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3,594,136

SMOKE SUPPRESSANT ADDITIVES

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12 Claims

ABSTRACT OF THE DISCLOSURE

A smoke and soot suppressant additive for liquid fuel comprises an ether and a Group II-A metal carbonate. An especially suitable additive is barium carbonate and an alkyl ether of ethylene glycol, such as the dimethyl ether of ethylene glycol. Generally the carbonate is employed in amounts from about 0.1 to 1% by weight and the ether is employed in amounts from 0.1 to 1% by weight.

BACKGROUND OF THE INVENTION

This invention relates to new fuel additives. In particular, it relates to new additives which reduce soot and smoke from fuels, particularly diesel fuel.

The petroleum industry has encountered serious problems in supplying the demand for middle distillate and heavy residual oils suitable for injecting into compression ignition engines which will not contribute materially to the pollution of the atmosphere through smoke and soot production. Coupled with the specific need for a diesel fuel additive, there is also an urgent need for a fuel additive suitable for suppressing soot and smoke in liquid hydrocarbon fuels, particularly those fuels employed in spark ignition and jet engines. Attempts have been made to reduce the soot formed during oxidation of liquid hydrocarbon fuels. By way of example, certain metallic smoke suppressant mixtures containing barium carbonate have been employed in compression ignition engines, but objections to these mixtures are that they leave excessive deposits in engine crankcases as a result of blowby from cylinders, can be unduly expensive to produce and package, and can form undesirable combustion products in proportion to their content of metal. The metal content of typical commercial smoke suppressants is usually about 22% by weight.

Accordingly, there exists an urgent need to produce an improved hydrocarbon fuel additive, capable of suppressing smoke and soot formed by the operation of internal combustion engines and especially compression ignition engines, and having a reduced metal content.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a liquid hydrocarbon fuel additive and, particularly, a diesel fuel additive which can reduce visible black smoke and soot in exhausts of internal combustion engines.

It is another object of this invention to provide a barium carbonate containing smoke and soot suppressant of greater effectiveness with a reduced metal content.

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 fuel additive comprising an ether and a Group II-A metal carbonate. A preferred additive is barium carbonate and an alkyl ether of an alkylene glycol, said glycol ether having from 3 to 9 carbon atoms. An especially effective additive is a mixture of barium carbonate and the dimethyl ether of ethylene glycol, wherein the weight ratio of ether to barium carbonate is from about 2:1 to 1:2.

A fuel mixture having reduced soot and smoking

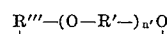
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characteristics is formed when the aforesaid Group II-A carbonate and ether mixtures are dispersed or dissolved in liquid hydrocarbon fuels. A preferred fuel mixture is a diesel fuel containing from about 0.1 to 1% by weight barium carbonate and from about 0.1 to 1% by weight of an alkyl ether of an alkylene glycol, said glycol ether having from about 3 to 9 carbon atoms.

It is a feature of this invention that the unexpected promotion of smoke and soot suppression in fuels obtained by employing the novel carbonate-ether additives disclosed herein permits a reduction in the metal content of commercial Group II-A metal carbonate, especially barium carbonate, fuel additives without sacrificing smoke suppression. Further the novel additives impart other beneficial properties to fuel mixtures, such as promotion of more uniform spray patterns and removal of deposits on injectors.

Typical Group II-A metal carbonates include beryllium carbonate, calcium carbonate, magnesium carbonate, and strontium carbonate. Basic Group II-A metal carbonates may also be employed. By way of example, basic beryllium carbonate, and basic magnesium carbonate are suitable. Further, hydrated forms of Group II-A metal carbonates and basic Group II-A metal carbonates are also employed, such as artinite and hydromagnesite. If desired, mixtures of the various Group II-A metal carbonates, basic carbonates and/or hydrated carbonates can also be employed.

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, usually between about 0 to 10 and preferably between about 1 to 3; R is a hydrocarbyl radical, R'' is either hydrogen or hydrocarbyl radical, when n is zero, R'' is a hydrocarbyl radical, when n is a whole integer, R'' is hydrogen or hydrocarbyl radical, and R' is a hydrocarbylene radical, such as methylene, ethylene or the like; and the total number of carbon atoms in a molecule is preferably less than about 30; and



wherein n' is an integer preferably having the value of 1 or 2, and R' and R''' are hydrocarbylene radicals.

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, 2-ethylhexyl, neodecyl, dodecyl, octadecyl, eicosyl, nonacosyl, phenyl, naphthyl, benzyl, tolyl, ethylphenyl, phenylhexyl, cyclohexyl, cyclopropyl, cyclopentyl, butenyl, octenyl, linoleyl, etc.

When R' and R''' are hydrocarbylene radicals, typical groups include for example: alkylene, arylen, alkarylene, aralkylene, alkenylene or alicyclene radicals. Suitable hydrocarbylene radicals are: methylene, ethylene, propylene, isohexylene, decylene, phenylene, cyclohexylene, pentenylene, etc.

Examples of simple ethers useful in this invention are: diethyl ether, isopropyl 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, diphenyl 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, dioxolane; 2-(3-heptyl) 1,3-dioxolane; 2-(3-heptyl) 1,3-dioxan-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 this invention employable in internal combustion engines include those formed by combining any Group II-A metal carbonate and any ether as set forth below.

Group II—A metal carbonates:

Beryllium carbonate
Strontium carbonate
Magnesium carbonate
Calcium carbonate
Barium carbonate

Ether:

Diethyl ether
Hexyl pentyl ether
Dipropyl ether of propylene glycol
Monomethyl ether of decylene glycol
Dibenzyl ether
Monomethyl ether of triethylene glycol

DESCRIPTION OF PREFERRED EMBODIMENTS

Enhanced reduction of smoke and soot from fuel combustion is obtained when a barium carbonate is employed as the Group II-A metal carbonate.

Generally the preferred ethers are those normally liquid mono or di ethers of polyols soluble in fuel. Examples of these ethers are: monomethyl ether of diethylene glycol, monoethyl ether of diethylene glycol, dimethyl ether of propylene glycol, monoethyl ether of triethylene glycol, diethyl ether of dipropylene glycol, monoethyl ether of triethylene glycol, diethyl ether of dipropylene glycol and alkylphenoxy polyethyleneoxy ethanols, 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: monoethyl ether of ethylene glycol, monopentyl ether of ethylene glycol, mono(2-ethylbutyl) ether of ethylene glycol, monopropyl ether of ethylene glycol, and monopropyl ether of propylene glycol; and the diethers of glycols and, particularly, of ethylene glycol, such as dibutyl ether of ethylene glycol.

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

Additionally, fuel mixtures of dialkyl ethers of ethylene glycol, and particularly of dimethyl ether of ethylene glycol, commonly called glyme, exhibit improved Cetane Numbers, as compared to diesel 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, diethyl ether of diethylene glycol, and dimethyl ether of triethylene glycol. Accordingly, such ethers comprise another particularly preferred class of ethers.

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, amine, nitro, nitrate, hydroxyl, and the like.

Preferred fuel additives include the following, especially the last two.

- (1) Barium carbonate; monomethyl ether of propylene glycol.
- (2) Barium carbonate; diethyl ether of pentylene glycol.
- (3) Barium carbonate; monomethyl ether of triethylene glycol.
- (4) Barium carbonate; monomethyl ether of ethylene glycol.
- (5) Barium carbonate; dimethyl ether of ethylene glycol.

Generally, the weight proportion of ether to Group II-A metal carbonate in the additives of this invention is from about 5:1 to 1:5 and preferably from 3:1 to 1:3. In the case of the barium carbonate and glycol ether ad-

ditive mixtures it is preferred that the weight ratio of ether to barium carbonate is from about 2:1 to 1:2.

Generally, the additive mixtures are employed in a quantity which produces significant reduction in the soot and smoke characteristics of the hydrocarbon fuel. For this purpose, generally about 0.05 to 5% by weight of Group II-A metal carbonate is employed and about 0.05 to 5% by weight of ether is employed. Although amounts in excess of 5% by weight of Group II-A metal carbonate may be employed, practical smoke and soot reductions are usually achieved with lesser amounts. Usually less than about 5% ether is employed, although greater amounts can be utilized.

Preferably the concentration of Group II-A metal carbonates is from about 0.1 to 1% by weight and the concentration of ether is from about 0.1 to 1% by weight.

It is particularly preferred that the Group II-A metal carbonate, especially barium carbonate, is employed in amounts from about 0.2 to 0.5% by weight and the ether, especially the alkyl ethers of alkylene glycols, is employed in amounts from about 0.2 to 0.5% by weight.

The previous weight percents are based upon the weight of metal carbonate or ether as compared to the total weight of the fuel mixtures.

In general, various methods can be employed for addition of the Group II-A metal carbonate and ether to fuel. For example, they can be added separately or individually or they can be premixed and then added. When the Group II-A metal carbonate is to be added separately to the fuel, it can be dispersed or suspended in the fuel by employing it in finely divided form, preferably below about 1 micron, and more preferably below 10^{-1} micron, and various surfactants and suspending agents can be employed to stabilize the dispersion, if necessary. Similarly, the Group II-A metal carbonate can be processed to a suitable particle size by employing conventional techniques, for example, mechanical disintegration, and then dispersed in the ether, aided by well known surfactants and suspending agents, and the resulting mix added to the fuel.

However, because of the inherent difficulty encountered in solubilizing Group II-A metal carbonates in ether and fuels, an advantageous mode for incorporating the carbonate into the fuels is to form the Group II-A metal carbonate in situ as a colloidal dispersion in the base fuel. For example, one can hydrolyze urea at elevated temperatures in the presence of a Group II-A metal oxide or hydroxide slurried in a solution of the base fuel with a suitable surface active material with addition of water to the mixture, and thereafter dehydrate the reaction mix, such method being more fully described, for example, in U.S. Pat. 3,321,399, the disclosure of said patent to the extent applicable being incorporated herein by reference. Other methods for the preparation of stable colloidal dispersions of metal carbonates in hydrocarbon fuels well-known to the art, can also be employed. The ether can then be added to the dispersion formed and the resulting mix added to the fuel in the proportions and in accordance with the invention as described herein. Thus, it is within the purview of this invention to include in the additive compositions those materials normally associated with the in situ production of the stable colloidal dispersion of the metal carbonate.

In general, any liquid hydrocarbon fuel including heating fuels and, particularly, those fuels useful in internal combustion engines, can be employed as the fuel to which the novel additives may be added. It is preferred that the liquid hydrocarbon fuel be diesel fuel having an initial boiling point from about 300° F. to an end distillation point of about 750° F. Diesel fuels having a boiling range 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.

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Example I

In order to evaluate the smoke and soot suppressants of this invention a diesel fuel mixture was prepared containing about 0.2% by weight of the dimethyl ether of ethylene glycol and about 0.208% by weight of commercially available smoke suppressant, a mixture of barium and calcium carbonates (21.6% Ba, 1.1% Ca) and a surfactant, a phenol, in petroleum solvent. The ether and carbonates were separately added to the diesel fuel.

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 aromatics	31.0
Percent olefins	0
Percent 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, the raw smoke values obtained from the

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Smoke Meter were subtracted from the "no smoke" base of 30 to more clearly define the degree of smoke reduction obtained. Use of this method gave an Adjusted Hartridge Smoke Number, labeled herein by HSH and percent Smoke Reduction is then defined by:

$$\frac{[HSN_{base} - HSN_{additive}]}{[HSN_{base}]} \times 100\%$$

The following table illustrates the effectiveness of the novel fuel mixture. In the table the Adjusted Hartridge Smoke Meter was subtracted from the "no smoke" base three consecutive runs.

Additive in base fuel	Weight percent		Adjusted HSN of base fuel	Adjusted HSN of fuel mixture	Percent visible smoke reduction
	Additive in fuel	Metal in fuel			
Metal carbonates (21.1% Ba 1.1% Ca)	0.208	0.04	33	10	70
Dimethylether of ethylene glycol	0.200				
Total	0.408				
Metal carbonates	0.208	0.04	31	12	61
Dimethyl ether of ethylene glycol	0.200		33	33	0

It should be noted that the components of the fuel mixture, when tested individually, showed less effectiveness in reducing visible soot and smoke than the combination thereof. This demonstrates that unexpected promotion of smoke and soot suppression is obtained when Group II-A metal carbonates and others are admixed in fuels.

The results of the preceding example demonstrate the enhanced effectiveness of fuel mixtures of Group II-A metal carbonates and of alkyl ethers of ethylene glycol, and especially fuel mixtures of dimethyl ether of ethylene glycol and barium carbonate, in reducing smoke and soot. Similar results are also obtained when other combinations of ethers and Group II-A carbonates are substituted for the carbonate and ether of the above example. Satisfactory results are obtained when other ethers such as methyl ethyl ether, diethyl ether of diethylene glycol, dioxane, and dibenzyl ether are substituted for the dimethyl ether of ethylene glycol, and other carbonates such as a beryllium carbonate and a strontium carbonate are substituted for the carbonate employed.

Example II

When the monomethyl ether of ethylene glycol was substituted for dimethyl ether of ethylene glycol in the previous fuel mixture and the resulting mixture tested according to the procedure of Example I, results are as follows:

Additive in base fuel	Weight percent		Adjusted HSN of base fuel	Adjusted HSN of fuel mixture	Percent visible smoke reduction
	Additive in fuel	Metal in fuel			
Metal carbonates (21.1% Ba 1.1% Ca)	0.208	0.04	32	10	69
Monomethyl ether of ethylene glycol	0.200				
Total	0.408				
Metal carbonates	0.208	0.04	31	12	61
Monomethyl ether of ethylene glycol	0.200		34	34	0

In the preceding examples, the ethers employed were assigned a zero rating for individual smoke reduction for comparative purposes.

Example III

In order to further demonstrate the effectiveness of the smoke and soot suppressants of this invention, selected quantities of a commercial barium carbonate smoke suppressant (22.5% Ba) and an ether were separately admixed with the No. 2 diesel fuel of Example I, and tested according to the procedure of Example I. The following results were obtained.

Additive in base fuel	Weight percent		Adjusted HSN of base fuel	Adjusted HSN of fuel mixture	Percent visible smoke reduction
	Additive in fuel	Metal in fuel			
Metal carbonate (22.5% Ba)...	0.2	0.04	34	13	62
Monomethyl ether of ethylene glycol.....	0.2	-----	-----	-----	-----
Total.....	0.4	-----	-----	-----	-----
Metal carbonate (22.5% Ba)...	0.2	0.04	33	13	61
Dimethyl ether of ethylene glycol.....	0.2	-----	-----	-----	-----
Total.....	0.4	-----	-----	-----	-----
Metal carbonate.....	0.2	0.04	34	15	56

The ethers employed were rated at 0% smoke reduction. The results clearly show that unexpected enhancement in smoke suppressancy of fuel mixtures of Group II-A metal carbonates occurs when ethers, particularly glycol ethers having from about 3 to 9 carbon atoms, are also employed.

If desired, the fuel compositions of this invention may additionally contain oxidation 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 formed from alcohols containing from 8 to 18 carbons, metal salts of di(2-ethylhexyl) sulfosuccinic acid, and especially Group II-A salts, particularly barium salts such as Group II-A metal phenoxides and sulfonates, and mixtures thereof may be additionally incorporated to the additives.

Mixtures of the Group II-A metal carbonates, such as barium carbonate and calcium carbonate, may be employed with the ethers of the invention. In this event the proportions of the Group II-A metal carbonates may vary widely.

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, I claim:

1. A smoke and soot suppressing additive suitable for hydrocarbon fuels comprising a Group II-A metal carbonate and an alkyl ether of an alkylene glycol, said glycol ether having up to 8 carbon atoms.

2. The composition of claim 1 in which the weight ratio of Group II-A metal carbonate to ether is from about 5:1 to 1:5.

3. The composition of claim 1 in which the Group II-A metal carbonate is barium carbonate.

4. A smoke and soot suppressing additive suitable for hydrocarbon fuels comprising an alkyl ether of an alkylene glycol, said glycol ether having up to 8 carbon atoms,

and barium carbonate wherein the weight ratio of ether to carbonate is from about 2:1 to 1:2.

5. The composition of claim 4 in which the ether is the dimethyl ether of ethylene glycol.

6. The composition of claim 4 in which the ether is the monomethyl ether of ethylene glycol.

7. A fuel composition having reduced smoking characteristics comprising a major portion of a liquid hydrocarbon fuel and a minor portion respectively of a Group II-A metal carbonate and an alkyl ether of an alkylene glycol, said glycol ether having up to 8 carbon atoms.

8. The composition of claim 7 in which the ether is present in amounts from about 0.05 to 5% by weight and the Group II-A metal carbonate is present in amounts from about 0.05 to 5% by weight wherein the weights are based on the total weight of the fuel mixture, and the liquid hydrocarbon fuel is a diesel fuel.

9. The composition of claim 8 in which the carbonate is a barium carbonate.

10. The composition of claim 9 in which the ether is present in amounts from about 0.1 to 1% by weight and the barium carbonate is present in amounts from about 0.1 to 1% by weight, based on the total weight of the fuel mixture.

11. A diesel fuel composition having reduced soot and smoke characteristics comprising diesel fuel, barium carbonate, and the dimethyl ether of ethylene glycol, wherein the barium carbonate is present in amounts from about 0.2 to 0.5% by weight and the ether is present in amounts from about 0.2 to 0.5% by weight wherein the weights are based on the total weight of the diesel fuel mixture.

12. The composition of claim 11 in which the monomethyl ether of ethylene glycol is substituted for the dimethyl ether of ethylene glycol.

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