of o-phosphoric acid that form quaternary ammonium salts suitable for the purposes of this invention are dilauryl acid

o-phosphate, dioleil acid o-phosphate, dimyristyl acid o-phosphate, dipalmityl acid o-phosphate, octyl di-acid o-phosphate, lauryl di-acid o-phosphate, and oleyl di-acid o-phosphate.

The sulfonic acids that form quaternary ammonium salts whose use is included by this invention are the oil-soluble hydrocarbon sulfonic acids. Such acids may be represented by the generic formula RSO_3H , where R is an organic radical of at least predominantly hydrocarbon character that is capable of imparting oil-solubility to the acid. These sulfonic acids may be oil-soluble aliphatic hydrocarbon sulfonic acids, including naphthenic hydrocarbon sulfonic acids, representative examples of the former of which are octyl, nonyl, decyl, undecyl, lauryl, tridecyl and myristyl sulfonic acids, and of the latter, the octyl-, dodecyl-, and dodecenyloxy-cyclopentyl and similarly substituted cyclohexyl sulfonic acids. Also satisfactory are the alkaryl sulfonic acids such as octyl, decyl, dodecyl and cetyl benzenesulfonic acids, as well as the so-called "keryl," or kerosene, and wax-alkyl benzenesulfonic acids, including the corresponding dialkyl benzenesulfonic acids. The preferentially oil-soluble petroleum sulfonic acids, normally referred to as "mahogany acids," in order to differentiate them from the preferentially water-soluble "green acids," are especially suitable for the purposes of this invention. As is well known in the art, oil-soluble petroleum sulfonic acids can be derived by sulfonation of higher boiling petroleum fractions, normally those having lubricating properties, with conventional sulfonating agents such as oleum, sulfur trioxide, or the like. The oil-soluble sulfonic acids are recoverable from the thus-treated oils by neutralization with aqueous alkali, such as aqueous caustic soda solution, extraction with alcohol or aqueous alcohol, distillation to remove the extraction solvent, and regeneration of the sulfonic acid by treatment of the residue with an equivalent amount of a mineral acid. Particularly suitable mahogany acids are those having an average molecular weight between about 400 and about 650.

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 (approx. 2.5 to 2.6 lbs./1000 bbls. gasoline). Preferably the anti-stalling addition agents disclosed herein will be employed in proportions of at least 0.006 percent by weight of the composition (approx. 15 lbs./1000 bbls. 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. Accordingly, we normally 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 more, such proportions are usually not necessary and normally produce no significant additional improvement in the stalling characteristics of the gasoline. In no instance should the antistalling addition agents disclosed herein be added to gasoline in amounts such as to produce a significant 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 gaso-

line. 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, and 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 important 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. However, it is obvious that some deviation from these limits can be tolerated without substantially changing the essential characteristics of a gasoline. Accordingly, the invention includes the use of borderline gasolines of this kind.

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 be 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, anti-gumming 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 dialkyl amine phosphates, dyes, and the like.

The utility of the gasoline motor fuel compositions of this invention has been demonstrated by two different test procedures. In one test, referred to hereinafter as the Mock Fuel System Test, test fuel is supplied at about 50° F. together with air at about 60° F. and about 75 percent relative humidity at controlled rates to the glass vaporizer chamber held at an absolute pressure of 12 inches of mercury (temperature initially at 50° F.), and by observing the time for icing to occur on a movable brass throttle plate positioned in the vaporizer chamber. Performance of a test fuel is determined by comparing the time for icing formation on the brass throttle plate with that required for the uninhibited fuel under the same test conditions. In these tests the base gasoline employed,

hereinafter referred to as Test Fuel A, had the following characteristics.

Inspections:

| | |
|---------------------------------|------|
| Gravity, ° API..... | 62.6 |
| Knock rating: | |
| Motor method, octane No..... | 84.2 |
| Research method, octane No..... | 94.4 |
| TEL, ml./gal..... | 3.19 |
| Vapor pressure, Reid, lbs..... | 8.4 |
| 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 |

According to the other test procedure employed, hereinafter referred to as the Cold Room Engine Test, a 216 cu. in. Chevrolet engine employing a standard Carter down-draft 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

isooctyl o-phosphoric acids, hereinafter referred to as Compound 3. Bis(dioctadecyldimethylammonium) isooctyl o-phosphate and dioctadecyldimethylammonium diisooctyl o-phosphate were the predominant components of Compound 3. The mixed acid esters of o-phosphoric acid employed in preparing Compound 3 comprised a mixture of diisooctyl acid o-phosphate and isooctyl diacid o-phosphate in approximately 1:1 mol proportions. This mixture of acids had an average molecular weight of about 266, a phosphorus content calculated as P₂O₅ of 27.0 percent, a specific gravity at 25° C./4° C. of 1.020, a refractive index at 25° C. of 1.4428. Another quaternary ammonium salt tested was the di(hydrogenated tallow alkyl)dimethylammonium salt of oil-soluble petroleum sulfonic acids, hereinafter referred to as Compound 4. An oil solution of the oil-soluble petroleum sulfonic acids employed in the separation of Compound 4 had an ash content of 0.25 percent and a neutralization number of 35.2. The petroleum sulfonic acids component of the solution had a calculated average molecular weight of about 460.

The results of the above-described tests are set forth in the following table:

Table A

| Example | Test Fuel A | 1 | 2 | Test Fuel B | 3 | 4 | 5 | 6 |
|--|-------------|-----|-----|-------------|-----|-----|-----|-----|
| Make-Up, Percent by Vol.: | | | | | | | | |
| Test Fuel A..... | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Test Fuel B..... | | | | | | | | |
| Added: Lb./1,000 Bbls.— | | | | | | | | |
| Compound 1..... | | | | | 25 | | | |
| Compound 2..... | | 25 | | | | 25 | | |
| Compound 3..... | | | 25 | | | | 25 | |
| Compound 4..... | | | | | | | | 25 |
| Inspections: | | | | | | | | |
| Mock Fuel System Test— | | | | | | | | |
| Time to Icing, Min..... | 1.5 | 7.0 | 5.5 | | | | | |
| Cold Room Engine Test— | | | | | | | | |
| Stalls Encountered During Warm-Up, No..... | | | | 10 | 5.5 | 3.5 | 3.0 | 6.8 |

for 20 seconds at 450 r.p.m. Air is supplied to the carburetor at ambient conditions and at approximately 85 percent relative humidity. The number of engine stalls is observed and reported as stalls per 20 cycles. The base gasoline employed in connection with this test procedure, hereinafter referred to as Test Fuel B, had the following characteristics.

Inspections:

| | |
|---------------------------------|------|
| Gravity, ° API..... | 64.4 |
| Knock rating: | |
| Motor method, octane No..... | 79.3 |
| Research method, octane No..... | 82.8 |
| Tel, ml./gal..... | 2.96 |
| Vapor pressure, Reid, lbs..... | 7.0 |
| Distillation, gasoline: | |
| Over point, ° F..... | 106 |
| End point, ° F..... | 388 |
| 10% evaporated at, ° F..... | 145 |
| 50% evaporated at, ° F..... | 206 |
| 90% evaporated at, ° F..... | 287 |

One of the compounds employed in the above-described tests was di(hydrogenated tallow alkyl)dimethylammonium naphthenate, hereinafter referred to as Compound 1. This salt was prepared from petroleum naphthenic acids boiling in the range 145° to 185° C. at 3 mm. Hg, having a neutralization value of 213 and an average molecular weight of about 381. The hydrogenated tallow alkyl radical consists essentially of a mixture of C₁₆H₃₃ and C₁₈H₃₇ radicals, with the latter predominating. Another salt employed in the tests was di(hydrogenated tallow alkyl)dimethylammonium p-tert-octyl phenate, hereinafter referred to as Compound 2. Another material tested was a mixture of neutral di(hydrogenated tallow alkyl)dimethylammonium salts of a mixture of isooctyl and di-

From the experimental results presented in the foregoing table it will be seen that the quaternary ammonium salts of the class disclosed herein are effective in reducing the carburetor icing tendencies of gasolines that normally tend to promote carburetor icing. The results obtained indicate that Compounds 2 and 3 are especially effective gasoline antistalling agents.

It will be understood that the invention is not limited to the specific compositions disclosed above and that good results can be obtained by the substitution of other normally stalling gasolines and by the substitution of other quaternary ammonium salts disclosed herein in the same or equivalent proportions for the corresponding components therein. For example good results can be obtained by incorporating into Test Fuel A and Test Fuel B in the proportions of 25 pounds per thousand barrels of gasoline of the dioctyldimethylammonium, the didodecyldimethylammonium, the dihexadecyldipropylammonium, and the dioctadecenyldimethylammonium salts of petroleum naphthenic, oleic, stearic, caprylic, and cyclohexylstearic acids, p-tert-amylphenol, p-sec-amylphenol, o-sec-amylphenol, o-tert-amylphenol, p-nonylphenol, cardanol, m-pentadecylphenol, 2,6-dimethyl-4-tert-butylphenol, 2-tert-amyl-4-methylphenol, 3-methyl-6-tert-butylphenol, 2-methyl-4,6-di-tert-butylphenol, 2,4-di-tert-butylphenol, diisooctyl o-phosphoric acid, isooctyl o-phosphoric acid, dilauryl o-phosphoric acid, dimyristyl o-phosphoric acid, didoleyl o-phosphoric acid, octyl o-phosphoric acid and ethyl lauryl o-phosphoric acid.

It is emphasized that the remarkable properties of the addition agents disclosed herein are attributable both to the nature of the covalent N-substituents and of the ionic N-substituent. Indicative of the importance of the character of the covalent N-substituents of the quaternary ammonium salts whose use is included by this invention is

the fact that benzyltrimethylammonium p-tert-octyl phenate and the tetramethyl ammonium salt of oil-soluble petroleum sulfonic acids were found to be substantially insoluble in benzene, even in low concentrations, thus indicating the unsuitability of these materials as gasoline additives. Indicative of the importance of the character of the ionic N-substituent is the fact that dihydrogenated tallow dimethylammonium chloride, even in the proportion of 250 pounds per thousand barrels of gasoline, was found to extend the time for icing in the Mock Fuel System Test to only three minutes, an unsatisfactory performance according to the test.

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, that has a 50 percent ASTM distillation point not greater than 220° F. and that normally tends to promote stalling of internal combustion engines and a minor amount, sufficient to reduce the engine stalling characteristics of said composition of a quaternary ammonium salt wherein two of the co-valent N-bonds are attached to aliphatic hydrocarbon substituents containing 8 to 22 carbon atoms and the remaining co-valent N-bonds are attached to saturated aliphatic hydrocarbon radicals containing 1 to 4 carbon atoms, and wherein the ionic N-bond is attached to an anionic salt forming radical derived from a member selected from the group consisting of (a) oil-soluble organic monocarboxylic acids containing 7 to 30 carbon atoms per molecule, (b) oil-soluble monohydric phenols having attached to the aromatic nucleus one to three hydrocarbon substituents containing at least four carbon atoms, and having not more than one substituent in the ortho position that contains more than one carbon atom, (c) oil-soluble mono- and di-acid esters of o-phosphoric acid having as one phosphato substituent an aliphatic hydrocarbon radical containing 8 to 22 carbon atoms, and as another a member

selected from the class consisting of hydrogen and aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms, and (d) oil-soluble hydrocarbon sulfonic acids.

2. The fuel composition of claim 1 where said minor amount is 0.001 to 0.1 percent by weight of the composition.

3. The fuel composition of claim 1 where said minor amount is about 15 to 50 pounds of said quaternary ammonium salt per thousand barrels of said hydrocarbon mixture.

4. The fuel composition of claim 1 where said quaternary ammonium salt is the di(hydrogenated tallow alkyl) dimethylammonium salt of petroleum naphthenic acids.

5. The fuel composition of claim 1 where said quaternary ammonium salt is di(hydrogenated tallow alkyl) dimethylammonium p-tert-octyl phenate.

6. The fuel composition of claim 1 where said quaternary ammonium salt is di(hydrogenated tallow alkyl) dimethylammonium diisooctyl o-phosphate.

7. The fuel composition of claim 1 where said quaternary ammonium salt is bis[di(hydrogenated tallow alkyl)] dimethylammonium isooctyl o-phosphate.

8. The fuel composition of claim 1 where the quaternary ammonium salt is a mixture of neutral di(hydrogenated tallow alkyl) dimethylammonium salts of isooctyl and diisooctyl o-phosphoric acids.

9. The fuel composition of claim 1 where said quaternary ammonium salt is the di(hydrogenated tallow alkyl) dimethylammonium salt of oil-soluble petroleum sulfonic acids.

References Cited in the file of this patent

UNITED STATES PATENTS

| | | | |
|----|-----------|------------------|----------------|
| 35 | 2,550,982 | Eberz | May 1, 1951 |
| | 2,563,506 | Werntz | Aug. 7, 1951 |
| | 2,582,733 | Zimmer et al. | Jan. 15, 1952 |
| | 2,632,694 | Watkins | Mar. 24, 1953 |
| | 2,706,677 | Duncan et al. | Apr. 19, 1955 |
| 40 | 2,819,954 | Gebelein et al. | Jan. 14, 1958 |
| | 2,843,464 | Gaston et al. | July 15, 1958 |
| | 2,862,800 | Cantrell et al. | Dec. 2, 1958 |
| | 2,863,742 | Cantrell et al. | Dec. 9, 1958 |
| | 2,905,541 | Gottshall et al. | Sept. 22, 1959 |

FOREIGN PATENTS

| | | | |
|--|---------|---------------|---------------|
| | 356,717 | Great Britain | Sept. 7, 1941 |
| | 791,394 | Great Britain | Mar. 5, 1958 |

OTHER REFERENCES

Petroleum Refining With Chemicals, by Kalichevsky et al., 1956, Elsevier Pub. Co., p. 480.