

1

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## SMOKE SUPPRESSANT ADDITIVES FOR PETROLEUM FUELS

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6 Claims

### ABSTRACT OF THE DISCLOSURE

The invention disclosed herein is a liquid fuel composition comprising a liquid hydrocarbon fuel having a tendency to form soot and smoke on combustion and a metal salt of an alkanic acid, wherein the concentration of metal salt is at least sufficient, usually from 0.05 to 5% by weight, to inhibit said tendencies. Especially suitable compositions include a diesel fuel having from about 0.3 to 2% by weight of barium 2-ethylhexanoate and a diesel fuel having from about 0.1 to 2% by weight of calcium 2-ethylhexanoate admixed therein. Further improvement in soot and smoke reduction is obtained in hydrocarbon fuels and particularly in diesel fuels, when an ether is additionally incorporated into the salt and fuel mixture. A diesel fuel having from about 0.1 to 0.5% by weight of barium 2-ethylhexanoate and from about 0.3 to 0.6% by weight of the monomethyl ether of ethylene glycol exhibits substantially reduced smoke and soot forming characteristics.

### BACKGROUND OF THE INVENTION

This invention relates to new liquid fuel compositions. In particular, it relates to new diesel fuel mixtures with reduced smoke and soot forming properties.

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 this specific need for a diesel fuel mixture with reduced smoking characteristics, there is also an urgent need for liquid hydrocarbon fuel mixtures having improved combustion characteristics for spark ignition and jet engines.

Attempts have been made to reduce the soot formed during the combustion of liquid hydrocarbon fuels. By way of example, certain metallic smoke suppressant mixtures have been employed in compression ignition engines, but an objection to these mixtures is that they leave deposits in engine crankcases as a result of blowby from cylinders, can be expensive to produce and package, and can form undesirable combustion products in proportion to their content of metal. Further, it has been additionally proposed to incorporate various materials into fuels to inhibit their soot, sludge and clogging tendencies. However, some of these materials have proven susceptible to emulsification upon storage and, in certain cases have shown a tendency to lower the Cetane Number of diesel fuels, or reduce the Octane Number of gasoline, while others have reduced the stability of fuels to oxidation during storage.

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

### SUMMARY OF THE INVENTION

It is an object of this invention to provide a liquid hydrocarbon fuel mixture and in particular a diesel fuel mixture,

2

which has reduced smoke and soot forming properties.

It is another object of this invention to provide a fuel mixture having reduced soot and smoke forming characteristics which produces a minimum of ash upon combustion.

It is another object of this invention to provide a fuel mixture having reduced smoke characteristics which has improved oxygen stability as compared to the base fuel.

It is another object of this invention to provide a fuel composition having a Cetane Number and water tolerance characteristics at least equivalent to that of the base fuel, yet which exhibits reduced smoke and soot properties as compared to the base fuel.

It is another object of this invention to provide an improved method for operating an internal combustion engine, and particularly, a compression ignition engine.

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

The objects of this invention are met by dispersing or dissolving in liquid hydrocarbon fuels having a tendency to form soot and smoke on combustion, a metal salt of an alkanic acid wherein the concentration of said metal salt is at least sufficient to inhibit said tendencies. Diesel fuels having from about 0.05 to 5% by weight, of Group II—A metal alkanates have particularly significant reduced soot and smoke forming properties. Mixtures of diesel fuels and from about 0.3 to 2% by weight of barium 2-ethylhexanoate, or from about 0.1 to 2% by weight of calcium 2-ethylhexanoate are especially effective.

The soot and smoke forming tendencies of liquid hydrocarbon fuels may be further reduced by incorporating an ether into the aforesaid metal salt-fuel mixtures. Glycol ethers and particularly the mono and dialkyl ethers of ethylene glycol are preferred. In general, the concentration of ether in the fuel mixture should be from about 0.05 to 5% by weight and in the case of the preferred alkanic ethers of glycols, said ether is preferably present in amounts from about 0.1 to 1% by weight. A particularly preferred mixture is a mixture of diesel fuel and from about 0.1 to 0.5% by weight of barium 2-ethylhexanoate and from about 0.3 to 0.6% by weight of the monomethyl ether of ethylene glycol.

Nonetheless, according to the invention, there is provided a method for operating an internal combustion engine which comprises passing liquid hydrocarbon fuel mixture of the invention through the fuel supply system to the combustion chamber of said engine and causing ignition of the fuel therein in normal fashion. In particular, there is provided a method for operating a compression ignition engine which comprises passing a diesel fuel mixture of the invention through the fuel supply system to the combustion chamber of said engine and causing ignition of the fuel therein in normal fashion.

In general, metals may be combined with any alkyl carboxylic acid to form the alkanates employed in this invention. Some specific examples of acids are: ethanoic, propanoic, isobutanoic, 3-ethylhexanoic, 4-methyloctanoic, decanoic, dodecanoic, eicosanoic, 6-ethylhexadecanoic, octadecanoic, tricontanoic, and the like.

Examples of some specific salts which may be combined with liquid hydrocarbon fuels, especially diesel fuel, to form smoke suppressant mixtures include those formed by combining any of the metals with any of the acids set forth in the following table.

3

| Metals    | Acids                      |
|-----------|----------------------------|
| Cesium    | Ethanoic acid              |
| Rubidium  | Butanoic acid              |
| Titanium  | Hexanoic acid              |
| Zirconium | 4-ethyloctanoic acid       |
| Vanadium  | 3-methylpentanoic acid     |
| Tungsten  | 2-propyldecanoic acid      |
| Manganese | Tetradecanoic acid         |
| Iron      | Hexadecanoic acid          |
| Cadmium   | Docosanoic acid            |
| Silver    | 6-methylheptacosanoic acid |
| Tin       | Tricontoic acid            |
| Bismuth   | 2-methyltetracosanoic acid |

## DESCRIPTION OF PREFERRED EMBODIMENTS

Enhanced reduction of soot and smoke in fuels is obtained when Group III-A metal salts and Rare Earth metal salts and, particularly, Group II-A metals salts are employed. Examples of suitable salts include those formed by combining any of the Group II-A, III-A, and Rare Earth metals with any of the acids set forth in the following table:

| Metals     | Acids                        |
|------------|------------------------------|
| Beryllium  | Isopropanoic acid            |
| Magnesium  | 3-methylhexanoic acid        |
| Aluminum   | Heptanoic acid               |
| Gallium    | 3-ethyloctanoic acid         |
| Lanthanum  | Decanoic acid                |
| Cerium     | 4,4-diethylundecanoic acid   |
| Gadolinium | 2-propylhexadecanoic acid    |
| Lutetium   | Octadecanoic acid            |
|            | 1,3-propylheptadecanoic acid |

Generally, it is preferred that the alkanolic acids forming the salts be soluble in the hydrocarbon fuel mixture. Low molecular weight alkanolic acids, particularly those acids having from about 4 to 12 carbon atoms, are especially preferred.

Further improvement in smoke suppression is obtained when the metal salts of alkanolic acids, especially alkanolates having from 4 to 12 carbon atoms and particularly the Group II-A salts thereof, are branched in the alpha position. Particularly preferred Group II-A salts, are barium and calcium salts.

Examples of preferred salts are set forth below in which any of the metals may be combined with any of the acids to form the salts:

| Metals    | Acids                            |
|-----------|----------------------------------|
| Barium    | 2-methylbutanoic acid            |
| Strontium | 2-ethylpentanoic acid            |
| Calcium   | 2,3-dimethylbutanoic acid        |
|           | 2,2-dimethylhexanoic acid        |
|           | 2-methylhexanoic acid            |
|           | 2,2,3,3-tetramethylbutanoic acid |
|           | 2-ethyloctanoic acid             |

An especially preferred salt additive is a Group II-A salt of 2-ethylhexanoic acid and particularly calcium 2-ethylhexanoate. A further preferred salt additive is barium 2-ethylhexanoate.

It is to be recognized that the di and polycarboxylic homologs of those monocarboxylates already described, may be substituted therefor. Examples of such homologs include: barium butanedioate, calcium 2-ethylhexanedioate, cerium octanedioate, aluminum 2-hydroxy 1,2,3-propanetricarboxylate, and the like.

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

In another embodiment of the invention, an ether is

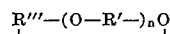
4

dissolved or dispersed in the mixtures of metal alkanolates and liquid hydrocarbon fuels hereinbefore described.

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;  $R$  is a hydrocarbyl radical,  $R'$  is either 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 0, 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, or alicyclic radicals. Examples of suitable hydrocarbyl radicals are: methyl, ethyl, propyl, butyl, isohexyl, 2-ethylhexyl, neodecyl, dodecyl, octadecyl, eicosyl, nonacosyl, phenyl, naphthyl, benzyl, cresyl, ethylphenyl, phenylhexyl, cyclohexyl, cyclopropyl, cyclopentyl, butenyl, octenyl, linoleyl, etc.

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

Examples of simple ethers useful in this invention are: ethyl 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, cyclobutyl 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, dioxolane, 2-(3-heptyl) 1,3-dioxolane; 2-(3-heptyl) 1,3-dioxan-5-ol, and such heterocyclic triethers as sym-trioxane, ethyltrioxane and the like.

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, monomethyl ether of triethylene glycol, diethyl ether of dipropylene glycol, and the like. Alkyl ethers of polyoxalkylene glycols having from about 3 to 10 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, mono(2-ethylhexyl) ether of ethylene glycol, monopentyl ether of ethylene glycol, and monopropyl ether of propylene glycol, and the diethers of glycols and, particularly, of ethylene glycol, such as dipropyl ether of ethylene glycol, diethyl ether of ethylene glycol, and dibutyl ether of ethylene glycol.

An ether producing unusually good soot and smoke reduction upon addition to diesel fuels 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 polyoxalkylene glycols as dimethyl ether of diethylene glycol, diethyl ether of diethylene glycol, dimethyl ether of triethylene glycol and dimethyl ether of tetraethylene 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, sub-

5

stituted 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.

Typical fuel mixtures of this embodiment of the invention, employable in internal combustion engines include those formed by combining any metal salt and any ether set forth below with a hydrocarbon fuel.

#### Salt:

Cesium propanoate  
Hafnium pentanoate  
Niobium heptanoate  
Molybdenum 3-propylheptanoate  
Rhenium 3-propylhexanoate  
Osmium 4-ethylundecanoate  
Rhodium tridecanoate  
Palladium 3-ethyl-5,5-dimethylhexadecanoate  
Gold eiconsanoate  
Mercury 3-methyl-4-ethylnonadecanoate  
Germanium tricontanoate  
Antimony 3-propyltetracosanoate

#### Ether:

Diethyl ether  
Methyl ethyl ether  
Propyl ether of propylene glycol  
Mono ethyl ether of decylene glycol  
Benzyl ether  
Benzyl ethyl ether  
Monophenyl ether of ethylene glycol  
Dioxane  
Trioxane  
Ethyldioxolane  
Diethyl ether of dipropylene glycol  
Monomethyl ether of tetrabutylene glycol

It is recognized, of course, that, as the fuel component of the mixture, such hydrocarbon fuels as diesel fuel, gasoline, jet fuel, benzene, etc., may be utilized, although diesel fuel is preferred.

Preferred fuel mixtures of this invention containing ethers include:

- (1) Calcium 2-methyldodecanoate; dioxane; hydrocarbon fuel.
- (2) Gallium heptanoate; methyl ethyl ether; hydrocarbon fuel.
- (3) Promethium 3-methyltridecanoate; cyclobutyl ether; hydrocarbon fuel.
- (4) Strontium 2-ethylundecanoate; monomethyl ether of triethylene glycol; hydrocarbon fuel.
- (5) Indium 4-ethylnonanoate; isopropyl ether; hydrocarbon fuel.
- (6) Samarium decanoate; tetrahydrofuran; hydrocarbon fuel.

Significant soot and smoke reductions are observed where the hydrocarbon fuel in the above fuel mixtures is a diesel fuel.

Especially suitable fuel mixtures of this invention include those formed by combining any of the barium salts and any of the ethers set forth below with a diesel fuel:

#### Salt:

Barium 2-ethylpentanoate  
Barium 2-methylhexanoate  
Barium 2-propyldecanoate  
Barium 2-ethyldecanoate

#### Ether:

Monomethyl ether of propylene glycol  
Dimethyl ether of ethylene glycol  
Monoethyl ether of dipropylene glycol  
Ethyl propyl ether of pentyleneglycol

A particularly preferred fuel composition is a mixture of diesel fuel, barium 2-ethylhexanoate, and the monomethyl ether of ethylene glycol.

6

Generally, the metal salts of this invention may be employed in amounts which produce effective soot and smoke suppression. For this purpose, a minor amount of salt, usually at least 0.05% by weight should be employed. Although greater amounts may be employed, generally it is not necessary to use more than about 5% by weight.

In the case of the preferred fuel mixtures, especially of barium 2-ethylhexanoate and diesel fuel, it has been found that best results are obtained when from about 0.3 to 2% by weight of salts is employed. In the case of the particularly preferred diesel fuel mixture of calcium 2-ethylhexanoate it has been found that best results are obtained when from about 0.1 to 2% by weight of salt is employed.

In the metal-salt fuel mixtures containing ethers, generally only a minor amount of salt, usually at least 0.01% by weight, need be employed. Although greater amounts may be employed, generally it is not necessary to use more than about 2% by weight.

In the preferred barium salt-diesel fuel mixtures containing ether, the salt should normally be employed in a concentration of about from 0.05 to 1% by weight.

In the case of the especially preferred diesel fuel mixture of ether and barium 2-ethylhexanoate, it has been found that best results are obtained when from about 0.1 to 0.5% by weight of salt is employed.

Generally, the ethers are employed in amounts necessary to produce a significant reduction in the smoke and soot characteristics of the fuel mixture. For this purpose, generally at least 0.05% by weight of ether should be used. Although amounts in excess of about 5% by weight may be employed, practical smoke and soot reductions are usually achieved with lesser amounts. For best results, it is preferred that the ether be employed in a concentration of from about 0.1 to 1% by weight.

In the case of the especially preferred diesel fuel mixture of barium 2-ethylhexanoate and monomethylether of ethylene glycol, it has been found that best results have obtained, when from about 0.3 to 0.6% by weight of the ether is employed and from about 0.2 to 0.5% by weight of salt is employed.

The weight percentage of salt additive is based upon the weight of salt as compared to the total weight of the fuel mixture. Similarly, the weight percentage of ether additive, is based on the weight of ether as compared to the total weight of the fuel mixture.

A synergistic effect resulting in improved soot and smoke reduction is observed when an ether is incorporated into the aforementioned salt-fuel mixtures. This effect is particularly evident when dialkyl ethers, particularly the mono and dialkyl ethers of ethylene glycol and, especially, the monomethyl ether of ethylene glycol, are employed.

To enhance the solution of metal salt in hydrocarbon fuels, particularly diesel fuels, it may be necessary to admix the metal salt with an inert petroleum solvent, such as petroleum ether, Varsol, White Oil, the aforementioned ethers, alcohols, especially glycols, and the like, and mixtures thereof, in amounts sufficient to form a liquid concentrate with greater solubility in these fuels. On the other hand, the salts can be dispersed in the fuel in finely divided form.

To prepare the fuel, salt, and ether mixtures advantageously, one may initially dissolve or disperse the metal salt in the ether and then combine said salt-ether concentrate with the liquid hydrocarbon fuel.

In general, any liquid hydrocarbon fuel including 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 300° F. and an end distillation point of about 750° F. Diesel fuels having a boiling range of from about 400° F. to 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 suppressants mixtures a, solution of barium 2-ethylhexanoate in the petroleum solvent (33% barium salt and 67% inert solvent) was added to a diesel fuel in appropriate amounts.

The diesel fuel employed was a No. 2 diesel fuel containing 110 parts per million of a known antioxidant additive, a 1,1-dimethylalkylamine added as a color stabilizer and antioxidant during fuel storage. The No. 2 diesel fuel possessed the following characteristics:

- (1) Cetane Number, minimum ----- 43
- (2) Flashpoint, ° F. minimum ----- 140
- (3) Distillation, 90% recovered, ° F. maximum -- 160
- (4) Viscosity, centistokes at 100° F. ----- 2.1-4.3
- (5) Carbon residue (10% bottoms) ----- 0.25

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 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 diesel fuel mixtures. In the table the Hartridge Smoke Number (HSN) values are given as the average of the three consecutive runs.

RESULT OF SMOKE SUPPRESSANT TESTS

| Additive in base fuel         | Weight percent of additive | HSN, base fuel | HSN' additive in base fuel |
|-------------------------------|----------------------------|----------------|----------------------------|
| Barium 2-ethylhexanoate-----  | 0.24                       | 55             | 36                         |
| Calcium 2-ethylhexanoate----- | 0.16                       | 45             | 19                         |
| Do-----                       | 1.3                        | 42             | 9                          |

The value of 100 on the Hartridge Smoke Number Scale represents completely black smoke, and 30 and below represents a clear exhaust acceptable under all running conditions.

The weight percent of additive is based on the weight of the salt as compared to the total weight of the diesel fuel mixture.

The results as set forth in the preceding examples demonstrate the effectiveness of diesel fuels containing Group II-A metal salt, and particularly barium 2-ethyl-

hexanoate or calcium 2-ethylhexanoate, in reducing soot and smoke formation. Similar results are obtained when other metal salts are substituted for the barium and calcium salts in the above example.

Thus, when the salts formed by the combination of the metals and acids listed below are substituted for the barium and calcium 2-ethylhexanoates employed in Example I, satisfactory results are obtained.

#### Metals:

Cesium  
Scandium  
Dysprosium  
Tantalum  
Chromium  
Technetium  
Ruthenium  
Cobalt  
Nickel  
Gold  
Cadmium  
Aluminum  
Tin  
Bismuth

#### Acids:

Isopropanoic acid  
Pentanoic acid  
Octanoic acid  
3,3-dimethylhexanoic acid  
2-ethyldecanoic acid  
2,2-diethylpentadecanoic acid  
2-ethyloctadecanoic acid  
3-propyleicosanoic acid  
Octacosanoic acid  
2,2-diethylundecanoic acid  
3-propyl-5-ethyloctanoic acid  
6-butylnonadecanoic acid  
2,2-diethylhexanoic acid  
2-ethyl-2-methylhexanoic acid

#### Example II

In order to demonstrate the smoke and soot reduction in mixtures of hydrocarbon fuels, metal salts and ethers, a diesel fuel mixture was prepared as follows:

About 33 parts by weight of barium 2-ethylhexanoate was admixed with about 66.7 parts by weight of the monomethyl of ethylene glycol. Selected quantities of this concentrate were mixed with the No. 2 Diesel Fuel described in Example I and introduced into a cetane engine according to the procedure of Example I. A mixture of the No. 2 Diesel Fuel of Example I and 0.7% by weight of a commercially available smoke suppressant was tested as a reference. This mixture was substituted in place of the additive mixtures in the cetane engine after each run.

The "Percent effectiveness" is represented by the equation.

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

and is a measure of the efficiency of the novel fuel mixtures, as compared to a commercial smoke suppressant fuel mixture. The weight percent of additive is based on the weight of the metal salts as compared to the total weight of the fuel and salts.

RESULTS OF SMOKE SUPPRESSANT TESTS

| Additive in base fuel                                                            | Weight percent of additive | HSN, base fuel | HSN, additive in base fuel | HSN, reference | Percent effectiveness |
|----------------------------------------------------------------------------------|----------------------------|----------------|----------------------------|----------------|-----------------------|
| 1. Barium 2-ethylhexanoate and monomethyl ether of ethylene glycol solution----- | 0.64                       | 52             | 7                          | 10             | 107                   |
| 2. Barium 2-ethylhexanoate and monomethyl ether of ethylene glycol solution----- | 0.41                       | 37             | 7                          | 5              | 91                    |
| 3. Monomethyl ether of ethylene glycol-----                                      | 0.50                       | 42             | 38                         | 8              | 12                    |
| 4. Barium 2-ethylhexanoate-----                                                  | 0.27                       | 55             | 36                         | 67             | 38                    |

It should be noted that the components of the fuel mixtures of this example, when tested individually in diesel fuel, showed much less effectiveness in reducing soot and smoke than the combination thereof. This demonstrates that synergism is obtained when metal salt-fuel mixtures have ethers additionally incorporated therein.

The results of the preceding example also demonstrate the effectiveness of fuel mixtures of alkyl ethers of ethylene glycol, and especially the monomethyl ether of ethylene glycol and of barium salts of low molecular weight alkanolic acids, particularly those branched in the alpha position in reducing smoke and soot. Similar results are also obtained when other combinations of ethers and Group II—A and Group II—B metal salts of organic acids are substituted for the salts and ethers in 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 monomethyl ether of ethylene glycol.

When other liquid hydrocarbon fuels, such as jet fuel, heating fuel, gasoline, etc., are substituted for the diesel fuel tested, the smoke and soot properties of these fuels are beneficially improved.

### Example III

In order to test the tolerance of the novel fuel additive mixtures of this invention to water, the additive mixture appearing in the table below was dissolved in 100 millimeters of the No. 2 Diesel Fuel previously described in Example I and 10 millimeters of water was added. The diesel fuel mixture was at room temperature when tested. The water and diesel fuel additive mixtures were shaken vigorously and allowed to settle. The mixture was observed at periodic intervals for ten (10) days. The results of the test after 15 minutes are described in the table below.

| Additives in base fuel               | Weight percent of additive | Water break at oil water interface | Oil phase |
|--------------------------------------|----------------------------|------------------------------------|-----------|
| Barium 2-ethylhexanoate.....         | 0.16                       | Sharp.....                         | Clear.    |
| Methyl ether of ethylene glycol..... | 0.41                       | Sharp.....                         | Do.       |
| No. 2 Diesel Fuel.....               |                            | Sharp.....                         | Do.       |

Upon standing for 10 days, no haze was observed in the oil phase.

### EXAMPLE IV

In order to determine the effect of the new salt-fuel mixtures on the Cetane Number of diesel fuel, a fuel mixture consisting of No. 2 Diesel Fuel of Example I, in admixture with 0.16% by weight of barium 2-ethylhexanoate and 0.1% by weight of the monomethyl ether of ethylene glycol was tested against the No. 2 Diesel Fuel of Example I. The Cetane Number of the No. 2 Diesel Fuel and the novel fuel mixture was determined by operating a single cylinder Cetane Test Engine in accordance with ASTM procedure D-613. The Cetane Number of the No. 2 base diesel fuel was  $43.0 \pm 1.0$ , while the Cetane Number of the aforementioned mixture was  $43.0 \pm 1.0$ .

### EXAMPLE V

In order to determine the relative stability of fuel mixtures of the invention under aging conditions involving air exposure and in order to evaluate the effectiveness of the additive in inhibiting residue formation and color degradation, the diesel fuel mixture described in the previous example was subjected to the Du Pont 300° F. Accelerated Fuel Oil Stability Test.

Fifty ml. of the diesel fuel mixture of Example IV 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 paper were washed with n-heptane under vacuum until free of fuel oil. The filter was air dried under vacuum and compared with reference standards. A fuel having a matching standard of No. 7 or lower is "passing." The No. 2 diesel fuel of Example IV was the base fuel. The results of the test showed that the base fuel had a Pad Rating of 7, while the base fuel additive mixture had a rating of 3.

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.

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 fuel composition comprising a liquid hydrocarbon fuel having a tendency to form soot and smoke on combustion, a Group II—A metal salt of an alkanolic acid, and an alkyl ether of a glycol having 3 to 10 carbon atoms, wherein said metal salt is present in amounts from about 0.01 to 2% by weight, said ether is present in amounts from about 0.05 to 5% by weight and the weight percentages of said salt and said ether are based on the total weight of the fuel mixture.

2. The composition of claim 1 wherein said alkanolic acid is branched in the alpha position, and said fuel is a diesel fuel.

3. The composition of claim 2 wherein said metal salt is a barium salt of a monoalkanoic acid having from about 4 to 12 carbon atoms, and said metal salt is present in amounts from about 0.05 to 1% by weight, said ether is present in amounts from 0.1 to 1% by weight, and the weight percentages of said salt and said ether are based on the total weight of the fuel mixture.

4. The composition of claim 3 wherein said metal salt is barium 2-ethylhexanoate, said ether is the monomethyl ether of ethyleneglycol, said barium salt is present in an amount from about 0.1 to 0.5% by weight, said ether is present in an amount from about 0.3 to 0.6% by weight and said weight percentages are based on the total weight of the fuel mixture.

5. In the method of operating an internal combustion engine wherein a liquid hydrocarbon fuel is passed through a fuel supply system into a combustion chamber of said engine and caused to ignite therein, the improvement comprising operating said engine on a liquid hydrocarbon fuel having a tendency to form soot and smoke on combustion containing a Group II—A metal salt of an alkanolic acid and an alkyl ether of a glycol having 3 to 10 carbon atoms wherein said metal salt is present in amounts from about 0.01 to 2% by weight, said ether is present in amounts from about 0.05 to 5% by weight and the weight percentages of said metal salt and said ether are based on the total weight of the fuel mixture.

6. In the method of operating a compression ignition engine wherein a diesel fuel is passed through a fuel supply system into a combustion chamber of said engine and caused to ignite therein, the improvement comprising operating said engine on a diesel fuel having a tendency to form soot and smoke on combustion containing barium 2-ethylhexanoate and the monomethyl ether of ethylene glycol, said barium salt is present in an amount from about 0.1 to 0.5% by weight, said ether is present in an amount from about 0.3 to 0.6% by weight and said weights are based on the total weight of the fuel mixture.

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11

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12

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44—70, 77