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ANTI-STALL GASOLINE COMPOSITION

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1 Claim. (Cl. 44—76)

This invention relates to gasoline fuel compositions for use in internal combustion engines and is particularly concerned with new gasoline compositions adapted to provide improved engine operation under cool and humid weather conditions.

A well known difficulty encountered in the operation of automobile engines in cool and humid weather is that of frequent engine stalling during the warm-up period. The trouble is most prevalent in northern climates during the fall and winter periods. Its cause has been traced to the formation of ice in the carburetor of the engine. Although the difficulty has existed for a long time, it has become more prevalent than ever in recent years due to the use of more highly-volatile, winter-grade gasolines. Thus, the evaporation of gasoline in the carburetor produces a considerable cooling effect which is more pronounced with the higher volatility gasolines. In cool, moist weather, this cooling effect is sufficient to cause condensation and freezing of the moisture present in the air entering the carburetor. Consequently, in the period before the engine becomes warm, ice is formed which restricts the air-intake openings and causes the engine to stall. It has been found that conditions particularly conducive to stalling difficulties due to ice formation in the carburetor are ambient temperatures of from about 30° F. to about 65° F., when the relative humidity is above about 65%. The stalling occurs most readily when the engine is idling and although the frequency of stalling is greater with gasolines of higher volatility, such as those provided for winter use in northern climates, the difficulty is experienced with all types of commercial gasolines in all types of cars.

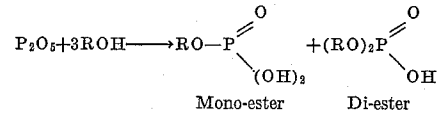
As is well known, a gasoline is a mixture of hydrocarbons having an initial boiling point varying between about 75° F. and about 135° F. and an end point varying between about 250° F. and about 450° F. and boiling substantially continuously therebetween. As aforementioned, gasolines vary in their volatility characteristics, the more volatile winter-grade gasolines being generally more susceptible to stalling due to carburetor icing than the less volatile. It has been recognized, in particular, that gasolines having relatively low mid-boiling points are more susceptible to stalling due to carburetor icing than those having relatively high mid-boiling points. However, all gasolines are prone to stalling under conditions conducive to carburetor icing and they are all substantially improved with respect to their anti-icing tendencies by application of the present invention.

It is the object of the invention to provide gasoline compositions having anti-icing properties such that substantially stall-free operation, under conditions which would normally induce stalling difficulties, is attained. Other and further objects of the invention will appear from the following detailed description thereof.

In accordance with this invention, it has been found that stalling difficulties due to the formation of ice in the carburetor of an engine can be substantially eliminated

by incorporating in the gasoline a small amount of a partial ester of phosphoric acid.

The partial esters contemplated by the invention are the mono- and di-esters of phosphoric acid, as distinguished from the (neutral) tri-esters. The partial esters of the invention are prepared by the reaction of a mono-hydroxy organic compound, such as an alcohol or a phenol, with phosphorus pentoxide, in a mol ratio of approximately 3:1, at a temperature of from about 100° C. to about 150° C. and for a time sufficient to complete the reaction, i.e., from about 3 to about 6 hours. The general reaction is represented by the following emperical equation:



where R represents the hydrocarbon portion of the hydroxy compound utilized in the reaction. As shown by the equation, the partial ester products thus produced are mixtures comprising the mono- and di-esters in a mol ratio of 1:1.

The partial esters contemplated herein may be of the aliphatic type or of the aromatic type. Thus, they may be aliphatic esters prepared from mono-hydroxy alcohols having from 4 to about 18 carbon atoms. Specific esters are, for example, the mono- and di-esters of butyl, hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl alcohols. The partial esters prepared from mixtures of such alcohols are also suitable. The esters may also be prepared from aromatic hydroxy compounds, such as alkyl-substituted phenols and naphthols in which the alkyl substituents contain a total of from about 4 to about 18 carbon atoms. Specific esters are, for example, the mono- and di-esters of butyl phenol, di-butyl phenol, mono-amyl phenol, di-amyl phenol, octyl phenol, di-octyl phenol, decyl phenol, dodecyl phenol, tetradecyl phenol, hexadecyl phenol and octadecyl phenol. The esters may also be those derived from mixtures of aliphatic and aromatic hydroxy compounds of the foregoing types.

It has been found that of the various mono- and di-esters contemplated herein those derived from the relatively high molecular weight, straight-chained, aliphatic alcohols exhibit the highest effectiveness as anti-icing additives, the oleyl mono- and di-ester product being particularly outstanding.

It is recognized that phosphate esters have been used heretofore as addition agents in gasoline. Thus, the prior art has shown the use of the neutral phosphate esters as antioxidants, gum inhibitors and pre-ignition additives. As far as the present applicant is aware, however, it has not been recognized heretofore that the partial esters of phosphoric acid would function as anti-icing agents. Indeed, the fact that the partial phosphate esters do so function is quite surprising as the corresponding neutral esters exhibit little or no effectiveness in this respect.

The following specific examples and test results will serve to illustrate the invention.

EXAMPLE I

A 1:1 mixture of the mono- and di-alkyl esters of phosphoric acid was prepared by reacting 3 mol proportions of an alcohol mixture consisting of about 50 weight percent octyl alcohol, about 30 weight percent decyl alcohol and about 20 weight percent dodecyl alcohol, with 1 mol proportion of P_2O_5, for a period of 5 hours, at a temperature of 125° C.

EXAMPLE II

A 1:1 mixture of mono- and di-oleyl phosphoric acid esters was prepared by reacting 3 mol proportions of

oleyl alcohol with 1 mol proportion of P_2O_5 at 125° C. for 5 hours.

EXAMPLE III

A 1:1 mixture of mono- and di-(diamyl phenyl) phosphoric acid esters was prepared by reacting 3 mol proportions of diamyl phenol with 1 mol proportion of P_2O_5 at 125° C. for 5 hours.

EXAMPLE IV

For comparative purposes, a trioleyl ester of phosphoric acid was prepared by reacting 2 mols (1 mol excess) of oleyl alcohol with ⅓ mol $POCl_3$, in the presence of pyridine, for 12 hours at 125° C. Excess oleyl alcohol was removed by distillation at low pressure.

EXAMPLE V

For further comparison, trioleyl phosphite was prepared by reacting 1 mol proportion of oleyl alcohol with ⅓ mol proportion of PCl_3 in the presence of pyridine, for 10 hours at a temperature of 125° C.

Carburetor icing tests

The ability of the partial esters contemplated herein to prevent engine stalling under conditions conducive to carburetor icing has been demonstrated by means of a series of cold-starting tests.

The test procedure was as follows. A standard, six cylinder Chevrolet engine was installed in a "cold" room, equipped with temperature and humidity controls was used in the tests. With the room temperature maintained at approximately 44° F. and the relative humidity at approximately 97%, the engine was started and operated for one minute at 2000 r.p.m., with no load. At the end of the one minute operation, the engine speed was reduced to 500 r.p.m. and the time required for the engine to stall was noted. In evaluating an anti-icing additive, the base fuel is first tested followed by a test on a blend of the base fuel with the additive. Any improvement caused by the additive is reflected in a longer run time before stalling, the more effective the additive, the longer the run time. The base gasoline utilized in the tests was a blended gasoline comprising 20% straight run component and 80% cracked component. It had a boiling range of approximately 94° F. to 387° F. The test results are tabularized below.

Product Added	Concentration (lbs./1,000 bbls.)	Run Time to Stalling (Seconds)
None	0	30
Example I	125	60
Example II	125	115
Example III	125	65
Example IV	125	35
Example V	125	35

It will be seen from the test results that the partial phosphate esters are effective anti-icing agents. Also, although the octadecyl partial ester product (Example II) is outstandingly effective, the neutral octadecyl ester (Example IV) is substantially ineffective. Likewise, the neutral phosphite ester (Example V) is ineffective.

The amount of the partial ester product to be incorporated into the gasoline will vary depending upon the gasoline to which it is added and the amount of improvement required. Thus, gasolines of relatively high volatility will ordinarily require the use of more of the partial esters than gasolines of relatively low volatility. In general, the amount to be used will vary from about 10 to about 200 pounds per 1000 barrels of gasoline, with the usual amount ranging from 100 to 150 pounds per 1000 barrels. In terms of weight percent, the amount used will range, broadly, from about 0.0025% to about 0.05%.

The gasoline may, of course, contain other additives designed to improve the properties thereof in other respects, along with the partial esters of this invention. Thus, it can also contain anti-knock agents, antioxidants, metal deactivators, anti-rust agents, foam inhibitors, solvent oils, upperlubes, dyes, etc.

Although the invention has been illustrated herein by means of specific materials and tests, it is not intended that its scope be limited in any way thereby, except as indicated in the appended claim.

What is claimed is:

A gasoline containing a minor amount, sufficient to improve the anti-icing properties thereof, of a mixture of mono- and di-oleyl esters of phosphoric acid in a mol ratio of approximately 1:1.

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