

1

3,577,228

SMOKE SUPPRESSANT FUEL MIXTURE

Charanjit Rai, Somerset, Sherman D. Collins, Edison, and Elmer J. Badin, Hightstown, N.J., assignors to Cities Service Oil Company, Tulsa, Okla.
No Drawing. Filed Jan. 3, 1969, Ser. No. 788,922
Int. Cl. C10I 1/18, 1/26

U.S. Cl. 44-76

25 Claims

ABSTRACT OF THE DISCLOSURE

A liquid fuel mixture having reduced soot and smoking characteristics comprises a major portion of a hydrocarbon fuel and a minor portion of a Group II-A metal organyl orthophosphate. Preferably, a barium salt of a dialkyl orthophosphoric acid is employed in amounts from about 0.1 to 2% by weight. Further improvement results when an ether, particularly a glycol ether, is additionally incorporated into the orthophosphate and fuel mixture.

BACKGROUND OF THE INVENTION

This invention relates to smoke and soot suppressant compositions. In particular, it relates to new metal orthophosphate smoke suppressants.

The petroleum industry has encountered serious problems in supplying the demand for middle distillate and heavy residual fuel oils suitable for injecting into compression ignition engines, which will not contribute materially to the pollution of the atmosphere through soot and smoke production. Coupled with this specific need for a diesel fuel mixture with reduced smoking characteristics, there is also an urgent need for liquid hydrocarbon fuel mixtures having reduced soot and smoke forming properties for spark ignition and jet engines.

Generally, the visible black soot and smoke emitted from engine exhausts, rather than the blue smoke occasionally emitted, is considered to be the major contributor to atmospheric pollution.

It has been proposed to employ certain metallic smoke suppressants in fuels, particularly diesel fuel, to reduce smoke and soot production; but a serious objection to these additives is that owing to their limited solubility in fuels, certain laborious, costly, and undesirable procedures are generally required to form a homogeneous fuel mixture of these additives acceptable to the petroleum industry.

Additionally, various agents have been added to fuels in order to provide added stability to the fuel while under storage or to aid in eliminating sludge formation under oxidizing conditions. Normally these agents vary in effectiveness and it is often necessary to use a number of additives in a single composition.

Accordingly, there exists an urgent need to produce a fuel mixture with reduced soot and smoke forming properties, free of side effects and deficiencies of the prior art.

SUMMARY OF THE INVENTION

It is an object of the invention to provide liquid hydrocarbon fuel mixtures, especially a diesel fuel mixture with reduced smoke and soot forming properties.

It is another object of this invention to provide a soot and smoke suppressant additive for fuels.

It is yet another object of this invention to provide an additive for internal combustion engines which reduces sludge formation in fuels.

It is an additional object of this invention to provide an easily formed fuel mixture, particularly a diesel fuel mixture, having reduced smoke and soot forming characteristics.

2

It is a further object of this invention to provide an additive which promotes stability toward water haze formation in fuels.

Other aspects, objects and advantages of this invention will be evident to those skilled in the art in view of this disclosure.

The above and other objects of this invention are met by a liquid fuel composition which comprises a major portion of a hydrocarbon fuel and a minor portion of a Group II-A metal organyl orthophosphate. Mixtures of diesel fuels and a salt having the following formula:



wherein each R is a hydrocarbyl group having from 1 to about 30 carbon atoms, M is a divalent Group II-A metal, n and n' each are integers from 0 to 2 and the total of n and n' is equal to 2, have particularly significant reduced smoke and soot forming properties. An especially effective mixture is a diesel fuel in admixture with from about 0.1 to 2% by weight of barium (II) bis[(di-2-ethylhexyl) orthophosphate].

Liquid hydrocarbon fuels having especially reduced soot and smoke characteristics are obtained when a fuel additive, comprising the aforesaid orthophosphates and an ether, is employed therein. Glycol ethers, particularly mono and dialkyl ethers of ethylene glycol, are the preferred ethers. Generally, the concentration of ether in the orthophosphate-fuel mixture is from about 0.05 to about 5% by weight. A particularly preferred mixture is a mixture of diesel fuel and from about 0.1 to 2% by weight, each, and especially from about 0.2 to 1% by weight each, of a Group II-A metal bis[dialkyl orthophosphate] and a glycol ether having from about 3 to 9 carbon atoms.

Use of a glycol ether as coadditive with the metal compound causes an unpredicted synergism of the effectiveness of the metal compound. Particularly useful in this synergism is the dimethyl ether of ethylene glycol.

In general, the Group II-A metals may be combined with any organyl orthophosphoric acid to form the salts employed in this invention. Such salts can be aliphatic or aromatic orthophosphates. For the purposes of this invention at least one acid group of the orthophosphate salt must be esterified and all or a portion of the acid groups of said salt may be esterified.

Illustrative of the Group II-A metal organyl orthophosphates are such monoacid trihydrocarbyl orthophosphates as:

beryllium[monoethyl monoacid orthophosphate][diethyl orthophosphate],
barium[monobutyl monoacid orthophosphate][dido-decyl orthophosphate],
calcium[monohexadecyl monoacid orthophosphate][dihexadecyl orthophosphate],
magnesium[monobenzyl monoacid orthophosphate][dicyclobutyl orthophosphate],
strontium[(mono-3-octylphenyl)monoacid orthophosphate][(di-3-octylphenyl) orthophosphate],
barium[monolinoleyl monoacid orthophosphate][dilinoleyl orthophosphate],
strontium[monopropenyl monoacid orthophosphate][di-2,4-dimethylhexyl) orthophosphate], and the like.

In the case of the Group II-A metal diacid dihydrocarbyl orthophosphates, wherein two phosphate moieties are connected to a divalent Group II-A metal, the free acid groups can both be present in one phosphate moiety or one free acid group can be present in each phosphate moiety.

Examples of the diacid dihydrocarbyl orthophosphates wherein the free acidic hydrogens are both present in one

phosphate moiety, said moiety being designated as a [diacid orthophosphate], are:

beryllium[diacid orthophosphate][diethyl orthophosphate],
magnesium[diacid orthophosphate][dioctacosyl orthophosphate],
strontium[diacid orthophosphate][dibenzyl orthophosphate],
calcium[diacid orthophosphate][(cyclohexyl)(oleyl) orthophosphate],
barium[diacid orthophosphate][(octynyl)(tetradecyl) orthophosphate], and the like.

Illustrative of the diacid dihydrocarbyl orthophosphates wherein there is one free acidic hydrogen per phosphate moiety, said moiety being designated as a [monohydrocarbyl monoacid orthophosphate], are:

barium bis[(mono-2,2,4-trimethylpentyl) monoacid orthophosphate],
calcium bis[(mono-3-methylhexyl) monoacid orthophosphate],
strontium bis[monoheptenyl monoacid orthophosphate],
magnesium[monononyl monoacid orthophosphate] [(mono-o-cresyl) monoacid orthophosphate],
beryllium bis[monocyclooctyl monoacid orthophosphate], and the like.

Exemplary of the triacid monohydrocarbyl orthophosphates are:

barium[diacid orthophosphate][monoisopentyl monoacid orthophosphate],
calcium[diacid orthophosphate][mono-octadecyl monoacid orthophosphate],
strontium[diacid orthophosphate][mononaphthyl monoacid orthophosphate],
magnesium[diacid orthophosphate][(mono-butylphenyl) monoacid orthophosphate],
magnesium[diacid orthophosphate][(mono-phenylhexyl) monoacid orthophosphate],
beryllium[diacid orthophosphate][(mono-2-ethylhexenyl) monoacid orthophosphate],
barium[diacid orthophosphate][(mono-2-ethylhexenyl) monoacid orthophosphate],
barium[diacid orthophosphate][monohexynyl monoacid orthophosphate], and the like.

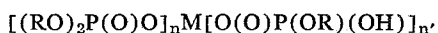
Illustrative of the fully esterified tetrahydrocarbyl orthophosphates are:

strontium bis[di(methylphenyl) orthophosphate],
calcium bis[di(p-pentylphenyl) orthophosphate],
barium bis[(2-ethylhexyl)(methylphenyl) orthophosphate],
magnesium bis[dioctenyl orthophosphate],
strontium bis[(butyl)(pentyl) orthophosphate],
barium bis[(isodecyl)(hexacosyl) orthophosphate], and the like.

It is to be understood, of course, that mixtures of Group II-A metal organyl orthophosphates may be employed wherein the Group II-A metal cations and/or the organyl orthophosphate anions are identical or different. For example, mixtures of the mono, di, tri, and tetra hydrocarbyl orthophosphates illustrated hereinbefore may be employed. The above salts are admixed with fuels, especially diesel fuels, to provide fuel mixtures with reduced soot and smoke forming properties.

DESCRIPTION OF PREFERRED EMBODIMENTS

Enhanced reduction of smoke and soot in fuels is obtained when the Group II-A metal salt employed has the following formula:



wherein each R is a hydrocarbyl group having from 1 to about 30 carbon atoms, M is a divalent Group II-A

metal, n and n' each are integers from 0 to 2 and the total of n and n' is 2.

Exemplary hydrocarbyl groups may include, for instance, aromatic and aliphatic groups such as: alkyl, aryl, alkaryl, aralkyl, alkenyl, alkynyl, or alicyclic hydrocarbyl radicals. Examples of suitable hydrocarbyl radicals are: ethyl; propyl; isopropyl; butyl; isobutyl; tert-butyl; pentyl; neopentyl; hexyl; isohexyl; heptyl; isoheptyl; 3-methylhexyl; 3,3-dimethylpentyl; octyl; 2,3-dimethylhexyl; 2,4-dimethylhexyl; 2-ethylhexyl; 2-ethylbutyl; nonyl; decyl; undecyl; dodecyl; tridecyl; tetradecyl; pentadecyl; hexadecyl; heptadecyl; octadecyl; nonadecyl; eicosyl; hencosyl; docosyl; tricosyl; tetracosyl; pentacosyl; hexacosyl; heptacosyl; octacosyl; nonacosyl; triacontyl; phenyl; naphthyl; benzyl; o-tolyl; p-cresyl; m-tolyl; dodecylphenyl; octylphenyl; ethylphenyl; diphenyl; phenylethyl; 2-phenylhexyl; cyclohexyl; cyclobutyl; cyclodecyl; cyclopentyl; butenyl; octenyl; 2,3-dimethylpentyl; 2-ethylhexenyl; linoleyl; oleyl; propynyl; pentynyl; 5-ethyl-1-hexynyl; and the like.

When $n'=2$ and $n=0$, typical salts include;

barium bis[monoheptyl monoacid orthophosphate],
strontium bis[(mono-hexacosyl) monoacid orthophosphate],
calcium bis[(mono-2-ethylphenyl) monoacid orthophosphate],
magnesium bis[(mono-3-ethylcyclohexyl) monoacid orthophosphate], and the like.

When $n'=1$ and $n=1$, illustrative salts are;

beryllium[dineopentyl orthophosphate][monoisobutyl monoacid orthophosphate],
barium[(di-2,2-dipropylhexyl) orthophosphate][mono-2,2-dipropylhexyl monoacid orthophosphate],
strontium[(di-3-dodecynyl) orthophosphate][(mono-3-dodecynyl) monoacid orthophosphate],
calcium[(propenyl)(decyl) orthophosphate][monodecyl monoacid orthophosphate],
magnesium[(di-3,3-diethylheptyl) orthophosphate][mono-3,3-diethylheptyl monoacid orthophosphate], and the like.

Enhanced results are obtained, and accordingly it is preferred when $n'=0$ and $n=2$. Exemplary salts are:

barium bis[(di-tetradecyl) orthophosphate],
strontium bis[(di-2-ethylnonyl) orthophosphate],
calcium bis[(phenyl)(butenyl) orthophosphate],
magnesium bis[dicyclopentyl orthophosphate],
beryllium bis[(di-β-methylnaphthyl) orthophosphate],
barium bis[(di-hencosyl) orthophosphate], and the like.

It is further preferred that each R is an alkyl group having from about 4 to 20 carbon atoms. Generally, branched chain aliphatic radicals and particularly those alkyl radicals branched in the alpha position are preferable, especially 2-ethylhexyl radicals. A mixture of diesel fuel and strontium (II) bis[(di-2-ethylhexyl) orthophosphate] exhibits especially reduced soot and smoke formation.

A particularly preferred orthophosphate is a barium orthophosphate, particularly a barium (II) bis[dialkyl orthophosphate]. Diesel fuel mixtures of such salts show unexpectedly enhanced smoke and soot suppression. Typical fuel mixtures include a diesel fuel and the following particularly preferred salts:

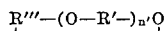
Barium bis[(di-2-methylpropyl) orthophosphate]
Barium bis[(di-2-ethylbutyl) orthophosphate]
Barium bis[(di-2-propylhexyl) orthophosphate]
Barium bis[(di-2-neopentyl) orthophosphate]
Barium bis[(di-2,2-dimethyldecyl) orthophosphate]
Barium bis[(di-2-methylnonadecyl) orthophosphate]

An especially preferred fuel mixture is a diesel fuel and barium (II) bis[(di-2-ethylhexyl) orthophosphate].

In another and more preferred embodiment of the invention, an ether is admixed with the aforementioned Group II-A metal organyl orthophosphates to form a

smoke and soot suppressant concentrate suitable for use in hydrocarbon fuels, particularly diesel fuels.

The ethers employed in the present invention are, in general, those having the following structural formula: $R(O-R')_nOR''$ wherein n is an integer preferably between about 0 to 10 and especially between about 1 to 3; R is a hydrocarbyl radical, R'' is hydrogen or hydrocarbyl radical, such that when n is a whole integer, R'' is hydrogen or hydrocarbyl, and when n is 0, R'' is hydrocarbyl, and R' is a hydrocarbylene radical, such as methylene, ethylene, or the like; and



wherein n' is an integer preferably having the value of 1 or 2, and R' and R'' are hydrocarbylene radicals; wherein the total number of carbon atoms in the molecule is preferably less than about 30.

Thus, when R and R'' are hydrocarbyl radicals, typical groups include, for instance: alkyl, alkenyl, aryl, alkaryl, aralkyl, or alicyclic radicals. Examples of suitable hydrocarbyl radicals are: methyl, ethyl, propyl, butyl, isohexyl, 2-ethylhexyl, neodecyl, dodecyl, octadecyl, eicosyl, nonacosyl, phenyl, naphthyl, benzyl, *o*-tolyl, ethylphenyl, phenylhexyl, cyclohexyl, cyclopropyl, cyclopentyl, butenyl, octenyl, linoleyl, etc.

When R' and R'' are hydrocarbylene radicals, typical groups include, for example: alkylene, arylene, alkarylene, aralkylene, alkenylene, or alicyclenyl radicals. Suitable hydrocarbylene radicals are: methylene, ethylene, tolylene, benzylidene, decylene, phenylene, cyclohexylene, pentenylene, etc.

Examples of simple ethers useful in this invention are: diethyl ether, diisopropyl ether, methyl tert-butyl ether, ethyl *n*-butyl ether, decyl butyl ether, nonacosyl methyl ether, allyl ethyl ether, vinyl isobutyl ether, cyclopropyl methyl ether, dicyclobutyl ether, methyl ethyl ether, benzyl methyl ether, benzyl ethyl ether, phenyl ether, anisole, bis(2-chloroisopropyl)ether, and the like.

Examples of heterocyclic ethers useful in this invention are: such heterocyclic monoethers as tetrahydrofuran; ethylene oxide; propylene oxide; furan; such heterocyclic diethers as para-dioxane; meta-dioxane; dioxolanes; 2-(3-heptyl) 1,3-dioxolane; 2-(3-heptyl) 1,3-dioxane-5-ol; 2-(3-heptyl) 1,3-dioxolane-4-methanol; and such heterocyclic triethers as sym-trioxane; ethyltrioxane; and the like.

Typical fuel additives of the invention include an ether and a Group II-A metal organyl orthophosphate, selected from the following examples, which may be admixed with a liquid hydrocarbon fuel to reduce smoke and soot therefrom.

Ether	Group II-A Orthophosphate
Diethyl ether.....	Barium(mono-heptadecyl) monoacid orthophosphate] [(di-heptadecyl) orthophosphate],
Hexyl pentyl ether.....	Strontium bis[(mono-phenylbutyl) monoacid orthophosphate],
Dipropyl ether of propylene glycol.	Calcium bis[(di-2-ethylhexyl) orthophosphate].
Monoethyl ether of decylene glycol.	Magnesium[diacid orthophosphate][dicyclopentyl orthophosphate].
Dibenzyl ether.....	Beryllium[dibenzyl orthophosphate][dihexenyl orthophosphate].
Benzyl ethyl ether.....	Barium bis[(di-2-ethylhexyl) orthophosphate].

Generally, the preferred ethers are those normally liquid mono- or diethers of polyols soluble in fuel, especially diesel fuel. Examples of these ethers are: monomethyl ether of diethylene glycol, monoethyl ether of diethylene glycol, dimethyl ether of propylene glycol, monomethyl ether of triethylene glycol, dimethyl ether of dipropylene glycol, and the like. Alkyl ethers of polyoxyalkylene glycols having from about 3 to 9 carbon atoms are particularly preferred.

Especially suitable ethers are the monoalkyl ethers of glycols, and in particular of ethylene glycol, such as: monoethylether of ethylene glycol, mono-2-ethylbutyl ether of ethylene glycol, mono-2-ethylpentyl ether of ethylene glycol, mono-2-methylhexyl ether of ethylene glycol, monoethyl ether of ethylene glycol, and monopropyl ether of propylene glycol; and the dialkyl ethers of glycols and, particularly, of ethylene glycol, such as dipropyl ether of ethylene glycol, diethyl ether of ethylene glycol, and ethyl butyl ether of ethylene glycol.

Fuel mixtures of Group II-A metal organyl orthophosphates and dialkyl ethers of ethylene glycol, and particularly of dimethyl ether of ethylene glycol, commonly called glyme, generally exhibit improved Cetane Numbers, as compared to liquid fuels without said ethers, as well as effective soot and smoke reductions. This improvement is also seen in such dialkyl ethers of polyoxyethylene glycols, as dimethyl ether of diethylene glycol, methyl ethyl ether of diethylene glycol, diethyl ether of diethylene glycol, and dimethyl ether of triethylene glycol, and the like. Accordingly, such ethers comprise another particularly preferred class of ethers.

An ether producing unusually good soot and smoke reduction in fuels in conjunction with the organyl orthophosphates is the monomethyl ether of ethylene glycol.

It will be recognized that the derivatives of the aforementioned ethers having groups, preferably polar, substituted in place of hydrogen may also be incorporated into fuels. Such substituents must be essentially non-reactive to fuel and include such polar groups as halogen, amino, nitro, nitrate, hydroxyl, and the like.

Preferred mixtures of the invention include the following and especially the last two mixtures.

- (1) Monomethyl ether of propylene glycol
Barium bis[(di-tridecyl) orthophosphate]
Diesel fuel
- (2) Diethyl ether of pentylene glycol
Barium bis[(di-2-propyldecyl) orthophosphate]
Diesel fuel
- (3) Monomethyl ether of triethylene glycol
Barium bis[(phenyl)(butyl) orthophosphate]
Diesel fuel
- (4) 1-methoxy-2-propanol
Barium bis[(di-2-ethylpentyl) orthophosphate]
Diesel fuel
- (5) Monomethyl ether of ethylene glycol
Barium bis[(di-2-butylhexadecyl) orthophosphate]
Diesel fuel
- (6) Monomethyl ether of ethylene glycol
Barium bis[(di-2-ethylhexyl) orthophosphate]
Diesel fuel
- (7) Dimethyl ether of diethylene glycol
Barium bis[(di-2-ethylhexyl) orthophosphate]
Diesel fuel

Generally, the Group II-A metal organyl orthophosphates of this invention are employed in fuels in amounts which produce effective visible black smoke and soot suppression. For this purpose, a minor amount of salt, usually about 0.05% by weight is employed. Although greater amounts may be employed, generally it is not necessary to use more than about 5% by weight.

It is preferred that the salts be employed in amounts from about 0.1 to 2% by weight. For best results it is preferred that the salts are employed in amounts from about 0.2 to 1% by weight. In the aforesaid fuel mixtures the weight percent of additive is based upon the weight of additives as compared to the total weight of the fuel mixture.

A synergistic interaction between the ethers and Group II-A metal organyl orthophosphates in fuel, resulting in unexpectedly greater smoke suppression, has been discovered. Though the weight ratio of ether to orthophosphate may vary widely, synergism is enhanced when the weight ratio of ether to orthophosphate is from about

10:1 to 1:10 and preferably from about 3:1 to 1:3. An increased synergistic interaction is obtained, especially in the case of the preferred glycol ether and barium hydrocarbyl orthophosphate concentrates, when the weight ratio of ether to orthophosphate is from about 2:1 to 1:2, and particularly about 1:1.

Usually the orthophosphate-ether concentrates are employed in fuels in amounts which provide significant smoke and soot suppression. Generally about at least 0.05% by weight each of ether and orthophosphate is employed. Although amounts in excess of about 5% by weight each of ether and orthophosphate is employed, practical smoke and soot suppression is obtained usually with lesser amounts.

It is preferred that the ethers, especially glycol ethers, and orthophosphates, particularly barium bis[di-alkyl orthophosphates], are each employed in amounts from about 0.1 to 2% by weight, and, for most practical purposes, from 0.2 to 1% by weight, wherein the above weights are based on the weight of component as compared to the total weight of the fuel mixture.

In order to enhance the solution of Group II-A metal salts in fuels, it may be necessary to premix the metal salt with a solubilizer, for instance, an inert petroleum solvent, such as petroleum ether, Varsol, white oil, ketones, alcohols, particularly glycols, other surfactants, dialkyl phthalates, and the like and mixtures thereof, in amounts sufficient to form a liquid concentrate with greater solubility in the fuel. On the other hand, the salt can be dispersed or dissolved in the fuel.

In order to form the ether-orthophosphate concentrates, the orthophosphates are generally dissolved or dispersed in the ether. If necessary, a solubilizer similar to those previously illustrated, may be employed to enhance the solution of the orthophosphate in the ether. Fuel mixtures of the ether and orthophosphate additives are formed generally, by either premixing the ethers and orthophosphates and adding the resulting concentrate to the fuel, or separately adding the ether and orthophosphate to the fuel.

In general, any liquid hydrocarbon fuel including gasolines and heating fuels, and particularly those fuels useful in internal combustion engines can be employed as the fuel component of the compositions of this invention. It is preferred that the liquid hydrocarbon fuel be a diesel fuel having an initial boiling point of about 300° F. and an end distillation point of about 750° F. Diesel fuels having a boiling range of from about 400° F. to about 675° F., such as No. 2 diesel fuel, are especially preferred.

The following examples are given to further illustrate the nature of the invention and are not limitative of scope.

EXAMPLE I

In order to evaluate the new smoke suppressant fuel mixtures, 0.258% by weight of barium (II) bis[di-2-ethylhexyl] orthophosphate] was dissolved in a diesel fuel at room temperature, and 0.252% by weight of strontium (II) bis[(di-2-ethylhexyl) orthophosphate] was dissolved in another portion of diesel fuel.

Synthesis of barium (II) bis[(di-2-ethylhexyl) orthophosphate] was carried out in the following manner: a solution of 1 mole di-2-ethylhexyl orthophosphoric acid in 2500 ml. benzene was mixed with a solution of 0.5 mole Ba(OH)₂·8H₂O in 1500 ml. water, the mixture was mechanically stirred at 50° C. for 2 hrs. after which it was cooled to room temperature and washed with 13 successive portions of water, the benzene solutions was clarified by filtration through diatomaceous earth, solvent removal was done by distillation in vacuo, and the white solid product remaining as residue was pulverized and dried in a vacuum desiccator. Yield of product was greater than 90%, and analysis of purified product showed 17.5% Ba as compared with 17.6% Ba theory. The strontium (II) analog was prepared in similar fashion. The metal compounds used in this example, and in following examples, were prepared by this procedure.

The diesel fuel employed was a No. 2 diesel fuel possessing the following characteristics:

(1) Gravity, ° API	32.9
(2) Flash point, ° F.	108
(3) Distillation:	
10% recovered, ° F.	419
90% recovered, ° F.	587
Residue, percent	1.5
(4) FIA, percent—	
Aromatic	31.0
Olefins	0
Saturates	69.0

The novel smoke suppressant mixtures were evaluated in a 4-cylinder John Deere Model 3020 tractor engine equipped with a Hartridge smoke meter. An exhaust probe was inserted in the exhaust pipe about 4 feet from the exhaust manifold. The probe was connected to a 2-way valve of the smoke meter.

Firstly, the engine was warmed up on the base fuel at a condition wherein no visible smoke was observed in the exhaust gases. The fuel flow was increased until it was about 22 pounds per hour corresponding generally to the appearance of visible black smoke in the exhaust gases.

The smoke suppressant fuel mixture of the invention was then substituted for the base fuel and the engine was run about 5 minutes to allow stabilization. The smoke meter reading was then recorded. The cycle of base fuel and additive fuel was repeated two additional times.

On the Hartridge Scale, the value of 100 represents completely black smoke while 30 and below represents a clear exhaust acceptable under all running conditions. Accordingly, each of the smoke meter readings was adjusted by subtracting from it the "no smoke" base of 30 to more clearly define the degree of smoke reduction obtained. This supplies an "adjusted Hartridge Smoke Number," denoted by "HSN_{adj.}" in the following expression which defines "Percent Visible Smoke Reduction."

$$\left[\frac{\text{HSN}_{\text{adj. base}} - \text{HSN}_{\text{adj. additive}}}{\text{HSN}_{\text{adj. base}}} \right] 100$$

The following table illustrates the effectiveness of the novel fuel mixtures. In the table the "adjusted Hartridge Smoke Numbers" are given as the average of three consecutive runs.

Additive in base fuel	Weight percent additive in fuel	HSN _{adj. base fuel}	HSN _{adj. fuel mixture}	Percent visible smoke reduction
Barium bis[(di-2-ethylhexyl) orthophosphate].....	0.258	32	23	28
Strontium bis[(di-2-ethylhexyl) orthophosphate].....	0.252	33	25	24

The results of the preceding example demonstrate the effectiveness of fuel mixtures of Group II-A metal hydrocarbyl orthophosphates, and especially diesel fuel mixtures of barium alkyl orthophosphates, in reducing smoke and soot. Similar results are also obtained when other Group II-A metal hydrocarbyl orthophosphates are substituted for the orthophosphates of the above example.

Illustrative of such orthophosphates are: beryllium bis[monobutyl monoacid orthophosphate], magnesium [diacid orthophosphate][dibenzyl orthophosphate], calcium bis[dipropenyl orthophosphate], barium bis[(di-2-ethylpentadecyl) orthophosphate], and barium[dicyclopentyl orthophosphate][(heptynyl)(tolyl) orthophosphate].

EXAMPLE II

In order to demonstrate the unexpectedly enhanced smoke and soot suppression obtained by the novel orthophosphate-ether additives, a selected quantity of barium (II) bis[(di-2-ethylhexyl) orthophosphate] was dissolved in the dimethyl ether of ethylene glycol, and the resulting liquid homogeneous concentrate was admixed with the

diesel fuel of Example I and tested according to the procedure of Example I. To show the unexpected enhancement in smoke and soot reduction obtained, separate tests were run on the individual components. The following table shows the results of the tests.

Additive in base fuel	Weight percent additive in fuel	HSN _{adj.} base fuel	HSN _{adj.} fuel mixture	Percent visible smoke reduction
Barium bis[(di-2-ethylhexyl) orthophosphate].....	0.258	28	16	43
Dimethyl ether of ethylene glycol.....	0.258			
Total.....	0.516			
Barium bis[(di-2-ethylhexyl) orthophosphate].....	0.258	32	23	28

When a solution of dimethyl ether of ethylene glycol in diesel fuel was tested, a smoke reduction much less than 1% was obtained, and, for the purpose of this test, the mix was rated at 0%. The results of this test demonstrate the synergism, resulting in enhanced smoke suppression, between Group II-A metal organyl orthophosphates and ethers in fuels, especially diesel fuels. When other combinations of orthophosphates and ethers are substituted for the barium dialkyl orthophosphate and glycol ether employed above, similar results are obtained. Exemplary of such ether-orthophosphate additive concentrates are:

- Barium bis[(mono-2,3-diethylhexadecyl)monoacid orthophosphate]
- Diethyl ether of ethylene glycol
- Strontium bis[(di-p-tolyl) orthophosphate]
- Monomethyl ether of propylene glycol
- Calcium bis[monobenzylmonoacid orthophosphate]
- Tetrahydrofuran
- Magnesium[diacid orthophosphate][dicyclohexyl-orthophosphate]
- Diethyl ether
- Beryllium[diacid orthophosphate][(di-2-ethyloctenyl)-orthophosphate]
- Anisole
- Barium bis[di-2,2-dibutyldodecyl] orthophosphate]
- Dimethyl ether of diethylene glycol

EXAMPLE III

In order to additionally demonstrate the smoke and soot suppressant fuel mixtures of this invention, a diesel fuel mixture was prepared by admixing selected quantities of barium (II) bis[(di-2-ethylhexyl) orthophosphate] and the monomethyl ether of ethylene glycol to form an additive concentrate, and thereafter dissolving said additive concentrate in a diesel fuel having similar characteristics to the fuel employed in Example I, and, in addition, containing 100 p.p.m. of an amine antioxidant.

The smoke suppressants were evaluated in a single cylinder cetane-type diesel engine equipped with a Hartridge Smoke Meter. An exhaust probe was inserted in the exhaust pipe about 4 feet from the exhaust manifold. The probe was connected to a 2-way valve of the smoke meter. Typical engine temperatures were:

	° F.
Intake air	150
Gallery oil	120-140
Coolant	212

Firstly, the engine was warmed up on the base fuel at a condition wherein no visible black smoke was observed in the exhaust gases. The fuel flow was increased until the fuel flow was about 13 cubic centimeters per minute, corresponding to the appearance of visible black smoke in the exhaust gases and a Hartridge Smoke Number (HSN) reading of about 40.

The smoke suppressant fuel mixture of the invention was then substituted for the base fuel and the engine was

run for about 5 minutes to allow stabilization. The smoke meter reading was then recorded. The cycle of base fuel and additive fuel was repeated two additional times.

The following table illustrates the effectiveness of the novel additive mixtures. In the table, the Hartridge Smoke number values, not adjusted, are given as the average of three consecutive runs. The "% Smoke Reduction" is defined by

$$\left[\frac{\text{HSN}_{\text{base}} - \text{HSN}_{\text{additive}}}{\text{HSN}_{\text{base}}} \right] 100$$

which is a measure of the efficiency of the novel fuel mixtures. The weight percent of additive is based on the weight of the metal orthophosphate as compared to the total weight of the fuel mixture. The results of the tests are set forth below.

Additive in base fuel	Weight percent additive in fuel	HSN, base fuel	HSN, fuel mixture	Percent smoke reduction
Barium bis[(di-2-ethylhexyl) orthophosphate].....	0.937	48	27	44
Monomethyl ether of ethylene glycol.....	0.937			
Total.....	1.874			
Barium bis[(di-2-ethylhexyl) orthophosphate].....	0.469			
Monomethyl ether of ethylene glycol.....	0.469	52	39	25
Total.....	0.938			

The results set forth in the preceding example further illustrate the effectiveness of Group II-A metal organyl orthophosphates and ethers in fuels.

EXAMPLE IV

In order to determine the stability of the novel fuel additives of this invention toward water contamination, a multiple-contact emulsion test was performed. This test measures the tendency for a treated fuel particularly a diesel fuel to form a fuel-in-water emulsion on contact with water.

In this test 0.937% by weight of barium bis[(di-2-ethylhexyl) orthophosphate] and 0.911 weight percent of monomethyl ether of ethylene glycol were admixed in diesel fuel. 100 milliliters of the diesel fuel mixture and 10 milliliters of distilled water were placed in an 8 ounce narrow neck bottle and shaken for about 5 minutes. Later the bottle was placed in an upright position in the dark and at the end of 24 hours the appearance of the fuel layer, fuel-water interface, and water layer were observed. After observation, the fuel layer was syphoned off and replaced with 100 ml. of fresh diesel fuel mixture test fuel. This procedure was repeated for a total of ten times and at the end of each 24 hour period the sample was rated according to the following scale, for which only the first four ratings are described although ratings go to 11.

Rating:	Description
0 -----	Clean break on the interface of fuel and water.
1 -----	Very slight skin on the fuel-water interface that does not break on tilting the bottle.
2 -----	Skin at fuel-water interface, heavier than rating 1 and usually accompanied with dirt and bubbles on the skin. No evidence of any white emulsion.
3 -----	First sign of white emulsion. Usually forms at the bottom and in the center of the bottle. It is circular in shape and approximately 1/4" to 1" in diameter.

As the ratings increase from 4 to 11, the emulsion formed becomes more extensive, and finally, at 11, is a mayonnaise type solid emulsion.

The treated fuel had a rating of 0. When the untreated fuel, the No. 2 diesel fuel of Example III was tested, the rating showed a value of 1, or a greater tendency to emulsify, than the treated fuel.

EXAMPLE V

In order to determine the relative stability of fuel additives of the invention under aging conditions involving air exposure and in order to evaluate the effectiveness of the novel fuel mixtures in inhibiting sludge formation and color degradation, the diesel fuel mixture described in the Example IV was subjected to the "300° F. Accelerated Fuel Oil Stability Test."

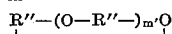
50 ml. of the diesel fuel mixture was filtered and aged in an oil bath held at 300° F. for 90 minutes. The sample was filtered under vacuum (16" hg.) through a 4.25 cm. No. 1 whatman paper held in millipore filter holder. The test tube that held the aged sample was rinsed with 3 ml. portions of n-heptane, each wash being transferred to the filter holder. The filter holder and papers were washed with n-heptane under vacuum until free of fuel oil. The filters were air dried under vacuum and compared with Pad Ratings of reference standards. A fuel having a Pad Rating of 7 or preferably lower is "passing." The results of the test showed that the base fuel had a Pad Rating of 6, while the base fuel-additive mixture had Pad Rating about 1.

If desired, the fuel compositions of this invention may additionally contain oxidation inhibitors, corrosion inhibitors, antifoam agents, other smoke suppressants, sludge inhibitors, color stabilizers, and other additional agents adapted to improve the fuels in one or more respects. Further, detergents, such as metal salts of monoesters of sulfuric acid with n-aliphatic alcohols containing from 8 to 18 carbons, metal salts of di-2-ethylhexyl sulfosuccinate, and especially Group II-A metals salts, particularly barium salts, and mixtures thereof may be additionally incorporated to the additives.

It will be understood that the specific embodiments set forth hereinabove are illustrative only and that the invention is not to be limited except as set forth in the following claims.

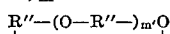
Therefore, we claim:

1. A smoke and soot suppressant additive suitable for liquid hydrocarbon fuels comprising a Group II-A metal hydrocarbyl orthophosphate and an ether selected from the group consisting of ethers having the structural formulas $R'(O-R'')_mOR'''$ and

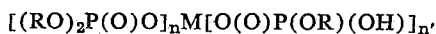


wherein m is an integer from 0 to about 10, m' is an integer from 1 to about 2, R' is a hydrocarbyl radical, R'' is a hydrocarbylene radical, and R''' is selected from the group consisting of hydrogen and a hydrocarbyl radical, and the weight ratio of ether to orthophosphate is from about 10:1 to 1:10.

2. A smoke and soot suppressant additive suitable for liquid hydrocarbon fuels comprising an ether selected from the group consisting of ethers having the structural formulas $R'(O-R'')_mOR'''$ and



wherein m is an integer from 0 to about 10, m' is an integer from 1 to about 2, R' is a hydrocarbyl radical, R'' is a hydrocarbylene radical, and R''' is selected from the group consisting of hydrogen and a hydrocarbyl radical; and a Group II-A metal hydrocarbyl orthophosphate having the following formula:



wherein each R is a hydrocarbyl group having from 1 to about 30 carbon atoms, M is a divalent Group II-A metal, n and n' each are integers from 0 to 2, such that the total of n and n' is equal to 2, and the weight ratio of ether to orthophosphate is from about 10:1 to 1:10.

3. The composition of claim 2 in which the Group II-A metal is barium.

4. The composition of claim 3 in which n is 2 and n' is 0 and the ether is a polyol ether having up to about 30 carbon atoms.

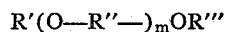
5. The composition of claim 4 in which the orthophosphate is a barium bis[dialkyl orthophosphate] wherein each alkyl group has from about 2 to about 20 carbon atoms and the ether is an alkyl ether of an alkylene glycol, said glycol ether having from about 3 to about 9 carbon atoms.

6. The composition of claim 5 in which the weight ratio of ether to orthophosphate is from about 2:1 to 1:2.

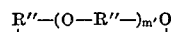
7. The composition of claim 6 in which the orthophosphate is barium bis[(di-2-ethylhexyl)orthophosphate] and the ether is the monomethyl ether of ethylene glycol.

8. The composition of claim 7 in which the dimethyl ether of ethylene glycol is substituted for the monomethyl ether of ethylene glycol.

9. A liquid fuel composition having reduced smoke and soot forming characteristics comprising a major portion of a liquid hydrocarbon fuel and a minor portion, respectively, of a Group II-A metal hydrocarbyl orthophosphate and an ether selected from the group consisting of ethers having the structural formulas

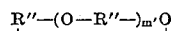


and



wherein m is an integer from 0 to about 10, m' is an integer from 1 to about 2, R' is a hydrocarbyl radical, R'' is a hydrocarbylene radical, and R''' is selected from the group consisting of hydrogen and a hydrocarbyl radical, and the weight ratio of ether to orthophosphate is from about 10:1 to 1:10.

10. A liquid fuel composition having reduced smoke and soot forming characteristics comprising a major portion of a diesel fuel and a minor portion, respectively, of an ether selected from the group consisting of ethers having the structural formulas $R'(O-R'')_mOR'''$ and



wherein m is an integer from 0 to about 10, m' is an integer from 1 to about 2, R' is a hydrocarbyl radical, R'' is a hydrocarbylene radical, and R''' is selected from the group consisting of hydrogen and a hydrocarbyl radical; and a Group II-A metal hydrocarbyl orthophosphate having the following structural formula:



wherein each R is a hydrocarbyl group having from 1 to about 30 carbon atoms, M is a divalent Group II-A metal, n and n' each are integers from 0 to 2, such that the total of n and n' is equal to 2, and the weight ratio of ether to orthophosphate is from about 10:1 to 1:10.

11. The composition of claim 10 in which the Group II-A metal hydrocarbyl orthophosphate and ether each are present in amounts from about 0.05 to about 5% by weight, wherein the weights are based on the total weight of the fuel mixture.

12. The composition of claim 11 in which the Group II-A metal is barium and the ether is a polyol ether having up to about 30 carbon atoms.

13. The composition of claim 12 in which n is 2 and n' is 0.

14. The composition of claim 13 in which each R is an alkyl group having from about 2 to about 20 carbon atoms and the ether is an alkyl ether of an alkylene glycol, said glycol ether having from about 3 to about 9 carbon atoms.

15. The composition of claim 14 in which the orthophosphate and ether are each present in amounts from about 0.1 to 2% by weight based on the total weight of the fuel mixture.

13

16. The composition of claim 15 in which the orthophosphate is barium bis[di-2-ethylhexyl] orthophosphate] and the ether is the monomethyl ether of ethylene glycol.

17. The composition of claim 16 in which the dimethyl ether of ethylene glycol is substituted for the monomethyl ether of ethylene glycol.

18. The composition of claim 2 in which the Group II-A metal is calcium.

19. The composition of claim 18 in which the orthophosphate is calcium bis[(di-2-ethylhexyl) orthophosphate] and the ether is selected from the group consisting of the monomethyl ether of ethylene glycol and the dimethyl ether of ethylene glycol.

20. The composition of claim 10 in which the Group II-A metal is calcium and the ether is a polyol ether having up to about 30 carbon atoms.

21. The composition of claim 20 in which the orthophosphate is calcium bis[(di-2-ethylhexyl) orthophosphate] and the ether is selected from the group consisting of the monomethyl ether of ethylene glycol and the dimethyl ether of ethylene glycol.

22. The composition of claim 2 in which the Group II-A metal is strontium.

23. The composition of claim 22 in which the orthophosphate is strontium bis[(di-2-ethylhexyl) orthophosphate] and the ether is selected from the group consisting of the monomethyl ether of ethylene glycol and the dimethyl ether of ethylene glycol.

14

24. The composition of claim 10 in which the Group II-A metal is strontium and the ether is a polyol ether having up to about 30 carbon atoms.

25. The composition of claim 24 in which the orthophosphate is strontium bis[(di-2-ethylhexyl) orthophosphate] and the ether is selected from the group consisting of the monomethyl ether of ethylene glycol and the dimethyl ether of ethylene glycol.

References Cited

UNITED STATES PATENTS

2,221,839	11/1940	Lipkin	44-57X
2,697,033	12/1954	Ambrose et al.	44-68
2,763,537	9/1956	Barusch et al.	44-57
3,334,978	8/1967	Revukas	44-68X
3,401,184	9/1968	Revukas	44-68X
3,437,465	4/1969	Le Suer	44-51
3,445,206	5/1969	Revukas	44-68X

DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. CI. X.R.

44-77