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STABILIZED FUEL ADDITIVE CONCENTRATES CONTAINING ALKYL AND/OR ALKYL ARYL PHOSPHATES

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8 Claims. (Cl. 44—72)

This invention relates to an improved fuel additive concentrate. In another aspect, this invention relates to a multipurpose gasoline fuel additive concentrate containing alkyl and alkyl aryl phosphates.

It has been found highly desirable to employ additives in the preparation of internal combustion motor fuels to substantially improve the performance of the engines employing these fuels. Generally, several additives are employed in the preparation of, for example, premium gasoline fuels. For simplicity and convenience, these fuel additives are generally premixed to form additive concentrates or "packages." This mixture of additives is then blended into the fuel at the appropriate time and place. The term "additive concentrate" as hereinafter employed refers to mixtures of those additives other than the lead or lead scavenger additives. The lead-lead scavenger mixture is generally kept separate from the other additive mixtures and is normally added to the fuel at a point much earlier in the fuel blending process.

The use of phosphorous in the preparation of an internal combustion motor fuel has been found to be highly effective in preventing surface ignition and as a spark plug anti-foulant. Alkyl and alkyl aryl phosphates are effective and attractive sources of phosphorous for use in internal combustion motor fuels. Methyl diphenyl phosphate, for example, is more economical, on a cost per pound of phosphorous basis, than other wholly aryl phosphates such as cresyl diphenyl phosphate or tricresyl phosphate. Alkyl phosphates suffer from the disadvantage, however, of being susceptible to decomposition by hydrolysis. They are known to hydrolyze and result in precipitate formation in the presence of water and iron. Fuel additives are conventionally stored in contact with steel containers. Under these conditions, the alkyl phosphate additive tends to decompose with the formation of heavy precipitates which, of course, cannot be tolerated in internal combustion motor fuels.

Diethylene glycol monomethyl ether, hereinafter referred to as methyl Carbitol, has been found to be particularly effective as a de-icer and is employed as an additive in internal combustion motor fuels to prevent fuel line freezeup. When methyl Carbitol and other hereinafter described anti-icing additives are mixed with alkyl and alkyl aryl phosphates in the preparation of a fuel additive concentrate, the anti-icing additive appears to contribute to the hydrolysis of the phosphate.

Accordingly, an object of my invention is to provide an improved fuel additive concentrate.

Another object of my invention is to provide improved fuel additive concentrates containing alkyl and alkyl aryl phosphates.

Another object of my invention is to provide improved fuel additive concentrates containing an alkyl phosphate or an alkyl aryl phosphate and an anti-icing additive.

Another object of my invention is to provide a process for improving the stability of alkyl and alkyl aryl phosphates.

Other objects, advantages and features of my invention will be readily apparent to those skilled in the art from the following description and appended claims.

By my invention I have provided an improved fuel additive concentrate comprising a material selected from the

group consisting of alkyl and alkyl aryl phosphates and a selected surfactant material hereinafter described. The addition of the selected surfactant material inhibits the decomposition of the phosphate, thereby providing a fuel additive concentrate that can effectively be employed in the preparation of high performance internal combustion motor fuels. In a second embodiment, an improved fuel additive concentrate comprising a material selected from the group consisting of alkyl and alkyl aryl phosphates, an anti-icing additive, and a selected surfactant material is provided.

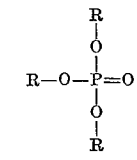
The anti-icing additive employed in the preparation of the fuel additive concentrate consists essentially of a blend of (1) a saturated acyclic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 2 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula $R(OCH_2CH_2)_xOH$, wherein: R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl and tolyl groups; where R is hydrogen, x is an integer of from 2 to 4; and when R is other than hydrogen, x is an integer of from 1 to 4. Suitable proportions of said alcohol and said ether in the anti-icing additive are usually from 0 to 49 weight percent of the said alcohol and from 100 to 51 weight percent of said ether.

Examples of saturated acyclic polyhydroxy alcohols which can be used in the practice of the invention include the following: 1,2-dihydroxypropane; 1,3-dihydroxypropane; glycerol; 1,2,3-trihydroxybutane; 1,2,4-trihydroxybutane; 2-(hydroxymethyl)-1,3-hydroxypropane; erythritol; pentaerythritol; 1,2,3,4-tetrahydroxypentane; 1,2,3,5-tetrahydroxypentane; 1,2,4,5-tetrahydroxypentane; 2-(hydroxymethyl)-1,3,4-trihydroxybutane; and 1,2,3,4,5-pentahydroxypentane.

Examples of said glycol ethers which can be used in the practice of the invention include, among others, the following: methyl ether of ethylene glycol (methyl Cellosolve); ethyl ether of ethylene glycol (ethyl Cellosolve); butyl ester of ethylene glycol (butyl Cellosolve); methyl ether of diethylene glycol (methyl Carbitol); ethyl ether of diethylene glycol (ethyl Carbitol); butyl ether of diethylene glycol (butyl Carbitol); methyl ether of triethylene glycol; ethyl ether of triethylene glycol; phenyl ether of ethylene glycol; tolyl ether of ethylene glycol; phenyl ether of diethylene glycol; tolyl ether of diethylene glycol; phenyl ether of triethylene glycol; tolyl ether of triethylene glycol; diethylene glycol; triethylene glycol; and tetraethylene glycol.

The fuel additive base of my invention consists of 5–100 volume percent of a material selected from the group consisting of alkyl and alkyl aryl phosphates and 0–95 volume percent of the anti-icing additive and/or diluent. To this fuel additive base is added a hereinafter described surfactant to provide a concentration of surfactant in the produced fuel additive concentrate in the range of 1–50 volume percent.

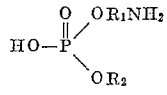
The phosphates employed in the preparation of the fuel additive concentrate are those having the formula:



where R is selected from the group consisting of alkyl radicals having up to and including 6 carbon atoms, phenyl radicals, and cresyl radicals, at least one R being an alkyl radical, and mixtures thereof. Specific examples of suitable phosphates include methyl diphenyl phosphate, dimethyl phenyl phosphate, trimethyl phosphate, tri-n-

hexyl phosphate, p-cresyl diethyl phosphate, and the like.

The surfactants which are applicable for use in the preparation of the inventive fuel additive concentrate are those surfactants which reduce the interfacial tension between two liquids. Preferably, the surfactants employed are detergent surfactants which will exhibit at least some anticorrosion properties. Surfactants which have been found to be of particular value in the preparation of the inventive fuel additive concentrate are the trialkylamines having alkyl groups ranging from 4–22 carbon atoms and the alkyl aminoalkyl phosphates having the following structure:



wherein R_1 is an alkylene group containing from 4–22 carbon atoms per molecule and R_2 is an alkyl group having 4–22 carbon atoms per molecule, and the sum of the carbon atoms in both the R_1 and R_2 radicals is in the range of 20–30.

Diluents can be employed in the preparation of the fuel additive concentrate of my invention. The diluents which are useful are inert materials which are solvents for the constituents of the fuel oil additive concentrate. Methyl Carbitol can be employed as a diluent. Other materials suitable as diluents are the xylenes, gasolines, naphthas, halogenated hydrocarbons, ethers, methyl alcohol, and the like. In those cases where methyl Carbitol is not employed in the preparation of the fuel additive concentrate, miscibility of the selected surfactant and the selected phosphate will eliminate the necessity of employing a diluent.

The fuel additive concentrates of my invention can be utilized in fuels for internal combustion engines. As employed in an internal combustion engine fuel, the fuel additive concentrate is effective in preventing surface ignition and operates to prevent spark plug fouling. In addition thereto, the fuel additive concentrate serves as a de-icer, thereby preventing fuel line freezeups, and further operates as a carburetor detergent.

The following example is presented to illustrate the objects and advantages of the invention. It is not intended, however, to limit the invention to the specific embodiments presented therein.

EXAMPLE

A number of runs were made in which storage stability test specimens were prepared employing the fuel additive concentrate of my invention. The fuel additive concentrates were prepared employing varying proportions of additives, placed in stoppered bottles, and the stoppered bottles placed in an oven maintained at 110° F. for a 60 day period of observation. A mild steel coupon was placed in each bottle, such that the fuel additive concentrate in that bottle was contacted with a steel area which was about 150 percent of that to which it would be exposed to in conventional metal drums. Water (0.5 weight percent of the concentrate) was added in some test bottles to determine the effect of water upon the storage stability of the particular fuel additive concentrate.

The bottles were periodically examined while in storage and the appearance of any instability as evidenced by precipitate in the bottles noted. The degree of precipitation was also noted. The composition of the fuel additive concentrate, percent water added to the fuel concentrate, and the results of the runs are presented below in Table I. Where noted, methyl alcohol and xylene were employed as diluents in the preparation of the fuel additive concentrate.

The surfactant identified in Table I as Du Pont DMA is an aminoalkyl alkyl phosphate diester in which the sum of the carbon atoms in the alkyl radicals is 27 carbon atoms and which contains 64.7 percent carbon, 2.2 percent hydrogen, 12.9 percent oxygen, 6.4 percent phosphorous and 3.0 percent nitrogen by weight. The Du Pont DMA additive containing 20 volume percent methanol is distributed by the Petroleum Chemicals Division of E. I. du Pont de Nemours & Co. of Wilmington. Del., and presented as DMA–4A in a bulletin dated Mar. 4, 1958. The surfactant labeled Lubrizol 545 is a tertiary alkyl amine having alkyl groups ranging from 12 to 14 carbon atoms and Lubrizol 575 is a commercial surfactant containing both nitrogen and phosphorous. Lubrizol 545 and Lubrizol 575 are distributed by Lubrizol Corporation of Cleveland, Ohio, and illustrated in Report No. 580, August 1962, and a bulletin dated Aug. 6, 1964, respectively.

TABLE I

Run No.	Composition of Fuel Additive Concentrate in Volume percent							0.5 wt. percent water added	Days to Form Precipitate		
	Methyl Diphenyl Phosphate	Du Pont DMA	Lubr. 545	Lubr. 575	Methyl Carbitol	Methyl Alcohol	Xylene		Light	Medium	Heavy
1	100.0							Yes	1	3-4	10
2	18.9				81.1			Yes	1	2-3	8-9
3	75.0					25.0		No	1	None	6
4	18.3	3.4			78.3			No	None	None	44-56
5	18.3	3.4			78.3			Yes	37-43	None	44-56
6	58.5	11.0				[1] 30.5		No	16.18	19-22	23-28
7	58.5	11.0				[1] 30.5		Yes	None	15-18	19-22
8	68.4		31.6					No	None	56-60	None
9	68.4		31.6					Yes	None	None	37-43
10	17.4		8.0		74.6			No	None	14-15	16-18
11	17.4		8.0		74.6			Yes	None	14-15	16-18
12	13.8			4.1	59.0		[1] 23.1	No	None	None	None
13	13.8			4.1	59.0		[1] 23.1	Yes	None	None	44-56
14	51.1			15.5		[1] 33.4		No	None	None	None
15	51.1			15.5		[1] 33.4		Yes	12-14	None	16-18

[1] Volume percent solvent required to prevent separation into two phases at 0° F.

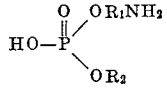
Referring to Table I, Run 1 illustrates that methyl diphenyl phosphate will begin to decompose in less than 1 day in the presence of water and Runs 3 and 4 illustrate that methyl diphenyl phosphate will begin to decompose forming a precipitate in a matter of hours in the presence of steel and either methyl Carbitol or methanol when unprotected in the presence of steel. Runs 4, 5, 6 and 7 show that the use of the Du Pont DMA surfactant in preparation of the fuel additive concentrate substantially inhibits decomposition as evidenced by the greatly increased interval before precipitation was observed. Runs 5 and 7 illustrate that even in the presence of added water, the Du Pont DMA surfactant substantially inhibits decomposition.

Runs 8, 9, 10 and 11 illustrate the beneficial effect of employing the Lubrizol 545 surfactant. As therein noted, the Lubrizol surfactant substantially inhibits the decomposition of methyl diphenyl phosphate in the fuel additive concentrate. Similarly, Runs 12, 13, 14 and 15 show that the Lubrizol 575 surfactant is also effective in extending the storability of methyl diphenyl phosphate-containing concentrate.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of the foregoing disclosure, without departing from the spirit or scope thereof.

I claim:

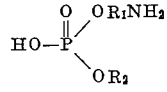
1. A fuel additive concentrate adapted to be diluted many times upon addition to a fuel, which concentrate contains a phosphate material selected from the group consisting of alkyl and alkyl aryl phosphates, an anti-icing additive consisting essentially of (1) a saturated acyclic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 2 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula $R(OCH_2CH_2)_xOH$, wherein: R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, and tolyl groups; where R is hydrogen, x is an integer of from 2 to 4; and when R is other than hydrogen, x is an integer of from 1 to 4, wherein the concentration of said alcohol in said anti-icing additive is in the range from about 0 to about 49 weight percent of said anti-icing additive and the concentration of said ether is in the range from about 100 to 51 weight percent of said anti-icing additive, and a surfactant consisting essentially of an aminoalkyl alkyl phosphate having the following structure:



wherein R_1 is an alkylene group containing from 4 to 22 carbon atoms per molecule and R_2 is an alkyl group having 4 to 22 carbon atoms per molecule, and the sum of the carbon atoms in both the R_1 and R_2 radicals is in the range of 20 to 30.

2. The fuel additive concentrate of claim 1 further comprising an inert diluent.

3. A fuel additive concentrate adapted to be diluted many times upon addition to a fuel, which concentrate contains a material selected from the group consisting of alkyl and alkyl aryl phosphates and an aminoalkyl alkyl phosphate having the following structure:

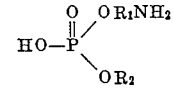


wherein R_1 is an alkylene group containing from 4 to 22 carbon atoms per molecule and R_2 is an alkyl group having 4 to 22 carbon atoms per molecule, and the sum of the carbon atoms in both the R_1 and R_2 radicals is in the range of 20 to 30.

4. The fuel additive concentrate of claim 3 wherein said aminoalkyl alkyl phosphate is methyl diphenyl phosphate.

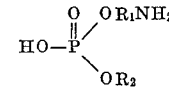
5. The fuel additive concentrate of claim 3 wherein the concentration of said aminoalkyl alkyl phosphate is from about 1 to about 50 volume percent.

6. A fuel additive concentrate consisting essentially of (1) a material selected from a group consisting of alkyl and alkyl aryl phosphates; (2) a glycol ether having the formula: $R(OCH_2CH_2)_xOH$, wherein R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, and tolyl groups; where R is hydrogen, x is an integer from 2 to 4; and when R is other than hydrogen, x is an integer of from 1 to 4; and (3) an aminoalkyl alkyl phosphate having the following structure:



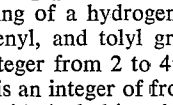
wherein R_1 is an alkylene group containing from 4 to 22 carbon atoms per molecule and R_2 is an alkyl group having 4 to 22 carbon atoms per molecule, and the sum of the carbon atoms in both the R_1 and R_2 radicals is in the range of 20 to 30.

7. A fuel additive concentrate adapted to be diluted many times upon addition to a fuel, which concentrate contains a first material selected from the group consisting of alkyl and alkyl aryl phosphates, a second material consisting essentially of (1) a saturated acyclic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 2 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula $R(OCH_2CH_2)_xOH$, wherein: R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, and tolyl groups; where R is hydrogen, x is an integer from 2 to 4; and when R is other than hydrogen, x is an integer of from 1 to 4, wherein the concentration of said alcohol in said second material is in the range of from about 0 to about 49 weight percent of said second material and the concentration of said ether is in the range of about 100 to 51 weight percent of said second material, and a third material consisting essentially of an aminoalkyl alkyl phosphate having the following structure:



wherein R_1 is an alkylene group containing from 4 to 22 carbon atoms per molecule and R_2 is an alkyl group having 4 to 22 carbon atoms per molecule, and the sum of the carbon atoms in both the R_1 and R_2 radicals is in the range of 20 to 30, and wherein the concentration of said first material is from about 5 to about 100 volume percent of the total concentration of said first material and said second material, the concentration of said second material is from about 0 to about 95 volume percent of the total concentration of said first material and said second material, and the concentration of said third material is from about 1 to about 50 volume percent of said fuel additive concentrate.

8. A fuel additive concentrate adapted to be diluted many times upon addition to a fuel, which concentrate contains a first material selected from the group consisting of alkyl and alkyl aryl phosphates, a second material consisting essentially of (1) a saturated acyclic polyhydroxy alcohol containing from 3 to 5 carbon atoms, from 2 to 5 OH groups each attached to different carbon atoms and wherein the ratio of OH groups to carbon atoms is in the range of 0.66:1 to 1:1, and (2) a glycol ether having the formula $R(OCH_2CH_2)_xOH$, wherein: R is selected from the group consisting of a hydrogen atom, methyl, ethyl, propyl, butyl, phenyl, and tolyl groups; where R is hydrogen, x is an integer from 2 to 4; and when R is other than hydrogen, x is an integer of from 1 to 4, wherein the concentration of said alcohol in said second material is in the range of from about 0 to about 49 weight percent of said second material and the concentration of said ether is in the range of about 100 to 51 weight percent of said second material, and a third material consisting essentially of an aminoalkyl alkyl phosphate having the following structure:



wherein R_1 is an alkylene group containing from 4 to 22 carbon atoms per molecule and R_2 is an alkyl group having 4 to 22 carbon atoms per molecule, and the sum of the carbon atoms in both the R_1 and R_2 radicals is in the range of 20 to 30, and an inert diluent, wherein the concentration of said first material is from about 5 to about 100 volume percent of the total concentration of said first material, said second material, and said inert diluent, the concentration of second material and said inert diluent is from about 0 to about 95 volume percent of the total concentration of said first material, said second material, and said inert diluent, and the concentration of said third material is

from about 1 to about 50 volume percent of said fuel additive concentrate.

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