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(11) **EP 1 431 374 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
23.06.2004 Bulletin 2004/26

(51) Int Cl.7: **C10L 1/22, C10L 10/02**

(21) Application number: **03255769.6**

(22) Date of filing: **16.09.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: **20.12.2002 US 328115**

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(54) **A method of reducing particulate emissions in internal combustion engines**

(57) A method of reducing the particulate emissions in an internal combustion engine, said method comprising operating the internal combustion engine with a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an ef-

fective particulate emission-reducing amount of an alkylene oxide-adducted hydrocarbyl amide having from about 3 to 50 moles of alkylene oxide per mole of hydrocarbyl amide.

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Description

[0001] This invention relates to a method for reducing particulate emissions in an internal combustion engine. More particularly, this invention relates to a method for reducing particulate emissions in an internal combustion engine which comprises operating the internal combustion engine with a particulate emission-reducing fuel composition of the present invention.

BACKGROUND OF THE INVENTION

[0002] Millions of internal combustion engines are in operation worldwide for the purposes of transportation, power generation, and so on. These engines rely almost exclusively on hydrocarbon fuels such as gasoline or diesel. One of the drawbacks of the operation of these types of engines is due to the emissions they produce. Particulate emissions are solid or liquid emissions (which may form from emission gases either before or after emission from the engine exhaust system). Of particular concern are particles which are emitted in the size range below 100 nanometers. Particles in this size range are referred to as "ultrafine" and are the focus of a great deal of attention due to potential environmental and public health concerns.

[0003] In the past, changes in engine technology have been relied upon to reduce particulate emissions. Some examples of this are improved combustion chamber design, high pressure injection systems, and advanced engine control strategies. In addition, fuel and lube oil compositions have been changed in some cases (primarily through reduction of sulfur levels) to reduce these emissions. Currently, exhaust particulate filters are being proposed for use on a widespread basis to further reduce levels of particulate emissions.

[0004] One of the most fundamental methods for reducing particulate emissions is by improving the combustion properties of a fuel itself. Historically, the use of additives has been a common technique for improving the combustion performance of a given fuel for use in internal combustion engines. Although such additives (e.g. Ferrocene, Tetra-Ethyl Lead, MTBE, etc.) have been widely used, they often possess serious drawbacks (harmful to public health and the environment, excessive cost, hazardous storage/handling issues, damage to engine and exhaust system components, etc.). The additive disclosed and employed herein possesses none of these drawbacks, and can be used with a wide variety of other existing additives.

[0005] In order to produce a finished hydrocarbon fuel, the producer must highly refine a base feedstock (e.g. crude oil) to create a final product. The final properties of this fuel are largely determined by the refining process used in its production. By improving combustion performance, the additive employed in the present invention may be added to lower quality fuels to maintain adequate combustion performance of the finished fuel composition. This allows for a lower degree of base stock refining, thus reducing the total cost per volume required to produce a finished fuel.

SUMMARY OF THE INVENTION

[0006] The present invention provides a method for reducing particulate emissions in an internal combustion engine. More particularly, this invention relates to a method for reducing particulate emissions in an internal combustion engine which comprises operating the internal combustion engine with a fuel composition comprising:

- a). a major amount of hydrocarbons boiling in the gasoline or diesel range and
- b). an effective particulate emission-reducing amount of an alkylene oxide-adducted hydrocarbyl amide having from 3 to 50 moles of alkylene oxide per mole of hydrocarbyl amide.

[0007] In an alternative embodiment, the present invention is directed to the use of an alkylene oxide-adducted hydrocarbyl amide in a fuel composition to reduce particulate emissions in an internal combustion engine.

[0008] Among other factors, the present invention is based on the discovery that particulate emissions can be effectively reduced in internal combustion engines by employing the unique method described herein. Moreover, the method of the present invention is suitable for use in removing such particulate emissions in spark ignition engines (including conventional port fuel injection and direct injection spark ignition engines) and in compression ignition engines (including direct and indirect injection diesel engines as well as homogeneous charge compression ignition engines).

DETAILED DESCRIPTION OF THE INVENTION

[0009] As stated above, the present invention involves a method for reducing the particulate emissions in an internal combustion engine, such as gasoline or diesel engines, particularly port fuel injected spark ignition engines, direct injection spark ignition engines or compression ignition engines.

[0010] Prior to discussing the present invention in detail, the following terms will have the following meanings unless expressly stated to the contrary.

Definitions

[0011] The term "amino" refers to the group: -NH_2 .

[0012] The term "hydrocarbyl" refers to an organic radical primarily composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl or alkaryl. Such hydrocarbyl groups may also contain aliphatic unsaturation, i.e., olefinic or acetylenic unsaturation, and may contain minor amounts of heteroatoms, such as oxygen or nitrogen, or halogens, such as chlorine. When used in conjunction with carboxylic fatty acids, hydrocarbyl will also include olefinic unsaturation.

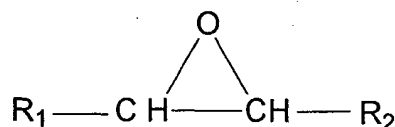
[0013] The term "alkyl" refers to both straight- and branched-chain alkyl groups.

[0014] The term "lower alkyl" refers to alkyl groups having 1 to about 6 carbon atoms and includes primary, secondary and tertiary alkyl groups. Typical lower alkyl groups include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

[0015] The term "polyalkyl" refers to alkyl groups which are generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene, butylene, and the like. Preferably, the mono-olefin employed will have from about 2 to 24 carbon atoms, and more preferably, from about 3 to 12 carbon atoms. More preferred mono-olefins include propylene, butylene, particularly isobutylene, 1-octene, and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, especially polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

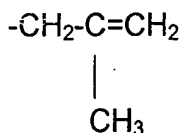
[0016] The term "alkenyl" refers to an alkyl group with unsaturation.

[0017] The term "alkylene oxide" refers to a compound having the formula:



wherein R_1 and R_2 are each independently hydrogen or lower alkyl having from 1 to about 6 carbon atoms.

[0018] The term "highly reactive polyisobutene" refers to a polyisobutene wherein at least about 20% of the residual olefinic double bonds are of the vinylidene type, i.e., represented by the formula:



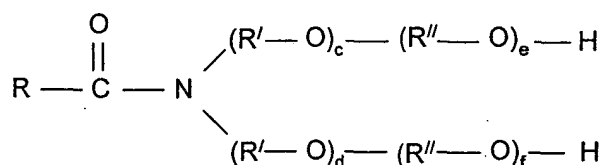
[0019] The term "succinimide" is understood in the art to include many of the amide, imide, etc. species that are also formed by the reaction of a succinic anhydride with an amine and is so used herein. The predominant product, however, is succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl- or alkyl-substituted succinic acid or anhydride with a polyamine. Alkenyl or alkyl succinimides are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 2,992,708; 3,018,250; 3,018,291; 3,024,237; 3,100,673; 3,172,892; 3,219,666; 3,272,746; 3,361,673; 3,381,022; 3,912,764; 4,234,435; 4,612,132; 4,747,965; 5,112,507; 5,241,003; 5,266,186; 5,286,799; 5,319,030; 5,334,321; 5,356,552; 5,716,912, the disclosures of which are hereby incorporated by reference.

[0020] The term "particulate emissions" refers to solid or liquid emissions which may form either from incomplete oxidation of carbon in the combustion chamber, or from precursors contained in the emission gases (either before or after emission from the engine exhaust system). Of particular concern are particles which are emitted in the size range below 100 nanometers.

[0021] The term "fuel" or "hydrocarbon-based fuel" refers to normally liquid hydrocarbons having boiling points in the range of gasoline and diesel fuels.

The Alkylene Oxide-Adducted Hydrocarbyl Amide

[0022] In its broadest aspect, the present invention employs a fuel composition containing an alkylene oxide-adducted hydrocarbyl amide having from about 3 to 50 moles, preferably from about 3 to 20 moles, more preferably from about 4 to 15 moles, of alkylene oxide per mole of hydrocarbyl amide. The alkylene oxide-adducted hydrocarbyl amides will have the following structure:



wherein,

R is a hydrocarbyl group having from about 4 to 75, preferably from about 6 to 24, most preferably from about 6 to 20, carbon atoms;

R' is a divalent alkylene group having from 1 to about 10, preferably from about 2 to 5, more preferably from about 2 to 3, carbon atoms;

R'' is a divalent alkylene group having from about 2 to 5, preferably from about 2 to 3, carbon atoms;

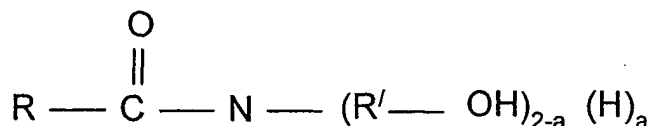
c and d are independently 0 or 1, preferably both are 1; and

e and f are independently integers from about 0 to 50, such that the total of e plus f ranges from about 3 to 50.

[0023] Preferably, the hydrocarbyl group, R, is alkyl or alkenyl, more preferably, alkyl.

[0024] Preferably, e and f are independently integers from about 0 to 20, such that the total of e plus f ranges from about 3 to 20. More preferably, e and f are independently integers from about 0 to 15, and that the total of e plus f ranges from about 4 to 15.

[0025] The hydrocarbyl amide of the present invention is typically the reaction product of a C₄ to C₇₅, preferably C₆ to C₂₄, more preferably C₆ to C₂₀, fatty acid or ester, and ammonia, or a mono- or di-hydroxy hydrocarbon amine, wherein the hydrocarbyl amide has the following structure:



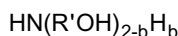
wherein R and R' are as defined above and a is an integer from about 0 to 2. Preferably, a is 0.

[0026] The acid moiety may preferably be RCO- wherein R is preferably an alkyl or alkenyl hydrocarbon group containing about 5 to 19 carbon atoms typified by caprylic, caproic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, etc. Preferably the acid is saturated although unsaturated acid may be present.

[0027] Preferably, the reactant bearing the acid moiety may be natural oil: coconut, babassu, palm kernel, palm, olive, castor, peanut, rape, beef tallow, lard, lard oil, whale blubber, sunflower, etc. Typically the oils which may be employed will contain several acid moieties, the number and type varying with the source of the oil.

[0028] The acid moiety may be supplied in a fully esterified compound or one which is less than fully esterified, e. g., glyceryl tri-stearate, glyceryl di-laurate, glyceryl mono-oleate, etc. Esters of polyols, including diols and polyalkylene glycols may be employed such as esters of mannitol, sorbitol, pentaerythritol, polyoxyethylene polyol, etc.

[0029] Ammonia or a mono- or di-(hydroxyhydrocarbon) amine with a primary or secondary amine nitrogen may be reacted to form the hydrocarbyl amides of the present invention. Typically, the mono- or di-(hydroxyhydrocarbon) amines may be characterized by the formula:



wherein R' is as defined above and b is 0 or 1.

[0030] Typical amines may include, but are not limited to, ethanolamine, diethanolamine, propanolamine, isopropa-

nolamine, dipropanolamine, diisopropanolamine, butanolamines etc.

[0031] Reaction may be effected by heating the oil containing the acid moiety and the amine in equivalent quantities to produce the desired product. Reaction may typically be effected by maintaining the reactants at about 100 °C. to 200 °C., preferably about 120 °C. to 150 °C. for 1 to about 10 hours, preferably about 4 hours. Reaction may be carried out in a solvent, preferably one which is compatible with the ultimate composition in which the product is to be used.

[0032] Typical reaction products which may be employed in the practice of this invention may include those formed from esters having the following acid moieties and alkanolamines:

TABLE 1

Acid Moiety in Ester	Amine
Lauric Acid	propanolamine
Lauric Acid	diethanolamine
Lauric Acid	ethanolamine
Lauric Acid	dipropanolamine
Palmitic Acid	diethanolamine
Palmitic Acid	ethanolamine
Stearic Acid	diethanolamine
Stearic Acid	ethanolamine

[0033] Other useful mixed reaction products with alkanolamines may be formed from the acid component of the following oils: coconut, babassu, palm kernel, palm, olive, castor, peanut, rape, beef tallow, lard, whale blubber, corn, tall, cottonseed, etc.

[0034] In one preferred aspect of this invention, the desired reaction product may be prepared by the reaction of (i) a fatty acid ester of a polyhydroxy compound (wherein some or all of the OH groups are esterified) and (ii) diethanolamine.

[0035] Typical fatty acid esters may include esters of the fatty acids containing about 6 to 20, preferably about 8 to 16, more preferably about 12, carbon atoms. These acids may be characterized by the formula RCOOH wherein R is an alkyl hydrocarbon group containing about 7 to 15, preferably about 11 to 13, more preferably about 11 carbon atoms.

[0036] Typical of the fatty acid esters which may be employed may be glyceryl tri-laurate, glyceryl tri-stearate, glyceryl tri-palmitate, glyceryl di-laurate, glyceryl mono-stearate, ethylene glycol di-laurate, pentaerythritol tetra-stearate, pentaerythritol tri-laurate, sorbitol mono-palmitate, sorbitol penta-stearate, propylene glycol mono-stearate.

[0037] The esters may include those wherein the acid moiety is a mixture as is typified by the following natural oils: coconut, babassu, palm kernel, palm, olive, castor, peanut, rape, beef tallow, lard (leaf), lard oil, whale blubber.

[0038] The preferred ester is coconut oil which contains the following acid moieties:

TABLE 2

Fatty Acid	Moiety Wt. %
Caprylic	8.0
Capric	7.0
Lauric	48.0
Myristic	17.5
Palmitic	8.2
Stearic	2.0
Oleic	6.0
Linoleic	2.5

[0039] Examples of desirable alkyl amides suitable for the present invention include, but are not limited to, octyl amide (capryl amide), nonyl amide, decyl amide (caprin amide), undecyl amide dodecyl amide (lauryl amide), tridecyl amide, tetradecyl amide (myristyl amide), pentadecyl amide, hexadecyl amide (palmityl amide), heptadecyl amide, octadecyl amide (stearyl amide), nonadecyl amide, eicosyl amide (alkyl amide), or docosyl amide (behenyl amide). Examples of desirable alkenyl amides include, but are not limited to, palmitolein amide, oleyl amide, isooleylyl amide, elaidyl amide, linolyl amide, linoleyl amide. Preferably, the alkyl or alkenyl amide is a coconut oil fatty acid amide.

[0040] The preparation of hydrocarbyl amides from fatty acid esters and alkanolamines is described, for example, in U.S. Patent No. 4,729,769 to Schlicht et al., the disclosure of which is incorporated herein by reference.

[0041] The alkylene oxide which is adducted to the hydrocarbyl amide is derived from an alkylene group having from about 2 to 5 carbon atoms. Preferably, the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, and pentylene oxide. Ethylene oxide and propylene oxide are particularly preferred. In addition, mixtures of alkylene oxides are desirable in which, for example, a mixture of ethylene oxide and propylene oxide may be used to form the alkylene oxide-adducted hydrocarbyl amide of the present invention. A respective molar ratio of from about 1:5 to 5:1 may be used in the case of a mixture of ethylene oxide and propylene oxide.

[0042] A desirable number of moles of the alkylene oxide to be adducted to the hydrocarbyl amide will be in the range of from about 3 to 50 moles of alkylene oxide per 1 mole of hydrocarbyl amide. More preferably, the range of from about 3 to 20 moles is particularly desirable. Most preferably, the range of from about 4 to 15 moles is most preferable as a molar range of the alkylene oxide per mole of hydrocarbyl amide.

[0043] Preferably, the alkylene oxide-adducted hydrocarbyl amide is derived from an alkylene oxide-adduction reaction involving a coconut oil fatty acid amide with ethylene oxide and propylene oxide. However, the alkylene oxide adducted hydrocarbyl amides useful as fuel additives in the present invention can be also a mixed product wherein various types and different moles of alkylene oxide and can be adducted to various types of hydrocarbyl amides.

[0044] The amount of alkylene oxide-adducted hydrocarbyl amide added in a hydrocarbon-based fuel will typically be in a range of from about 10 to 10,000 ppm by weight per weight (active component ratio). Preferably, the desired range is from about 10 to 5,000 ppm by weight, more preferably a range of from about 10 to 1,000 ppm by weight and most preferably a range from about 50 to 500 ppm by weight, based on the total weight of the fuel composition.

Other Additives

[0045] The fuel composition employed in the method of the present invention may also contain at least one nitrogen-containing detergent additive. Suitable detergent additives for use in this invention include, for example, aliphatic hydrocarbyl amines, hydrocarbyl-substituted poly(oxyalkylene) amines, hydrocarbyl-substituted succinimides, Mannich reaction products, nitro and amino aromatic esters of polyalkylphenoxyalkanols, polyalkylphenoxyaminoalkanes, polyalkylpyrrolidines, and mixtures thereof.

[0046] The aliphatic hydrocarbyl-substituted amines which may be employed in the present invention are typically straight or branched chain hydrocarbyl-substituted amines having at least one basic nitrogen atom and wherein the hydrocarbyl group has a number average molecular weight of about 700 to 3,000. Preferred aliphatic hydrocarbyl-substituted amines include polyisobutenyl and polyisobutyl monoamines and polyamines.

[0047] The aliphatic hydrocarbyl amines employed in this invention are prepared by conventional procedures known in the art. Such aliphatic hydrocarbyl amines and their preparations are described in detail in U.S. Patent Nos. 3,438,757; 3,565,804; 3,574,576; 3,848,056; 3,960,515; 4,832,702; and 6,203,584, the disclosures of which are incorporated herein by reference.

[0048] Another class of detergent additives suitable for use in the present invention are the hydrocarbyl-substituted poly(oxyalkylene) amines, also referred to as polyether amines. Typical hydrocarbyl-substituted poly(oxyalkylene) amines include hydrocarbyl poly(oxyalkylene) monoamines and polyamines wherein the hydrocarbyl group contains from 1 to about 30 carbon atoms, the number of oxyalkylene units will range from about 5 to 100, and the amine moiety is derived from ammonia, a primary alkyl or secondary dialkyl monoamine, or a polyamine having a terminal amino nitrogen atom. Preferably, the oxyalkylene moiety will be oxypropylene or oxybutylene or a mixture thereof. Such hydrocarbyl-substituted poly(oxyalkylene) amines are described, for example, in U.S. Patent No. 6,217,624 to Morris et al., and U.S. Patent No. 5,112,364 to Rath et al., the disclosures of which are incorporated herein by reference.

[0049] A preferred type of hydrocarbyl-substituted poly(oxyalkylene) monoamine is an alkylphenyl poly(oxyalkylene) monoamine wherein the poly(oxyalkylene) moiety contains oxypropylene units or oxybutylene units or mixtures of oxypropylene and oxybutylene units. Preferably, the alkyl group on the alkylphenyl moiety is a straight or branched-chain alkyl of 1 to about 24 carbon atoms. An especially preferred alkylphenyl moiety is tetrapropenylphenyl, that is, where the alkyl group is a branched-chain alkyl of about 12 carbon atoms derived from propylene tetramer.

[0050] An additional type of hydrocarbyl-substituted poly(oxyalkylene)amine finding use in the present invention are hydrocarbyl-substituted poly(oxyalkylene) aminocarbamates disclosed for example, in U.S. Patent Nos. 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930; 4,233,168; 4,197,409; 4,243,798 and 4,881,945, the disclosure of each of which are incorporated herein by reference.

[0051] These hydrocarbyl poly(oxyalkylene)aminocarbamates contain at least one basic nitrogen atom and have an average molecular weight of about 500 to 10,000, preferably about 500 to 5,000, and more preferably about 1,000 to 3,000. A preferred aminocarbamate is alkylphenyl poly(oxybutylene) aminocarbamate wherein the amine moiety is derived from ethylene diamine or diethylene triamine.

[0052] A further class of detergent additives suitable for use in the present invention are the hydrocarbyl-substituted succinimides. Typical hydrocarbyl-substituted succinimides include polyalkyl and polyalkenyl succinimides wherein the polyalkyl or polyalkenyl group has an average molecular weight of about 500 to 5,000, and preferably about 700 to

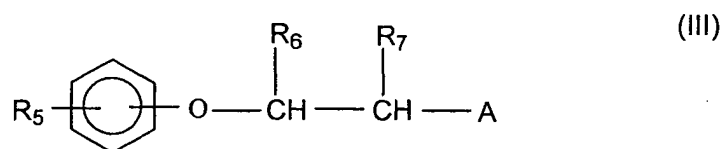
3,000. The hydrocarbyl-substituted succinimides are typically prepared by reacting a hydrocarbyl-substituted succinic anhydride with an amine or polyamine having at least one reactive hydrogen bonded to an amine nitrogen atom. Preferred hydrocarbyl-substituted succinimides include polyisobutenyl and polyisobutanyl succinimides, and derivatives thereof.

[0053] The hydrocarbyl-substituted succinimides finding use in the present invention are described; for example, in U.S. Patent Nos. 5,393,309; 5,588,973; 5,620,486; 5,916,825; 5,954,843; 5,993,497; and 6,114,542, and British Patent No. 1,486,144, the disclosure of each of which are incorporated herein by reference.

[0054] Yet another class of detergent additives which may be employed in the present invention is Mannich reaction products which are typically obtained from the Mannich condensation of a high molecular weight alkyl-substituted hydroxyaromatic compound, an amine containing at least one reactive hydrogen, and an aldehyde. The high molecular weight alkyl-substituted hydroxyaromatic compounds are preferably polyalkylphenols, such as polypropylphenol and polybutylphenol, especially polyisobutylphenol, wherein the polyalkyl group has an average molecular weight of about 600 to 3,000. The amine reactant is typically a polyamine, such as alkylene polyamines, especially ethylene or polyethylene polyamines, for example, ethylene diamine, diethylene triamine, triethylene tetramine, and the like. The aldehyde reactant is generally an aliphatic aldehyde, such as formaldehyde, including paraformaldehyde and formalin, and acetaldehyde. A preferred Mannich reaction product is obtained by condensing a polyisobutylphenol with formaldehyde and diethylene triamine, wherein the polyisobutyl group has an average molecular weight of about 1,000.

[0055] The Mannich reaction products suitable for use in the present invention are described, for example, in U.S. Patent Nos. 4,231,759 and 5,697,988, the disclosures of each of which are incorporated herein by reference.

[0056] A still further class of detergent additive suitable for use in the present invention are polyalkylphenoxyaminoalkanes. Preferred polyalkylphenoxyaminoalkanes include those having the formula:



wherein:

R_5 is a polyalkyl group having an average molecular weight in the range of about 600 to 5,000;

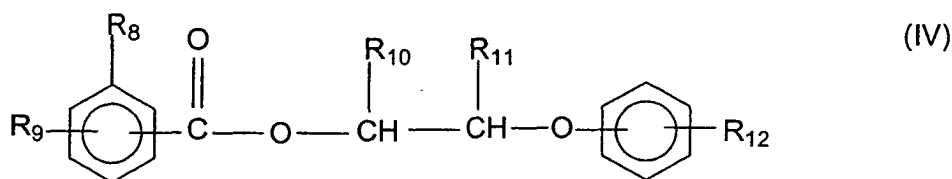
R_6 and R_7 are independently hydrogen or lower alkyl having 1 to about 6 carbon atoms; and

A is amino, N-alkyl amino having 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to 12 amine nitrogen atoms and about 2 to 40 carbon atoms.

[0057] The polyalkylphenoxyaminoalkanes of Formula III above and their preparations are described in detail in U.S. Patent No. 5,669,939, the disclosure of which is incorporated herein by reference.

[0058] Mixtures of polyalkylphenoxyaminoalkanes and poly(oxyalkylene) amines are also suitable for use in the present invention. These mixtures are described in detail in U.S. Patent No. 5,851,242, the disclosure of which is incorporated herein by reference.

[0059] A preferred class of detergent additive finding use in the present invention are nitro and amino aromatic esters of polyalkylphenoxyalkanols. Preferred nitro and amino aromatic esters of polyalkylphenoxyalkanols include those having the formula:



wherein:

R_8 is nitro or $-(CH_2)_n-NR_{13}R_{14}$, wherein R_{13} and R_{14} are independently hydrogen or lower alkyl having 1 to about 6 carbon atoms and n is 0 or 1;

R_9 is hydrogen, hydroxy, nitro or $-NR_{15}R_{16}$, wherein R_{15} and R_{16} are independently hydrogen or lower alkyl having 1 to about 6 carbon atoms;

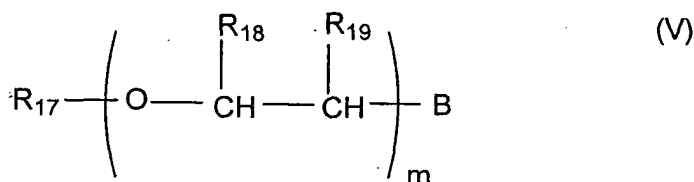
R_{10} and R_{11} are independently hydrogen or lower alkyl having 1 to about 6 carbon atoms; and

R_{12} is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

[0060] The aromatic esters of polyalkylphenoxyalkanols shown in Formula IV above and their preparations are described in detail in U.S. Patent No. 5,618,320, the disclosure of which is incorporated herein by reference.

[0061] Mixtures of nitro and amino aromatic esters of polyalkylphenoxyalkanols and hydrocarbyl-substituted poly(oxyalkylene) amines are also preferably contemplated for use in the present invention. These mixtures are described in detail in U.S. Patent No. 5,749,929, the disclosure of which is incorporated herein by reference.

[0062] Preferred hydrocarbyl-substituted poly(oxyalkylene) amines which may be employed as detergent additives in the present invention include those having the formula:



wherein:

R_{17} is a hydrocarbyl group having from 1 to about 30 carbon atoms;

R_{18} and R_{19} are each independently hydrogen or lower alkyl having about 1 to about 6 carbon atoms and each R_{18} and R_{19} is independently selected in each $-O-CH_{R_{18}}-CH_{R_{19}}-$ unit;

B is amino, N-alkyl amino having 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to 12 amine nitrogen atoms and about 2 to 40 carbon atoms; and

m is an integer from about 5 to 100.

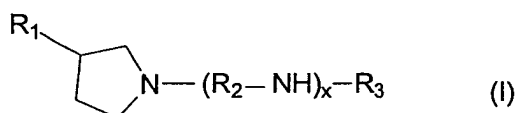
[0063] The hydrocarbyl-substituted poly(oxyalkylene) amines of Formula V above and their preparations are described in detail in U.S. Patent No. 6,217,624, the disclosure of which is incorporated herein by reference.

[0064] The hydrocarbyl-substituted poly(oxyalkylene) amines of Formula V are preferably utilized either by themselves or in combination with other detergent additives, particularly with the polyalkylphenoxyaminoalkanes of Formula III or the nitro and amino aromatic esters of polyalkylphenoxyalkanols shown in Formula IV. More preferably, the detergent additives employed in the present invention will be combinations of the hydrocarbyl-substituted poly(oxyalkylene) amines of Formula V with the nitro and amino aromatic esters of polyalkylphenoxyalkanols shown in Formula

IV. A particularly preferred hydrocarbyl-substituted poly(oxyalkylene) amine detergent additive is dodecylphenoxy poly(oxybutylene) amine and a particularly preferred combination of detergent additives is the combination of dodecylphenoxy poly(oxybutylene) amine and 4-polyisobutylphenoxyethyl para-aminobenzoate.

[0065] Another type of detergent additive suitable for use in the present invention are the nitrogen-containing carburetor/injector detergents. The carburetor/injector detergent additives are typically relatively low molecular weight compounds having a number average molecular weight of about 100 to 600 and possessing at least one polar moiety and at least one non-polar moiety. The non-polar moiety is typically a linear or branched-chain alkyl or alkenyl group having about 6 to 40 carbon atoms. The polar moiety is typically nitrogen-containing. Typical nitrogen-containing polar moieties include amines (for example, as described in U.S. Patent No. 5,139,534 and PCT International Publication No. WO 90/10051), ether amines (for example, as described in U.S. Patent No. 3,849,083 and PCT International Publication No. WO 90/10051), amides, polyamides and amide-esters (for example, as described in U.S. Patent Nos. 2,622,018; 4,729,769; and 5,139,534; and European Patent Publication No. 149,486), imidazolines (for example, as described in U.S. Patent No. 4,518,782), amine oxides (for example, as described in U.S. Patent Nos. 4,810,263 and 4,836,829), hydroxyamines (for example, as described in U.S. Patent No. 4,409,000), and succinimides (for example, as described in U.S. Patent No. 4,292,046).

[0066] Still other detergent additives useful in the present invention are polyalkylpyrrolidines, as described in U.S. Patent No. 6,033,446, the disclosure of which is incorporated herein by reference, having the following formula:



or a fuel-soluble salt thereof;
wherein

R_1 is a polyalkyl group having an average molecular weight in the range of from about 500 to 5,000;

R_2 is a straight- or branched-chain alkylene group having from about 2 to 6 carbon atoms;

R_3 is H or CH_3 ; and

x is an integer from 0 to about 4.

[0067] Preferably, R_1 is a polyalkyl group having an average molecular weight in the range of from about 500 to 3,000, more preferably from about 700 to 2,000, and most preferably from about 700 to 1,500.

[0068] In addition, R_1 is preferably a polyalkyl group derived from polypropylene, polybutene, or polyalphaolefin oligomers of 1-octene or 1-decene. More preferably, R_1 is a polyalkyl group derived from polyisobutene. Most preferably, R_1 is a polyalkyl group derived from a highly reactive polyisobutene containing at least about 20% of a methylvinylidene isomer.

[0069] Preferably, R_2 is a straight- or branched-chain alkylene group having from about 2 to 4 carbon atoms. Most preferably, R_2 contains about 2 or 3 carbon atoms.

[0070] Preferably, R_3 is H.

[0071] Preferably, x is an integer of from 0 to about 2. Most preferably, x is 0.

[0072] The fuel additive composition of the present invention can also be combined with one, two, or more other additives publicly known to be used in hydrocarbon-based fuels. Such additives include, but are not limited to, deposit control additives such as detergents or dispersants, corrosion inhibitors, oxidation inhibitors, metal deactivators, demulsifiers, static electricity preventing agents, anti-coagulation agents, anti-knock agents, oxygenates, flow improvers, pour point depressants, cetane improvers and auxiliary-solution agents.

[0073] Diesel fuels will typically contain various additives in conventional amounts. The additives include cold flow improvers, pour point depressants, storage stabilizers, corrosion inhibitors, anti-static agents, biocidal additives, combustion modifiers or smoke suppressants, dyes, and deodorants. Examples of such additives are known to the art as well as to the literature. Accordingly, only a few additives will be discussed in detail. Considering the storage stabilizers, they can include various antioxidants which prevent the accumulation of organic peroxides such as hindered phenols, N,N,-dialkyl paraphenylene diamines, paraamino phenols and the like. Color stabilizers constitute another group with specific examples including tertiary amines, secondary amines, imidazolines, tertiary alkyl primary amines, and the like. Another storage stabilizer group are the various metal deactivators for metals which serve as catalysts for oxidation during storage. Yet other storage stabilizers are the various dispersants which keep gummy, insoluble residues and other solids dispersed as small particles so that they do not interfere with the proper burning of the fuel. Such compounds can be oil soluble ethoxylated alkyl phenols, polyisobutylene alkylated succinimides, polyglycol, esters of alkylated succinic anhydrides, and the like.

[0074] Considering the corrosion inhibitors which generally retard the effects of oxygen and/or water, they are generally polar organic molecules which form a monomolecular protective layer over metal surfaces. Chemically, such corrosion inhibitors fall into three general classes: (1) complex carboxylic acids or their salts, (2) organic phosphorus acids and their salts, and (3) ammonium mahogany sulfonates.

[0075] Combustion modifiers for diesel fuel have been found to suppress the formation of black smoke, that is, unburned carbon particles, in the diesel engine. These additives are believed to not only catalyze the burning of carbon particles to CO₂, but also to suppress the formation of free carbon in the early stages of the combustion cycle. Generally, two different types of chemicals are effective in suppressing diesel smoke. The first type comprises barium and calcium salts in amine or sulfonate complexes while the other type consists of metal alkyls of transition elements such as manganese, iron, cobalt, nickel, and the like.

[0076] Amounts of the various fuel additives in the fuel can vary over a considerable range. Generally, a suitable amount of a diesel fuel stabilizer is from about 3 to about 300 ppm. A suitable amount of a corrosion inhibitor is from about 1 to about 100 ppm with a suitable amount of a smoke suppressant being from about 100 to about 5,000 ppm. Naturally, higher or lower amounts can be utilized depending upon the type of fuel, the type of diesel engine, and the like.

[0077] Diesel fuels may also contain various sulfur-free and sulfur-containing cetane improvers. Desirably, the sulfur-free compounds are nitrate cetane improvers which are known to the art as well as to the literature. For example, a description of such nitrate cetane improvers are set forth in U.S. Patent Nos. 2,493,284; 4,398,505; 2,226,298; 2,877,749; 3,380,815; an article "Means of Improving Ignition Quality of Diesel Fuels" by Nygarrrd et al, J. Inst. Petroleum, 27, 348-368 (1941); an article "Preliminary Reactions in Diesel Engines", Part 1, by Gardner et al, The Institute of Petroleum, Vol. 38, 341, May, 1952; and an article "Ignition Accelerators for Compression-Ignition Fuels" by Bogen et al, Petroleum Refiner 23, (7) 118-52 (1944), which are hereby fully incorporated by reference with regard to various types of nitrate cetane improvers. Generally, the cetane improvers are alkyl nitrates having from about 1 to about 18 carbon atoms and desirably from about 2 to about 13 carbon atoms. Examples of specific nitrate cetane improvers include ethyl nitrate, butyl nitrate, amyl nitrate, 2-ethylhexyl nitrate, polyglycol dinitrate, and the like. Amyl nitrate and 2-ethylhexyl nitrate are preferred. Sulfur-containing cetane improvers are described, for example, in U.S. Patent No. 4,943,303. Combinations of sulfur-containing cetane improvers with sulfur-free cetane improvers, such as nitrate cetane improvers, may also be employed in diesel fuels.

[0078] A fuel-soluble, nonvolatile carrier fluid or oil may also be used with the alkylene oxide-adducted hydrocarbyl amides employed in the present invention. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the nonvolatile residue (NVR), or solvent-free liquid fraction of the fuel composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, synthetic polyoxyalkylene-derived oils, such as those described, for example, in U.S. Pat. No. 4,191,537 to Lewis, and polyesters, such as those described, for example, in U.S. Pat. Nos. 3,756,793 and 5,004,478 to Robinson and Vogel et al., respectively, and in European Pat. Application Nos. 356,726 and 382,159, published Mar. 7, 1990 and Aug. 16, 1990, respectively.

EXAMPLES

[0079] The invention will be further illustrated by following examples, which set forth particularly advantageous method embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

Example 1

[0080] A method for measuring reduction in particulate emissions from an internal combustion engine using the current method for reduction of particulate emissions is described below. This example was performed using a 1998 Mitsubishi Carisma equipped with a 1.8 liter gasoline direct injection spark ignition engine. However, this is not limiting and such procedures could be modified by those with skill in the art to cover other engine types.

[0081] In order to simulate on-road operating conditions, the test vehicle is placed on a mileage accumulation chassis dynamometer. This dynamometer can be used to load the vehicle (according to a vehicle-specific road-load model) corresponding to cruising conditions at any desired speed.

[0082] In order to start the test, the vehicle fuel system is first drained, flushed of any residual fuel, then re-filled with the test fuel. At this point, the engine is started and the vehicle is operated at a speed of 50 kilometers per hour for 90 minutes to ensure that the engine and drivetrain are at full operating temperature.

[0083] Following this warm-up phase, the vehicle speed is brought to the first operating condition (see Table 3). The vehicle is allowed to operate at this condition for 15 minutes prior to the start of data collection. After the completion of data collection for the first condition, the vehicle is moved to each of the three remaining operating conditions sequentially, with data collection following the same 15 minute stabilization period. At the conclusion of data collection

for the final operating condition, the vehicle is run for 30 minutes at a speed of 50 kilometers per hour, then is shut down.

TABLE 3

Engine Test Operating Conditions		
Operating condition #	Vehicle Speed	Throttle position (% open)
1	40 km/h	3.7
2	60 km/h	4.9
3	80 km/h	6.5
4	100 km/h	13.9

[0084] To ensure that the vehicle is running properly, a number of critical engine temperatures and pressures (e.g. engine oil temperature and pressure, coolant temperature) are monitored throughout the test.

[0085] In order to measure particulate emissions, a portion of the engine exhaust gas is continuously extracted from the vehicle exhaust system (upstream of the catalytic converter) and is diluted with clean, filtered air to a ratio of approximately 500:1 in a standard free-jet dilution tunnel. A scanning mobility particle sizer (SMPS) is then used to measure the number-weighted particle size distribution in the size range from 5 to 80 nanometers. For each test operating condition, a total of ten size distribution measurements are collected; the total particle number concentration in this size range is then reported as an average of the ten measurements.

[0086] In order to evaluate reduction in particulate emissions, tests were conducted using two fuels. Fuel "A" was a typical, commercially available California reformulated base gasoline which contained no additives. Fuel "B" was the same base gasoline as fuel "A", with the addition of a coconut oil fatty acid diethanol amide adducted with 4 moles of propylene oxide at a concentration of 130 ppm. Each fuel was tested twice, in the following order: A - B - B - A. The results are shown in Table 4.

[0087] The results in Table 4 show a substantial reduction in the number of particles emitted by the engine in the size range from 5 to 80 nanometers when carrying out the method of the present invention.

TABLE 4
Measured particle number concentration and average particle
emissions reduction in the size range from 5 to 80 nm

Vehicle speed (km/h)	Particle conc., particles/cm ³ (Test #1, Fuel A)	Particle conc., particles/cm ³ (Test #2, Fuel B)	Particle conc., particles/cm ³ (Test #3, Fuel B)	Particle conc., particles/cm ³ (Test #4, Fuel A)	Average reduction in particulate emissions
40	1.44×10^6	1.37×10^5	3.98×10^5	9.41×10^5	77.5%
60	1.62×10^6	9.71×10^5	1.44×10^6	4.37×10^6	59.7%
80	7.23×10^5	6.92×10^4	6.54×10^4	2.05×10^6	95.1%
100	3.03×10^5	3.44×10^4	6.43×10^4	5.00×10^5	87.7%

Claims

- 5 **1.** A method of reducing the particulate emissions in an internal combustion engine, said method comprising operating the internal combustion engine with a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline or diesel range and an effective particulate emissions-reducing amount of an alkylene oxide-adducted hydrocarbyl amide having from about 3 to 50 moles of alkylene oxide per mole of hydrocarbyl amide.
- 10 **2.** The method according to Claim 1, wherein the alkylene oxide-adducted hydrocarbyl amide has from about 3 to 20 moles of alkylene oxide per mole of hydrocarbyl amide.
- 15 **3.** The method according to Claim 2, wherein the alkylene oxide-adducted hydrocarbyl amide has from about 4 to 15 moles of alkylene oxide per mole of hydrocarbyl amide.
- 20 **4.** The method according to Claim 1, wherein the alkylene oxide-adducted hydrocarbyl amide is derived from an alkyl or alkenyl amide having from about 4 to 75 carbon atoms.
- 25 **5.** The method according to Claim 4, wherein the alkylene oxide-adducted hydrocarbyl amide is derived from an alkyl or alkenyl amide having from about 8 to 22 carbon atoms.
- 30 **6.** The method according to Claim 5, wherein the alkyl or alkenyl amide is a coconut oil fatty acid amide.
- 35 **7.** The method according to Claim 6, wherein the coconut oil fatty acid amide is obtained by the reaction of coconut oil fatty acid or ester and diethanolamine.
- 40 **8.** The method according to Claim 1, wherein the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, or mixtures thereof.
- 45 **9.** The method according to Claim 8, wherein the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, or a mixture thereof.
- 50 **10.** The method according to Claim 1, wherein the alkylene oxide-adducted hydrocarbyl amide is derived from the reaction of a coconut oil fatty acid amide with ethylene oxide or propylene oxide.
- 55 **11.** The method according to Claim 1, wherein the fuel composition further comprises a nitrogen-containing detergent.
- 60 **12.** The method according to Claim 1, wherein the alkylene oxide-adducted hydrocarbyl amide is present in the fuel in the range of from about 10 to 10,000 ppm by weight.
- 65 **13.** The method according to Claim 12, wherein the alkylene oxide-adducted hydrocarbyl amide is present in the fuel in the range of from about 10 to 5,000 ppm by weight.
- 70 **14.** The method according to Claim 13, wherein the alkylene oxide-adducted hydrocarbyl amide is present in the fuel in the range of from about 10 to 1,000 ppm by weight.
- 75 **15.** The method according to Claim 14, wherein the alkylene oxide-adducted hydrocarbyl amide is present in the fuel in the range of from about 50 to 500 ppm by weight.
- 80 **16.** The method according to Claim 1, wherein the internal combustion engine is a port fuel injected spark ignition engine.
- 85 **17.** The method according to Claim 1, wherein the internal combustion engine is a direct injection spark ignition engine.
- 90 **18.** The method according to Claim 1, wherein the internal combustion engine is a compression ignition engine.
- 95 **19.** The method according to Claim 18, wherein the compression ignition engine is a diesel fuel engine.
- 100 **20.** The use of an alkylene oxide-adducted hydrocarbyl amide having from about 3 to 50 moles of alkylene oxide per mole of hydrocarbyl amide, in a fuel composition comprising major amount of hydrocarbons boiling in the gasoline

or diesel range, for the purpose of reducing the particulate emissions in an internal combustion engine.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 25 5769

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