

5                   **FUEL ADDITIVE COMPOSITION SUITABLE FOR**  
**CONTROL AND REMOVAL OF TENACIOUS ENGINE DEPOSITS**

**FIELD OF THE INVENTION**

10   This invention relates to fuel compositions employing a hydrocarbyl-substituted polyoxyalkylene amine and a glycol ether component useful for the prevention and control of engine deposits. Moreover, said fuel additive composition of the present invention can be used for the control and removal of existing tenacious engine deposits, and is particularly suited for controlling and removing piston ring groove deposits.

15                   **DESCRIPTION OF THE RELATED ART**

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports, intake valves, and combustion chambers, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art. However, even after employing fuel detergents, injectors and other components subject to heavy deposits and/or tenacious deposit regimes require occasional additional cleaning to maintain optimum performance.

30   For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing about 0.01 to about 0.25 volume percent of a high molecular weight aliphatic hydrocarbon-substituted

phenol in which the aliphatic hydrocarbon radical has an average molecular weight in the range of about 500 to about 3,500. This patent teaches that gasoline compositions containing minor amounts of an aliphatic hydrocarbon-substituted phenol not only prevent or inhibit the formation of intake valve and port deposits in a gasoline engine,  
5 but also enhance the performance of the fuel composition in engines designed to operate at higher operating temperatures with a minimum of decomposition and deposit formation in the manifold of the engine.

Polyether amine fuel additives are also well known in the art for the prevention and  
10 control of engine deposits. These polyether additives have a polyoxyalkylene "backbone", i.e., the polyether portion of the molecule consists of repeating oxyalkylene units. U.S. Patent No. 4,191,537, issued March 4, 1980 to Lewis et al., for example, discloses a fuel composition comprising a major portion of hydrocarbons boiling in the gasoline range and from 30 to 2,000 ppm of a hydrocarbyl  
15 polyoxyalkylene aminocarbamate having a molecular weight from about 600 to 10,000, and at least one basic nitrogen atom. The hydrocarbyl polyoxyalkylene moiety is composed of oxyalkylene units having from 2 to 5 carbon atoms in each oxyalkylene unit. These fuel compositions are taught to maintain the cleanliness of intake systems without contributing to combustion chamber deposits. Hydrocarbyl  
20 polyoxyalkylene aminocarbamate additives are further disclosed in U.S. Patent No. 4,881,945, issued November 21, 1989 to Buckley as well as U.S. Patent No. 4,270,930, issued June 2, 1981 to Campbell et al., discloses a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range and from 0.3 to 3 weight percent of a hydrocarbyl poly(oxyalkylene) aminocarbamate of  
25 molecular weight from about 600 to about 10,000 having at least one basic nitrogen atom, wherein the hydrocarbyl group contains from 1 to 30 carbon atoms.

U.S. Patent No. 5,112,364, issued May 12, 1992 to Rath et al., discloses gasoline-engine fuels which contain from 10 to 2,000 parts per million by weight of a  
30 polyetheramine and/or a polyetheramine derivative, wherein the polyetheramine is prepared by reductive amination of a phenol-initiated or alkylphenol-initiated polyether alcohol with ammonia or a primary amine.

- U.S. Patent No. 5,660,601, issued August 26, 1997 to Oppenlander et al., discloses fuels for gasoline engines containing from 10 to 2,000 mg per kg of fuel (i.e., 10 to 2,000 parts per million) of an alkyl-terminated polyetheramine, therein the alkyl group contains from 2 to 30 carbon atoms and the polyether moiety contains from 12 to 28 butylene oxide units. This patent further teaches that the polyetheramines are prepared by the reaction of an alcohol with butylene oxide, and subsequent amination with ammonia or an amine.
- 10 U.S. Patent No. 4,332,595, issued June 1, 1982 to Herbstman et al., discloses a gasoline detergent additive which is a hydrocarbyl-substituted polyoxypropylene diamine, wherein the hydrocarbyl substituent contains 8 to 18 carbon atoms. This patent further teaches that the additive is prepared by reductive amination of a hydrocarbyl-substituted polyoxypropylene alcohol with ammonia to give a
- 15 polyoxypropylene amine, which is subsequently reacted with acrylonitrile to give the corresponding N-2-cyanoethyl derivative. Hydrogenation in the presence of ammonia then provides the desired hydrocarbyl-substituted polyoxypropylene N-3-aminopropyl amine.
- 20 U.S. Patent No. 6,217,624, issued April 17, 2001 to Morris et al., discloses hydrocarbyl-substituted polyoxyalkylene amine prepared by reductive animation of the poly(oxyalkylene) alcohol. The additive is employed in concentrations in the fuel from 2,050 to about 10,000 parts per million by weight.
- 25 U.S. Patent No. 3,440,029, issued April 22, 1969 to Little et al., discloses a gasoline anti-icing additive which is a hydrocarbyl-substituted polyoxyalkylene amine, wherein the hydrocarbyl substituent contains 8 to 24 carbon atoms. This patent teaches that the additive may be prepared by known processes wherein a hydroxy compound is condensed with an alkylene oxide or mixture of alkylene oxides and
- 30 then the terminal amino group is attached by either reductive amination or by cyanoethylation followed by hydrogenation. Alternatively, the hydroxy compound or oxyalkylated derivative thereof may be reacted with bis(2-chloroethyl)ether and alkali to make a chlorine-terminated compound, which is then reacted with ammonia to

produce the amine-terminated final product. Similarly, U.S. Patent No. 5,089,029, issued February 18, 1992 to Hashimoto et al., discloses a fuel oil additive prepared by condensing an alcohol with an alkylene oxide followed by cyanoethylation and hydrogenation.

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U.S. Patent No. 4,247,301, issued January 27, 1981 to Honnen, discloses hydrocarbyl-substituted poly(oxyalkylene) polyamines, wherein the hydrocarbyl group contains from 1 to 30 carbon atoms and the polyamine moiety contains from 2 to 12 amine nitrogen atoms and from 2 to 40 carbon atoms. This patent teaches that the additives may be prepared by the reaction of a suitable hydrocarbyl-terminated polyether alcohol with a halogenating agent such as HCl, thionyl chloride, or epichlorohydrin to form a polyether chloride, followed by reaction of the polyether chloride with a polyamine to form the desired poly(oxyalkylene) polyamine. This patent also teaches at Example 6 that the polyether chloride may be reacted with ammonia or dimethylamine to form the corresponding polyether amine or polyether dimethylamine.

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U.S. Patent No. 5,749,929 issued May 12, 1998 to Cherpeck et al., discloses a fuel additive compositions containing an aromatic ester of polyalkylphenoxyalkanols with a poly(oxyalkylene) amine.

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U.S. Patent No. 5,752,991 issued May 19, 1998 to Plavac, discloses fuel compositions containing from about 50 to about 2,500 parts per million by weight of a long chain alkylphenyl polyoxyalkylene amine, wherein the alkyl substituent on the phenyl ring has at least 40 carbon atoms.

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#### SUMMARY OF THE INVENTION

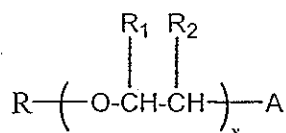
Disclosed herein are fuel compositions employing a hydrocarbyl-substituted polyoxyalkylene amine and a glycol ether component useful for the prevention and control of engine deposits. Moreover, said fuel additive composition can be used for the control and removal of existing tenacious engine deposits, and is particularly suited for controlling and removing piston ring groove deposits.

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Disclosed herein is a relatively high concentration of an additive package in a fuel, thus forming an effective deposit removing fuel composition.

In one aspect, there is provided a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range and

a) about 2,200 to 30,000 parts per million by weight of a hydrocarbyl-substituted polyoxyalkylene amine of the formula:



wherein:

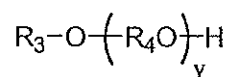
R is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or lower alkyl having from about 1 to about 6 carbon atoms and each R<sub>1</sub> and R<sub>2</sub> is independently selected in each -O-CHR<sub>1</sub>-CHR<sub>2</sub>- unit;

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

x is an integer from about 5 to about 100; and

b) about 1,000 to 60,000 parts per million by weight of at least one glycol ether component of the formula:



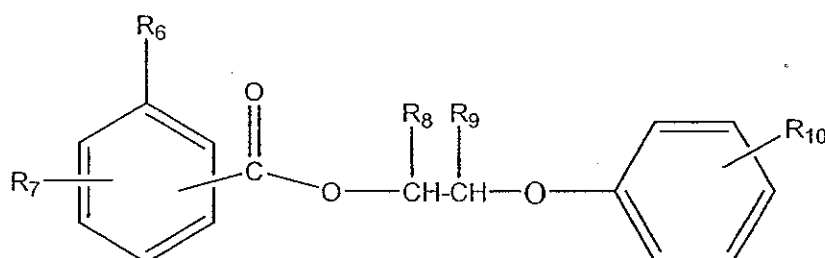
wherein:

R<sub>3</sub> is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

R<sub>4</sub> is a C<sub>2</sub> to C<sub>5</sub> alkylene group; and

y is an integer from 1 to 50.

- 5 In another embodiment disclosed herein, an additional component can be added to the fuel in conjunction with the hydrocarbyl-substituted polyoxyalkylene amine and glycol ether component described above. Also disclosed herein is a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range, components 1) and b) described herein above, and further comprising  
10 about 100 to 10,000 parts per million by weight of an aromatic ester compound of the formula:



- 15 wherein:

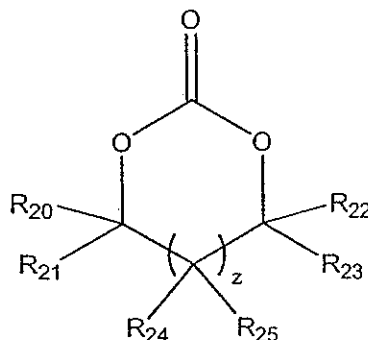
R<sub>6</sub> is nitro or -(CH<sub>2</sub>)<sub>n</sub>-NR<sub>11</sub>R<sub>12</sub>, wherein R<sub>11</sub> and R<sub>12</sub> are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and n is 0 or 1;

- 20 R<sub>7</sub> is hydrogen, hydroxy, nitro or -NR<sub>13</sub>R<sub>14</sub>, wherein R<sub>13</sub> and R<sub>14</sub> are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R<sub>8</sub> and R<sub>9</sub> are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

- 25 R<sub>10</sub> is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

In yet another embodiment, the disclosure is directed to a fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range, components a) and b) described herein above, and further comprising 100 to 15,000 parts per million by weight of a cyclic carbonate of the formula



wherein:

$R_{20}$ ,  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$ , and  $R_{25}$  are independently selected from hydrogen, hydroxy, hydroxymethyl, hydroxyethyl, hydrocarbyl group from about 1 to 6 carbon atoms; and  $z$  is an integer from zero to one.

Among other factors, the disclosure is based on the surprising discovery that fuel compositions containing high concentrations of certain hydrocarbyl-substituted polyoxyalkylene amines and at least one glycol ether component provide excellent control of engine deposits and is particularly suited for removal of deposits, especially piston ring groove deposits, piston top deposits, piston bowl deposits, as well as intake valve deposits and fuel injectors. Accordingly, the disclosed fuel compositions can be used for controlling or removing these deposits, especially piston ring deposits, by operating an engine with the disclosed fuel compositions.

#### DETAILED DESCRIPTION OF THE INVENTION

As used herein, the following terms have the following meanings unless expressly stated to the contrary.

#### DEFINITIONS:

The term "amino" refers to the group:  $--NH_2$ .

The term "N-alkylamino" refers to the group:  $--NHR_a$  wherein  $R_a$  is an alkyl group.

The term "N,N-dialkylamino" refers to the group:  $--NR_bR_c$ , wherein  $R_b$  and  $R_c$  are alkyl groups.

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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 are generally free of aliphatic unsaturation, i.e., olefinic or acetylenic unsaturation, but may contain minor amounts

10 of heteroatoms, such as oxygen or nitrogen, or halogens, such as chlorine.

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

The term "lower alkyl" refers to alkyl groups having 1 to about 6 carbon atoms and

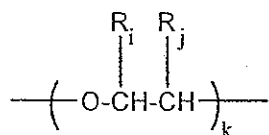
15 includes primary, secondary, and tertiary alkyl groups. Typical lower alkyl groups include, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, t-butyl, n-pentyl, n-hexyl, and the like.

The term "alkylene" refers to straight- and branched-chain alkylene groups having at

20 least 2 carbon atoms. Typical alkylene groups include, for example, ethylene ( $--CH_2CH_2--$ ), propylene ( $--CH_2CH_2CH_2--$ ), isopropylene ( $--CH(CH_3)CH_2--$ ), n-butylene ( $--CH_2CH_2CH_2CH_2--$ ), sec-butylene ( $--CH(CH_2CH_3)CH_2--$ ), n-pentylene ( $--CH_2CH_2CH_2CH_2CH_2--$ ), and the like.

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The term "polyoxyalkylene" refers to a polymer or oligomer having the general formula:



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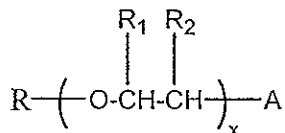
wherein:

$\text{R}_i$  and  $\text{R}_j$  are each independently hydrogen or lower alkyl groups, and  $k$  is an integer from about 5 to about 100. When referring herein to the number of oxyalkylene units in a particular polyoxyalkylene compound, it is to be understood that this number refers to the average number of oxyalkylene units in such compounds unless expressly stated to the contrary.

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The hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention have the general formula hydrocarbyl-substituted polyoxyalkylene amine of the formula:

15



wherein:

20  $\text{R}$  is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

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$\text{R}_1$  and  $\text{R}_2$  are each independently hydrogen or lower alkyl having from about 1 to about 6 carbon atoms and each  $\text{R}_1$  and  $\text{R}_2$  is independently selected in each  $\text{---O-CHR}_1\text{-CHR}_2\text{---}$  unit;  $\text{A}$  is amino, N-alkyl amino having about 1 to about 20 carbon atoms in the alkyl group, N,N-dialkyl amino having about 1 to about 20 carbon atoms in each alkyl group, or a polyamine moiety having about 2 to about 12 amine nitrogen atoms and about 2 to about 40 carbon atoms; and

x is an integer from about 5 to about 100.

Preferably, R is an alkyl or an alkylphenyl group, wherein the alkyl moiety is straight or branched chain. Preferably, one of R<sub>1</sub> and R<sub>2</sub> is lower alkyl of 1 to 4 carbon atoms, and the other is hydrogen. More preferably, one of R<sub>1</sub> and R<sub>2</sub> is methyl or ethyl, and the other is hydrogen. Yet, even more preferably R<sub>1</sub> is hydrogen and R<sub>2</sub> is methyl or ethyl and more preferably ethyl.

In general, A is amino, N-alkyl amino having from about 1 to about 20 carbon atoms in the alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms; N,N-dialkyl amino having from about 1 to about 20 carbon atoms in each alkyl group, preferably about 1 to about 6 carbon atoms, more preferably about 1 to about 4 carbon atoms; or a polyamine moiety having from about 2 to about 12 amine nitrogen atoms and from about 2 to about 40 carbon atoms, preferably about 2 to 12 amine nitrogen atoms and about 2 to 24 carbon atoms. More preferably, A is amino or a polyamine moiety derived from a polyalkylene polyamine, including alkylene diamine. Most preferably, A is amino or a polyamine moiety derived from ethylene diamine or diethylene triamine.

Preferably, x is an integer from about 5 to about 50, more preferably from about 8 to about 30, and most preferably from about 10 to about 25.

The hydrocarbyl-substituted polyoxyalkylene amines of formula I, will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200 °C - 250 °C). Typically, the molecular weight of these compounds will range from about 600 to about 10,000.

Fuel-soluble salts of the compounds of formula I can be readily prepared for those compounds containing an amino or substituted amino group and such salts are contemplated to be useful for preventing or controlling engine deposits. Suitable salts include, for example, those obtained by protonating the amino moiety with a strong organic acid, such as an alkyl- or arylsulfonic acid. Preferred salts are derived from toluenesulfonic acid and methanesulfonic acid.

A. Hydrocarbyl-substituted polyoxyalkylene amines -General Synthetic Procedures

5 The hydrocarbyl-substituted polyoxyalkylene amines employed in this invention may be prepared by the following general methods and procedures. It should be appreciated that where typical or preferred process conditions (e.g., reaction temperatures, times, mole ratios of reactants, solvents, pressures, etc.) are given, other process conditions may also be used unless otherwise stated. Optimum reaction  
10 conditions may vary with the particular reactants or solvents used, but such conditions can be determined by one skilled in the art by routine optimization procedures.

The hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention contain (A-1) a hydrocarbyl-substituted polyoxyalkylene component, and  
15 (A-2) an amine component; described herein below.

A-1. The Hydrocarbyl-Substituted Polyoxyalkylene Component

The hydrocarbyl-substituted polyoxyalkylene polymers which are utilized in  
20 preparing the hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention are monohydroxy compounds, i.e., alcohols, often termed hydrocarbyl "capped" polyoxyalkylene glycols and are to be distinguished from the polyoxyalkylene glycols (diols), which are not hydrocarbyl terminated, i.e., not capped. The hydrocarbyl-substituted polyoxyalkylene alcohols are produced by the  
25 addition of lower alkylene oxides, such as ethylene oxide, propylene oxide, or the butylene oxides, to the hydroxy compound, ROH, under polymerization conditions, wherein R is the hydrocarbyl group, as defined above, which caps the polyoxyalkylene chain. Preferred polyoxyalkylene polymers are those derived from C<sub>3</sub> to C<sub>4</sub> oxyalkylene units. Methods of production and properties of these polymers  
30 are disclosed in U.S. Patent No. 2,841,479 and Kirk-Othmer's "Encyclopedia of Chemical Technology", Volume 19, page 507. In the polymerization reaction, a single type of alkylene oxide may be employed, e.g., propylene oxide, in which case the product is a homopolymer, e.g., a polyoxypropylene alcohol. However, copolymers

are equally satisfactory and random copolymers are readily prepared by contacting the hydroxy-containing compound with a mixture of alkylene oxides, such as a mixture of propylene and butylene oxides. Block copolymers of oxyalkylene units also provide satisfactory polyoxyalkylene units for the practice of the present invention.

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The amount of alkylene oxide employed in this reaction will generally depend on the number of oxyalkylene units desired in the product. Typically, the molar ratio of alkylene oxide to hydroxy-containing compound will range from about 5:1 to about 100:1; preferably, from about 5:1 to about 50:1, more preferably from about 8:1 to about 30:1; even more preferably from about 10:1 to about 25:1.

10

Alkylene oxides suitable for use in this polymerization reaction include, for example, ethylene oxide; propylene oxide; and butylene oxides, such as 1,2-butylene oxide (1,2-epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane). Preferred alkylene  
15 oxides are propylene oxide and 1,2-butylene oxide, both individually and in mixtures thereof.

The hydrocarbyl moiety, R, which terminates the polyoxyalkylene chain will generally contain from about 1 to about 30 carbon atoms, preferably from about 2 to about 20 carbon atoms, and more preferably from about 4 to about 18 carbon atoms, and is generally derived from the monohydroxy compound, ROH, which is the initial site of the alkylene oxide addition in the polymerization reaction. Such monohydroxy compounds are preferably aliphatic or aromatic alcohols having from about 1 to about 30 carbon atoms, more preferably an alkanol or an alkylphenol, and most preferably an alkylphenol wherein the alkyl substituent is a straight or branched chain alkyl of from about 1 to about 24 carbon atoms. Preferred alkylphenols include those wherein the alkyl substituent contains from about 4 to about 24 carbon atoms, more preferably 12 to 16 carbon atoms. An especially preferred alkylphenol is one wherein the alkyl group is obtained by polymerizing propylene to an average of 4 propylene units, that is, about 12 carbon atoms, having the common name of propylene tetramer. The  
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30 resulting alkylphenol is commonly called tetrapropenylphenol or, more generically, dodecylphenol. Preferred alkylphenol-initiated polyoxyalkylene compounds may be termed either alkylphenylpolyoxyalkylene alcohols or polyalkoxylated alkylphenols.

## A-2. The Amine Component

As indicated above, the hydrocarbyl-substituted polyoxyalkylene amines employed in  
5 the present invention contain an amine component.

In general, the amine component will contain an average of at least about one basic nitrogen atom per molecule. A "basic nitrogen atom" is one that is titratable by a strong acid, for example, a primary, secondary, or tertiary amine nitrogen; as  
10 distinguished from, for example, an carbamyl nitrogen, e.g., --OC(O)NH--, which is not titratable with a strong acid. Preferably, at least one of the basic nitrogen atoms of the amine component will be primary or secondary amine nitrogen, more preferably at least one will be a primary amine nitrogen.

15 The amine component of the hydrocarbyl-substituted polyoxyalkylene amines employed in this invention is preferably derived from ammonia, a primary alkyl or secondary dialkyl monoamine, or a polyamine having a terminal amino nitrogen atom.

20 Primary alkyl monoamines useful in preparing compounds of the present invention contain 1 nitrogen atom and from about 1 to about 20 carbon atoms, more preferably about 1 to 6 carbon atoms, most preferably 1 to 4 carbon atoms. Examples of suitable monoamines include N-methylamine, N-ethylamine, N-n-propylamine, N-isopropylamine, N-n-butylamine, N-isobutylamine, N-sec-butylamine,  
25 N-tert-butylamine, N-n-pentylamine, N-cyclopentylamine, N-n-hexylamine, N-cyclohexylamine, N-octylamine, N-decylamine, N-dodecylamine, N-octadecylamine, N-benzylamine, N-(2-phenylethyl)amine, 2-aminoethanol, 3-amino-1-propanol, 2-(2-aminoethoxy)ethanol, N-(2-methoxyethyl)amine, N-(2-ethoxyethyl)amine and the like. Preferred primary amines are N-methylamine,  
30 N-ethylamine and N-n-propylamine.

The amine component of the presently employed fuel additive may also be derived from a secondary dialkyl monoamine. The alkyl groups of the secondary amine may

be the same or different and will generally each contain about 1 to about 20 carbon atoms, more preferably about 1 to about 6 carbon atoms, most preferably about 1 to about 4 carbon atoms. One or both of the alkyl groups may also contain one or more oxygen atoms.

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Preferably, the alkyl groups of the secondary amine are independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl and 2-methoxyethyl. More preferably, the alkyl groups are methyl, ethyl or propyl.

- 10 Typical secondary amines which may be used in this invention include N,N-dimethylamine, N,N-diethylamine, N,N-di-n-propylamine, N,N-diisopropylamine, N,N-di-n-butylamine, N,N-di-sec-butylamine, N,N-di-n-pentylamine, N,N-di-n-hexylamine, N,N-dicyclohexylamine, N,N-dioctylamine, N-ethyl-N-methylamine, N-methyl-N-n-propylamine,
- 15 N-n-butyl-N-methylamine, N-methyl-N-octylamine, N-ethyl-N-isopropylamine, N-ethyl-N-octylamine, N,N-di(2-hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine, N,N-di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine and the like. Preferred secondary amines are N,N-dimethylamine, N,N-diethylamine and N,N-di-n-propylamine.

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Cyclic secondary amines may also be used to form the additives employed in this invention. In such cyclic compounds, the alkyl groups, when taken together, form one or more 5- or 6-membered rings containing up to about 20 carbon atoms. The ring containing the amine nitrogen atom is generally saturated, but may be fused to one or

25 more saturated or unsaturated rings. The rings may be substituted with hydrocarbyl groups of from 1 to about 10 carbon atoms and may contain one or more oxygen atoms.

- Suitable cyclic secondary amines include piperidine, 4-methylpiperidine, pyrrolidine,
- 30 morpholine, 2,6-dimethylmorpholine and the like.

Suitable polyamines can have a straight- or branched-chain structure and may be cyclic or acyclic or combinations thereof. Generally, the amine nitrogen atoms of such

polyamines will be separated from one another by at least two carbon atoms, i.e., polyamines having an aminated structure are not suitable. The polyamine may also contain one or more oxygen atoms, typically present as an ether or a hydroxyl group. Polyamines having a carbon-to-nitrogen ratio of from about 1:1 to about 10:1 are particularly preferred.

In preparing the compounds employed in this invention using a polyamine where the various nitrogen atoms of the polyamine are not geometrically equivalent, several substitutional isomers are possible and each of these possible isomers is encompassed within this invention.

A particularly preferred group of polyamines for use in the present invention are polyalkylene polyamines, including alkylene diamines. Such polyalkylene polyamines will typically contain from about 2 to about 12 nitrogen atoms and from about 2 to about 40 carbon atoms, preferably about 2 to about 24 carbon atoms. Preferably, the alkylene groups of such polyalkylene polyamines will contain from about 2 to about 6 carbon atoms, more preferably from about 2 to about 4 carbon atoms.

Examples of suitable polyalkylene polyamines include ethylenediamine, propylenediamine, isopropylenediamine, butylenediamine, pentylenediamine, hexylenediamine, diethylenetriamine, dipropylenetriamine, dimethylaminopropylamine, diisopropylenetriamine, dibutylenetriamine, di-sec-butylenetriamine, triethylenetetraamine, tripropylenetetraamine, triisobutylenetetraamine, tetraethylenepentamine, pentaethylenhexamine, dimethylaminopropylamine, and mixtures thereof.

Particularly preferred polyalkylene polyamines are ethylenediamine, diethylenetriamine, triethylenetetraamine, and tetraethylenepentamine. Most preferred are ethylenediamine and diethylenetriamine, especially ethylenediamine.

Also contemplated for use in the present invention are cyclic polyamines having one or more 5- to 6-membered rings. Such cyclic polyamines compounds include piperazine, 2-methylpiperazine, N-(2-aminoethyl)piperazine,

N-2-hydroxyethyl)piperazine, 1,2-bis-(N-piperazinyl)ethane, 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the like. Among the cyclic polyamines, the piperazines are preferred.

- 5 Many of the polyamines suitable for use in the present invention are commercially available and others may be prepared by methods which are well known in the art. For example, methods for preparing amines and their reactions are detailed in Sidgwick's "The Organic Chemistry of Nitrogen", Clarendon Press, Oxford, 1966; Noller's "Chemistry of Organic Compounds", Saunders, Philadelphia, 2<sup>nd</sup> edition, 1957; and  
10 Kirk-Othmer's "Encyclopedia of Chemical Technology", 2<sup>nd</sup> edition., especially Volume 2, pp. 99-116.

#### A-3. Preparation of the Hydrocarbyl-Substituted Polyoxyalkylene Amine

- 15 The additives employed in this invention may be conveniently prepared by reacting a hydrocarbyl-substituted polyoxyalkylene alcohol, either directly or through an intermediate, with a nitrogen-containing compound, such as ammonia, a primary or secondary alkyl monoamine or a polyamine, as described herein.
- 20 The hydrocarbyl-substituted polyoxyalkylene alcohols used to form the polyoxyalkylene amines employed in the present invention are typically known compounds that can be prepared using conventional procedures. Suitable procedures for preparing such compounds are taught, for example, in U.S. Patent Nos. 2,782,240 and 2,841,479, as well as U.S. Patent No. 4,881,945, the disclosures of which are  
25 incorporated herein by reference.

Preferably, the polyoxyalkylene alcohols are prepared by contacting an alkoxide or phenoxide metal salt with from about 5 to about 100 molar equivalents of an alkylene oxide, such as propylene oxide or butylene oxide, or mixtures of alkylene oxides.

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Typically, the alkoxide or phenoxide metal salt is prepared by contacting the corresponding hydroxy compound with a strong base, such as sodium hydride, potassium hydride, sodium amide, and the like, in an inert solvent, such as toluene,

xylene, and the like, under substantially anhydrous conditions at a temperature in the range from about -10 °C to about 120 °C for from about 0.25 to about 3 hours.

5 The alkoxide or phenoxide metal salt is generally not isolated, but is reacted in situ with the alkylene oxide or mixture of alkylene oxides to provide, after neutralization, the polyoxyalkylene alcohol. This polymerization reaction is typically conducted in a substantially anhydrous inert solvent at a temperature of from about 30 °C to about 150 °C for from about 2 to about 120 hours. Suitable solvents for this reaction, include toluene, xylene, and the like. Typically, the reaction is conducted at a pressure  
10 sufficient to contain the reactants and the solvent, preferably at atmospheric or ambient pressure.

The hydrocarbyl-substituted polyoxyalkylene alcohol may then be converted to the desired polyoxyalkylene amine by a variety of procedures known in the art.

15 For example, the terminal hydroxy group on the hydrocarbyl-substituted polyoxyalkylene alcohol may first be converted to a suitable leaving group, such as a mesylate, chloride or bromide, and the like, by reaction with a suitable reagent, such as methanesulfonyl chloride. The resulting polyoxyalkylene mesylate or equivalent  
20 intermediate may then be converted to a phthalimide derivative by reaction with potassium phthalimide in the presence of a suitable solvent, such as N,N-dimethylformamide. The polyoxyalkylene phthalimide derivative is subsequently converted to the desired hydrocarbyl-substituted polyoxyalkylene amine by reaction with a suitable amine, such as hydrazine.

25 The polyoxyalkylene alcohol may also be converted to the corresponding polyoxyalkylene chloride by reaction with a suitable halogenating agent, such as HCl, thionyl chloride, or epichlorohydrin, followed by displacement of the chloride with a suitable amine, such as ammonia, a primary or secondary alkyl monoamine, or a  
30 polyamine, as described, for example, in U.S. Patent No. 4,247,301 to Honnen, the disclosure of which is incorporated herein by reference.

Alternatively, the hydrocarbyl-substituted polyoxyalkylene amines employed in the present invention may be prepared from the corresponding polyoxyalkylene alcohol by a process commonly referred to as reductive amination, such as described in U.S. Patent No. 5,112,364 to Rath et al. and U.S. Patent No. 4,332,595 to  
5 Herbstman et al., the disclosures of which are incorporated herein by reference.

In the reductive amination procedure, the hydrocarbyl-substituted polyoxyalkylene alcohol is aminated with an appropriate amine, such as ammonia or a primary alkyl monoamine, in the presence of hydrogen and a hydrogenation-dehydrogenation  
10 catalyst. The amination reaction is typically carried out at temperatures in the range of about 160 °C to about 250 °C and pressures of about 1,000 to about 5,000 psig, preferably about 1,500 to about 3,000 psig. Suitable hydrogenation-dehydrogenation catalysts include those containing platinum, palladium, cobalt, nickel, copper, or chromium, or mixtures thereof. Generally, an excess of the ammonia or amine  
15 reactant is used, such as about a 5-fold to about 60-fold molar excess, and preferably about a 10-fold to about 40-fold molar excess, of ammonia or amine.

When the reductive amination is carried out with a polyamine reactant, the amination is preferably conducted using a two-step procedure as described in European Patent  
20 Application Publication No. EP 0,781,793, published July 2, 1997, the disclosure of which is incorporated herein by reference in its entirety. According to this procedure, a polyoxyalkylene alcohol is first contacted with a hydrogenation-dehydrogenation catalyst at a temperature of at least 230 °C to provide a polymeric carbonyl intermediate, which is subsequently reacted with a polyamine at a temperature below  
25 about 190 °C in the presence of hydrogen and a hydrogenation catalyst to produce the polyoxyalkylene polyamine adduct.

#### EXAMPLE A3-1

##### Preparation of Dodecylphenoxy Poly(oxybutylene)poly(oxypropylene) Amine

30 A dodecylphenoxypoly(oxybutylene)poly(oxypropylene) amine was prepared by the reductive amination with ammonia of the random copolymer poly(oxyalkylene) alcohol, dodecylphenoxy poly(oxybutylene)poly(oxypropylene) alcohol, wherein the alcohol has a number average molecular weight of about 1598. The poly(oxyalkylene)

alcohol was prepared from dodecylphenol using a 75/25 weight/weight ratio of butylene oxide and propylene oxide, in accordance with the procedures described in U.S. Patent Nos. 4,191,537; 2,782,240; and 2,841,479, as well as in Kirk Othmer, "Encyclopedia of Chemical Technology", 4<sup>th</sup> edition, Volume 19, 1996, page 722.

- 5 The reductive amination of the poly(oxyalkylene) alcohol was carried out using conventional techniques as described in U.S. Patent Nos. 5,112,364; 4,609,377; and 3,440,029.

#### EXAMPLE A3-2

##### 10 Preparation of Dodecylphenoxy Poly(oxybutylene) Amine

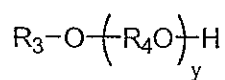
A dodecylphenoxy poly(oxybutylene) amine was prepared by the reductive amination with ammonia of a dodecylphenoxy poly(oxybutylene) alcohol having an average molecular weight of about 1600. The dodecylphenoxy poly(oxybutylene) alcohol was prepared from dodecylphenol and butylene oxide, in accordance with the procedures described in U.S. Patent Nos. 4,191,537; 2,782,240; and 2,841,479, as well as in Kirk Othmer, "Encyclopedia of Chemical Technology", 4<sup>th</sup> edition, Volume 19, 1996, page 722. The reductive amination of the dodecylphenoxy poly(oxybutylene) alcohol was carried out using conventional techniques as described in U.S. Patent Nos. 5,112,364; 4,609,377; and 3,440,029.

20

#### B. The Glycol Ether Component

The glycol ether employed in this invention can be represented by the formula:

25



B-I

wherein:

- 30  $R_3$  is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

$R_4$  is a  $C_2$  to  $C_5$  alkylene group; and

y is an integer such that the molecular weight of the glycol ether is from about 100 to about 5,000.

- 5 Preferably  $R_4$  is an alkylene group having 2 to 4 carbon atoms, and more particularly  $R_4O$  is derived from ethylene oxide, propylene oxide or butylene oxide or mixtures thereof. Preferably y is an integer from 1 to 50. Preferably,  $R_3$  is alkyl, phenyl, or alkylphenyl. Particularly preferred alkyl groups for  $R_3$  are straight and branched chain  $C_1$  to  $C_{15}$  alkyl groups. Preferred alkylphenyl group include those wherein the alkyl  
10 substituent contains from about 4 to about 24 carbon atoms and more preferably 12 to 16 carbon atoms. A particularly preferred alkylphenyl is dodecylphenyl.

- A sub-group of glycol ether compounds useful in the present invention is comprised of one or a mixture of high molecular weight glycol ethers, wherein the molecular  
15 weight of the glycol ether compound is from about 750 to about 3,000; and more preferably having a molecular weight from about 900 to about 1,500. These high molecular weight glycol ethers can be synthesized according to the description described hereinabove for the hydrocarbyl-substituted polyoxyalkylene component; and therefore, the number of oxyalkylene groups in formula B-I will be greater than 5,  
20 or stated in another fashion, in formula B-I, y is greater than 5. Preferably, y is an integer from 5-50, more preferably 8-30 and even more preferably from 10-25. In one aspect, y in formula B-I is selected to be substantially the same range in value as x in formula I. Preferred high molecular weight glycol ethers are characterized by having viscosities in their undiluted state of at least about 60 cSt, more preferably at least  
25 about 70 cSt, at 40 °C and at least about 11 cSt, more preferably at least about 13 cSt, at 100 °C. In addition, these high molecular weight glycol ether compounds used in the practice of this invention preferably have viscosities in their undiluted state of no more than about 400 cSt at 40 °C and no more than about 50 cSt at 100 °C. More preferably, their viscosities will not exceed about 300 cSt at 40 °C and will not exceed  
30 about 40 cSt at 100 °C. with particularly preferred compounds having viscosities of no more than about 200 cSt at 40°C, and no more than about 30 cSt at 100 °C. The high molecular weight (i.e. number average molecular weights from 750 to 3,000) are comprised of repeating units formed by reacting an alcohol or polyalcohol with an

alkylene oxide, such as propylene oxide and/or butylene oxide with or without use of ethylene oxide, and especially products in which at least 80 mole % of the oxyalkylene groups in the molecule are derived from 1,2-propylene oxide. Details concerning preparation of such poly(oxyalkylene) compounds are referred to, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, 3<sup>rd</sup> edition, Volume 18, pages 633-645 (Copyright 1982 by John Wiley & Sons), and in references cited therein, the foregoing excerpt of the Kirk-Othmer encyclopedia and the references cited therein being incorporated herein in by reference. U.S. Patent Nos. 2,425,755; 2,425,845; 2,448,664; and 2,457,139 also describe such procedures, and are fully incorporated herein by reference.

A particularly preferred sub-group of the glycol ether compounds employed in the present invention is comprised of one or a mixture of low molecular weight glycol ethers compounds; wherein the molecular weight of each of the glycol ether compound is from 100 to 450, more preferably from 115 to about 350, and even more preferably from about 115 to about 250. These low molecular weight glycol ethers are characterized by having viscosities in their undiluted state of less than about 40 cSt, more preferably less than about 30 cSt, at 25 °C. In these particularly preferred low molecular weight glycol ether compounds, the number of oxyalkylene units or y in the formula B-I above is an integer from 1 to 4, more preferably from 1 to 3, and even more particularly from 1 to 2. Commonly, these low molecular weight glycol ether compounds are synthesized by reacting one mole of an alcohol with one, two, three or four moles of an oxide (preferably ethylene or propylene) and are typically considered to be a derivative of ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol or tripropylene glycol, and the like. Thus, these low molecular weight glycol ethers include mono-glycol ethers, di-glycol ethers, and tri-glycol ethers. Examples of mono-glycol ethers include ethylene glycol monomethyl ether (Methyl Cellosolve), ethylene glycol monoethyl ether (Cellosolve), ethylene glycol monopropyl ether (Propyl Cellosolve), ethylene glycol monobutyl ether (Butyl Cellosolve), ethylene glycol monohexyl ether (Hexyl Cellosolve), ethylene glycol monophenyl ether (Dowanol EPH), propylene glycol monomethyl ether (Methyl Propasol), propylene glycol monopropyl ether (Propyl Propasol), propylene glycol monobutyl ether (Butyl Propasol), propylene glycol t-butyl ether

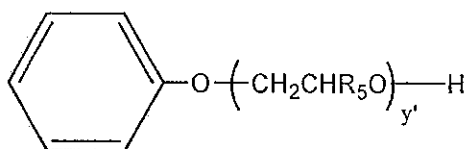
(Arcosolv PTB), and propylene glycol monophenyl ether (Dowanol PPH). Wherein as used herein, (Cellosolve, Carbitol and Dowanol) are trademarks of the Dow Chemical Company, (Arosolv) is the trademark of Lyondell Chemical Company, and (Propasol) is the trademark of Union Carbide.

5

Representative di-glycol ethers include diethylene glycol monomethyl ether (Methyl Carbitol), diethylene glycol monoethyl ether (Carbitol), diethylene glycol monopropyl ether (Propyl Carbitol), diethylene glycol monobutyl ether (Butyl Carbitol), diethylene glycol monoethyl ether (Hexyl Carbitol), dipropylene glycol monomethyl ether (Arcosolv DPM), and dipropylene glycol n-butyl ether (Dowanol DPNB).

Representative tri-glycol ethers include triethylene glycol monomethyl ether (Methoxytriglycol), triethylene glycol monoethyl ether (Ethoxytriglycol), tripropylene glycol monomethyl ether (Dowanol TPM), tripropylene glycol mono-n-propyl ether (Dowanol TPnP).

Particularly preferred glycol ethers are ethylene glycol monophenyl ether, diethylene glycol monophenyl ether, propylene glycol monophenyl ether, and dipropylene glycol monophenyl ether and the like; which accordingly are represented by the formula:



B-II

wherein:

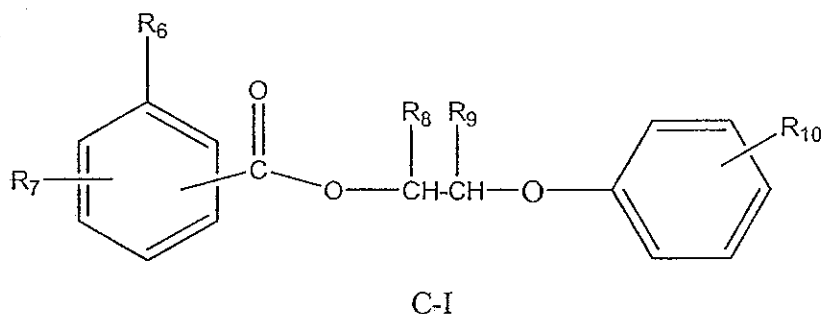
25  $\text{R}_5$  is selected from hydrogen or methyl; and

$y'$  is an integer from 1 to 3, and more preferably from 1 to 2.

### C. The Aromatic Ester Compound

The aromatic ester compound employed in the present invention can be represented by the formula:

5



wherein:

10  $R_6$  is nitro or  $-(CH_2)_n-NR_{11}R_{12}$ , wherein  $R_{11}$  and  $R_{12}$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and  $n$  is 0 or 1;

$R_7$  is hydrogen, hydroxy, nitro or  $-NR_{13}R_{14}$ , wherein  $R_{13}$  and  $R_{14}$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

15  $R_8$  and  $R_9$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and

$R_{10}$  is a polyalkyl group having a number average molecular weight in the range of about 450 to 5,000.

20

The aromatic esters of formula C-I and methods for synthesis are disclosed, for example, in U.S. Patent No. 5,749,929 incorporated by reference in its entirety. The preferred aromatics ester compounds of formula C-I employed in the present invention are those wherein  $R_6$  is nitro, amino, N-alkylamino, or  $-CH_2NH_2$  (aminomethyl). More preferably,  $R_6$  is a nitro, amino or  $-CH_2NH_2$  group. Most  
25 preferably,  $R_6$  is an amino or  $-CH_2NH_2$  group, especially amino. Preferably,  $R_7$  is hydrogen, hydroxy, nitro or amino. More preferably,  $R_7$  is hydrogen or hydroxy. Most preferably,  $R_7$  is hydrogen. Preferably,  $R_{10}$  is a polyalkyl group having an average molecular weight in the range of about 500 to 3,000, more preferably about 700 to

3,000, and most preferably about 900 to 2,500. Preferably, the aromatic ester compound has a combination of preferred substituents.

Preferably, one of  $R_8$  and  $R_9$  is hydrogen or lower alkyl of 1 to 4 carbon atoms, and  
5 the other is hydrogen. More preferably, one of  $R_8$  and  $R_9$  is hydrogen, methyl or ethyl, and the other is hydrogen. Most preferably,  $R_8$  is hydrogen, methyl or ethyl, and  $R_9$  is hydrogen.

When  $R_6$  and/or  $R_7$  is an N-alkylamino group, the alkyl group of the N-alkylamino  
10 moiety preferably contains 1 to 4 carbon atoms. More preferably, the N-alkylamino is N-methylamino or N-ethylamino.

Similarly, when  $R_6$  and/or  $R_7$  is an N,N-dialkylamino group, each alkyl group of the  
N,N-dialkylamino moiety preferably contains 1 to 4 carbon atoms. More preferably,  
15 each alkyl group is either methyl or ethyl. For example, particularly preferred N,N-dialkylamino groups are N,N-dimethylamino, N-ethyl-N-methylamino and N,N-diethylamino groups.

A further preferred group of aromatic ester compounds of formula C-I are those  
20 wherein  $R_6$  is amino, nitro, or  $-\text{CH}_2\text{NH}_2$  and  $R_7$  is hydrogen or hydroxy. A particularly preferred group of compounds are those wherein  $R_6$  is amino,  $R_7$ ,  $R_8$  and  $R_9$  are hydrogen, and  $R_{10}$  is a polyalkyl group derived from polyisobutene.

It is preferred that the  $R_6$  substituent is located at the meta or, more preferably, the  
25 para position of the benzoic acid moiety, i.e., para or meta relative to the carbonyloxy group. When  $R_7$  is a substituent other than hydrogen, it is particularly preferred that this  $R_7$  group be in a meta or para position relative to the carbonyloxy group and in an ortho position relative to the  $R_6$  substituent. Further, in general, when  $R_7$  is other than hydrogen, it is preferred that one of  $R_6$  or  $R_7$  is located para to the carbonyloxy group  
30 and the other is located meta to the carbonyloxy group. Similarly, it is preferred that the  $R_{10}$  substituent on the other phenyl ring is located para or meta, more preferably para, relative to the ether linking group.

The aromatic ester compounds of formula C-I employed in the present invention will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200 °C-250 °C). Typically, the molecular weight of the compounds employed in this invention will range from about 700 to  
5 about 3,500, preferably from about 700 to about 2,500.

#### EXAMPLE C-1.

Preparation of a 4-polyisobutylphenoxyethyl para-aminobenzoate

##### a) Polyisobutyl phenol

10 To a flask equipped with a magnetic stirrer, reflux condenser, thermometer, addition funnel and nitrogen inlet was added 203.2 grams of phenol. The phenol was warmed to 40.degree. C. and the heat source was removed. Then, 73.5 milliliters of boron trifluoride etherate was added dropwise. 1040 grams of Ultravis 10 Polyisobutene (molecular weight 950, 76% methylvinylidene, available from British Petroleum) was  
15 dissolved in 1,863 milliliters of hexane. The polyisobutene was added to the reaction at a rate to maintain the temperature between 22.degree. C. to 27.degree. C. The reaction mixture was stirred for 16 hours at room temperature. Then, 400 milliliters of concentrated ammonium hydroxide was added, followed by 2,000 milliliters of hexane. The reaction mixture was washed with water (3.times.2,000 milliliters), dried  
20 over magnesium sulfate, filtered and the solvents removed under vacuum to yield 1,056.5 grams of a crude reaction product. The crude reaction product was determined to contain 80% of the desired product by proton NMR and chromatography on silica gel eluting with hexane, followed by hexane: ethylacetate: ethanol (93:5:2).

##### b) 2-(4-polyisobutyl-phenoxy)-ethanol

25 1.1 grams of a 35 weight percent dispersion of potassium hydride in mineral oil and 4-polyisobutyl phenol (99.7 grams, prepared as in above) were added to a flask equipped with a magnetic stirrer, reflux condensor, nitrogen inlet and thermometer. The reaction was heated at 130 °C for one hour and then cooled to 100 °C. Ethylene carbonate (8.6 grams) was added and the mixture was heated at 160 °C for 16 hours.  
30 The reaction was cooled to room temperature and one milliliter of isopropanol was added. The reaction was diluted with one liter of hexane, washed three times with water and once with brine. The organic layer was dried over anhydrous magnesium

sulfate, filtered and the solvents removed in vacuo to yield 98.0 grams of the desired product as a yellow oil.

c) 4-polyisobutylphenoxyethyl para-nitrobenzoate

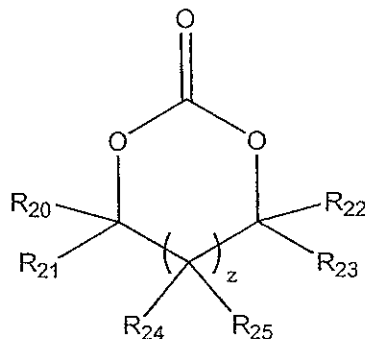
To a flask equipped with a magnetic stirrer, thermometer, Dean-Stark trap, reflux  
5 condensor and nitrogen inlet was added 15.0 grams of the  
2-(4-polyisobutyl-phenoxy)-ethanol, 2.6 grams of 4-nitrobenzoic acid and 0.24 grams  
of p-toluenesulfonic acid. The mixture was stirred at 130 °C for sixteen hours, cooled  
to room temperature and diluted with 200 mL of hexane. The organic phase was  
washed twice with saturated aqueous sodium bicarbonate followed by once with  
10 saturated aqueous sodium chloride. The organic layer was then dried over anhydrous  
magnesium sulfate, filtered and the solvents removed in vacuo to yield 15.0 grams of  
the desired product as a brown oil. The oil was chromatographed on silica gel, eluting  
with hexane/ethyl acetate (9:1) to afford 14.0 grams of the desired ester as a yellow  
oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.3 (AB quartet, 4H), 7.25 (d, 2H), 6.85 (d, 2H),  
15 4.7 (t, 2H), 4.3 (t, 2H), 0.7-1.6 (m, 137H).

d) A solution of 9.4 grams of the 4-polyisobutylphenoxyethyl para-nitrobenzoate  
product in 100 milliliters of ethyl acetate containing 1.0 gram of 10% palladium on  
charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure  
hydrogenator. Catalyst filtration and removal of the solvent in vacuo yield 7.7 grams  
20 of the desired product as a yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.85 (d, 2H),  
7.3 (d, 2H), 6.85 (d, 2H), 6.6 (d, 2H), 4.6 (t, 2H), 4.25 (t, 2H), 4.05 (bs, 2H),  
0.7-1.6 (m, 137H). Other compounds of formula C-I can be prepared by the similar  
methods as disclosed in U.S. Patent Nos. 5,407,452; 5,618,320; and 5,749,929  
incorporated herein by reference.

25

#### D. The Cyclic Carbonate

The cyclic carbonate employed in the invention can be represented by the formula:



5

D-I

wherein:

R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub>, and R<sub>25</sub> are independently selected from hydrogen, hydroxy, hydroxymethyl, hydroxyethyl, or a hydrocarbyl group of from about 1 to 6 carbon atoms; and z is an integer from zero to one.

10

Preferred cyclic carbonates for use in this invention are those of formula 1 above where z is zero and where R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub> are hydrogen and R<sub>23</sub> is methyl, ethyl or hydroxymethyl. Preferably when z is 1, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub>, R<sub>25</sub> are hydrogen. Most preferred are ethylene carbonate, propylene carbonate and the butylene carbonates which are defined below.

15

The following are examples of suitable cyclic carbonates for use in this invention as well as mixtures thereof: 1,3-dioxolan-2-one (also referred to as ethylene carbonate);

4-methyl-1,3-dioxolan-2-one (also referred to as propylene carbonate);

20 4-hydroxymethyl-1,3-dioxolan-2-one; 4,5-dimethyl-1,3-dioxolan-2-one;

4-ethyl-1,3-dioxolan-2-one; 4,4-dimethyl-1,3-dioxolan-2-one (previous three also referred to as butylenes carbonates); 4-methyl-5-ethyl-1,3-dioxolan-2-one;

4,5-diethyl-1,3-dioxolan-2-one; 4,4-diethyl-1,3-dioxolan-2-one; 1,3-dioxan-2-one;

4,4-dimethyl-1,3-dioxan-2-one; 5,5-dimethyl-1,3-dioxan-2-one;

25 5,5-dihydroxymethyl-1,3-dioxan-2-one; 5-methyl-1,3-dioxan-2-one;

4-methyl-1,3-dioxan-2-one; 5-hydroxy-1,3-dioxan-2-one;

5-hydroxymethyl-5-methyl-1,3-dioxan-2-one; 5,5-diethyl-1,3-dioxan-2-one;

5-methyl-5-propyl-1,3-dioxan-2-one; 4,6-dimethyl-1,3-dioxan-2-one; and 4,4,6-trimethyl-1,3-dioxan-2-one. Other suitable cyclic carbonates may be prepared from visconal diols prepared from C<sub>1</sub>-C<sub>30</sub> olefins by methods known in the art.

- 5 Several of these cyclic carbonates are commercially available such as 1,3-dioxolan-2-one or 4-methyl-1,3-dioxolan-2-one sold for example by Lyondell Chemical Company under the trade name ARCONATE. Alternatively, Huntsman Performance Chemicals also sells, ethylene carbonate, propylene carbonate, 1,2 butylene carbonate as well as mixtures thereof under the trade name
- 10 JEFFSOL. Cyclic carbonates may be readily prepared by known reactions. For example although not preferred, reaction of phosgene with a suitable alpha alkane diol or an alkan-1,3-diol yields a carbonate for use within the scope of this invention as for instance in U.S. Patent No. 4,115,206 which is incorporated herein by reference.
- 15 Likewise, the cyclic carbonates useful for this invention may be prepared by transesterification of a suitable alpha alkane diol or an alkan-1,3-diol with, e.g., diethyl carbonate under transesterification conditions. See, for instance, U.S. Patent Nos. 4,384,115 and 4,423,205 which are incorporated herein by reference for their teaching of the preparation of cyclic carbonates. Catalytic processes
- 20 employing Cr(III)- and Co(III)-based catalyst system can also be used for synthesis of cyclic carbonates from the coupling of CO<sub>2</sub> and terminal epoxides under mild conditions. For example, propylene oxide reacts with CO<sub>2</sub> in the presence of these complexes to afford propylene carbonate quantitatively. The reaction can be run with or without solvent, at modest temperatures (25-100°C), CO<sub>2</sub> pressures (1-5 atm), and
- 25 low catalyst level (0.075 mol%).

As used herein, the term "alpha alkane diol" means an alkane group having two hydroxyl substituents wherein the hydroxyl substituents are on adjacent carbons to each other. Examples of alpha alkane diols include 1,2-propanediol, 2,3-butanediol

30 and the like. Likewise, the term "alkan-1,3-diol" refers to an alkane group having two hydroxyl substituents wherein the hydroxyl substituents are beta substituted. That is, there is a methylene or a substituted methylene moiety between the hydroxyl

substituted carbons. Examples of alkan-1,3-diols include propan-1,3-diol, pentan-2,4-diol and the like.

5 The alpha alkane diols, used to prepare the 1,3-dioxolan-2-ones employed in this invention, are either commercially available or may be prepared from the corresponding olefin by methods known in the art. For example, the olefin may first react with a peracid, such as peroxyacetic acid or hydrogen peroxide to form the corresponding epoxide which is readily hydrolyzed under acid or base catalysis to the alpha alkane diol. In another process, the olefin is first halogenated to a dihalo  
10 derivative and subsequently hydrolyzed to an alpha alkane diol by reaction first with sodium acetate and then with sodium hydroxide. The olefins so employed are known in the art.

15 The alkan-1,3-diols, used to prepare the 1,3-dioxan-2-ones employed in this invention, are either commercially available or may be prepared by standard techniques, e.g., derivatizing malonic acid.

4-Hydroxymethyl 1,3-dioxolan-2-one derivatives and 5-hydroxy-1,3-dioxan-2-one derivatives may be prepared by employing glycerol or substituted glycerol in the  
20 process of U.S. Patent No. 4,115,206. The mixture so prepared may be separated, if desired, by conventional techniques. Preferably the mixture is used as is.

5,5-Dihydroxymethyl-1,3-dioxan-2-one may be prepared by reacting an equivalent of pentaerythritol with an equivalent of either phosgene or diethylcarbonate (or the like)  
25 under transesterification conditions.

5-hydroxymethyl-5-methyl-1,3-dioxan-2-one may be prepared by reacting an equivalent of trimethylolethane with an equivalent of either phosgene or diethylcarbonate (or the like) under transesterification conditions.

30

## E. Fuel Compositions

The hydrocarbyl-substituted polyoxyalkylene amine and glycol ether components employed in the present invention are particularly useful as additives in hydrocarbon  
5 fuels in the prevention and control of piston ring groove deposits. Additionally, this combination and concentration of additive as a fuel composition exhibits superior intake valve deposit control, superior injector clean-up, as well as excellent combustion chamber deposit removal and is particularly suited for use in direct injection spark ignition engines for piston bowl clean-up. Typically, the desired  
10 deposit control will be achieved by operating an internal combustion engine with a fuel composition containing a major amount of hydrocarbons boiling in the gasoline range and a deposit removing effective amount of the hydrocarbyl-substituted polyoxyalkylene amine and the glycol ether components. The proper concentration of additive necessary to achieve the desired deposit control varies depending upon the  
15 type of fuel employed, the type of engine, operating conditions, and the presence of other fuel additives.

In general, the concentration of the hydrocarbyl-substituted polyoxyalkylene amines of formula I employed in this invention in the hydrocarbon fuel will range from about  
20 2,200 to about 30,000 parts per million (ppm) by weight, preferably from about 3,000 to about 20,000 ppm, more preferably from about 6,000 to about 15,000 ppm, and even more preferably from about 12,000 to about 15,000 ppm. In one aspect, the present invention is directed to relatively high concentrations of the hydrocarbyl-substituted polyoxyalkylene amine thus the fuel composition will  
25 comprise greater than about 12,000 ppm of the hydrocarbyl-substituted polyoxyalkylene amine; and more preferably from 12,000 to 30,000 ppm, and even more preferably 15,000 to 25,000 ppm by weight in the fuel.

The glycol ether component of formula B-I of the present invention can be employed  
30 in the hydrocarbon fuel at concentrations as low as 100 ppm up to about 10 weight percent. Preferably the glycol ether component is employed from 100 to about 60,000 ppm, and more preferably from about 1,500 to about 40,000 ppm, and even more preferably from about 3,000 to about 30,000 ppm based upon weight percent in

the fuel composition and wherein the glycol ether component refers to sum of all glycol ethers in the composition.

5 In addition to the hydrocarbyl-substituted polyoxyalkylene amine and at least one glycol ether component described above, the fuel composition of the present invention can further employ from about 100 to about 10,000 parts per million by weight of an aromatic ester compound of formula C-I. Preferably the aromatic ester is employed from 150 to about 5,000 ppm, and even more preferably from 200 to about 3,000 ppm.

10

In yet another aspect, the fuel composition employing the hydrocarbyl-substituted polyoxyalkylene amine and the at least one glycol ether component described above, can further employ from about 100 to about 15,000 parts per million by weight of a cyclic carbonate of formula D-I. Preferably the cyclic carbonate is employed from 15 200 to about 7,000 ppm, and even more preferably from 200 to about 3,000 ppm, with 500 to 1,000 ppm by weight of the cyclic carbonate in the fuel composition being particularly preferred. Especially preferred is propylene carbonate.

20 The hydrocarbyl-substituted polyoxyalkylene amine and at least one glycol ether component employed in the present invention, as well as other embodiments may be formulated using an inert stable oleophilic (i.e., dissolves in gasoline) organic solvent boiling in the range of from about 65 °C to about 210 °C. Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene, or higher-boiling aromatics or aromatic thinners such as C<sub>9</sub> aromatic thinners being 25 particularly preferred. Aliphatic alcohols containing from about 6 to about 20 carbon atoms, such-as isopropanol, isobutylcarbinol, n-butanol, 2-ethyl hexanol, dodecyl alcohol and the like, in combination with hydrocarbon solvents are also suitable for use with the present additives. Particularly preferred are aralkyl alcohols such as benzyl alcohol, alpha and beta phenylethyl alcohol, and di- and tri-phenylmethanol; 30 with benzyl alcohol being particularly preferred. Typically, if such an oleophilic organic solvent is employed it is less than 0.5 wt percent of the fuel composition, more preferable in a lower concentration than the glycol ether component, such as a 0.1 to .5:1 weight ratio.

In gasoline fuels, other fuel additives may be employed with the additives of the present invention, including, for example, oxygenates, such as t-butyl methyl ether, ethanol, antiknock agents, such as methylcyclopentadienyl manganese tricarbonyl, and other dispersants/detergents, such as hydrocarbyl amines, Mannich reaction products, or succinimides. Additionally, antioxidants, metal deactivators, and demulsifiers may be present.

Optionally, a fuel-soluble, nonvolatile carrier fluid or oil may also be used with the hydrocarbyl-substituted polyoxyalkylene amine and glycol ether component employed in this 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 additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic fluid, such as mineral oil, refined petroleum oils, synthetic polyalkanes and alkenes, including hydrogenated and unhydrogenated polyalphaolefins, and synthetic polyoxyalkylene-derived fluids, such as those described, for example, in U.S. Patent No. 4,191,537 to Lewis and polyesters, such as those described, for example, in U.S. Patent Nos. 3,756,793 and 5,004,478, and in European Patent Application Nos. 356,726 and 382,159. These carrier fluids are believed to act as a carrier for the fuel additives of the present invention and to assist in removing and retarding certain deposits. The carrier fluid may also exhibit synergistic deposit control properties when used in combination with fuel composition of this invention. The carrier fluids may be employed in amounts ranging from about 50 to about 5,000 ppm by weight of the hydrocarbon fuel, preferably from about 400 to about 3,000 ppm of the fuel. Preferably, the ratio of carrier fluid to deposit control additive will range from about 0.01:1 to about 10:1, more preferably from about 0.1:1 to about 5:1.

### EXAMPLES

In order to further illustrate the advantages of this invention, the following illustrative examples are given. While the following examples illustrate specific embodiments of the present invention, they should not be interpreted as limitations upon the scope of the invention. The fuel additive formulations were prepared using a base fuel, which

is representative of a base commercial unleaded gasoline. The base fuel employed in these tests contained no fuel detergent.

#### Example 1

- 5 Approximately 20 gallons of a fuel composition of the present invention was prepared employing 20,000 ppma of a dodecylphenoxy poly(oxybutylene)amine and 5844 ppm 2-butoxy-ethanol and 5844 ppm of 2-phenoxy-ethanol in a base fuel. The dodecylphenoxy poly(oxybutylene)amine was prepared in accordance as described in Example A-3.2.

10

#### Performance Test in a 2.3 L Port Fuel Injected Engine:

- A 1994 four cylinder engine, having displacement volume of 2.3 liter was used to determine deposit clean up in the piston ring land area. The procedure included putting the engine through a dirty up phase for 100 hours. Thereafter, the engine was  
15 put through a clean up phase that included operating the engine with full amount of the above prepared fuel additive composition. Approximately 20 gallons of fuel additive composition was used. After the clean up phase, the engine was completely disassembled and piston ring land areas were photographed and rated for varnish by a trained technician using a standard Coordinating Research Council "CRC" rating  
20 method. Note that the CRC rating method used below assigns a numerical value of 10 to a perfectly clean metal surface (a new unused part). The data are included in Table 1. Unexpectedly, there is a dramatic improvement in varnish removal.

TABLE 1: Piston Ring Land Varnish Clean up Data from 2.3 L PFI Engine

|                 | CRC Varnish Rating<br>Before In-tank Clean up | CRC Varnish Rating After<br>In-tank Clean up |
|-----------------|-----------------------------------------------|----------------------------------------------|
| Piston Number 1 | 8.8                                           | 9.2                                          |
| Piston Number 2 | 9                                             | 9                                            |
| Piston Number 3 | 9                                             | 9.5                                          |
| Piston Number 4 | 9.2                                           | 9.5                                          |

25

#### Example 2

Approximately 25 gallons of a fuel composition was prepared employing 5,000 ppma of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1 and 6,500 ppm of 2-(2-hexyloxy-ethoxy)-ethanol [or diethylene glycol hexyl ether] in a base fuel.

5

#### Example 3

Approximately 25 gallons of a fuel composition was prepared employing 5,000 ppma of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1; 3823 ppm of 1-phenoxy-propan-2-ol [or propylene phenyl glycol ether]; 780 ppm of 2-butoxy-

10 ethanol; 900 ppm propylene carbonate and 1000 ppm benzyl alcohol in a base fuel.

#### Comparative Example A

Approximately 25 gallons of a comparative fuel composition was prepared employing 5,000 ppma of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1 and

15 5,450 ppm of an aromatic C<sub>9</sub> carrier fluid in a base fuel.

#### Example 4

Performance Example using a 2.4 L Port Fuel Injected Dynamometer Test:

A 1996 four cylinder engine, having a displacement volume of 2.4 liter was used for the dynamometer test. The performance evaluation program for the fuel compositions of Example 2, Example 3 and Comparative Example A was conducted by starting with a deposit-free engine and operating the engine for 100 hours to accumulate adequate level of engine deposits (referred to as dirty up phase). At the end of the dirty-up phase, the engine was disassembled and intake valve deposit weights were

25 measured and recorded. At the end of this stage, the engine was again assembled and put through a clean up phase that included 25 gallons of the fuel compositions listed in Example 2, Example 3 and Comparative Example A. It is noted that due to nature of these dynamometer experiments, a portion of the additized fuel was used to purge the fuel lines, leaving approximately 20 gallons of fuel for the clean up purposes.

30 Upon completion of the clean up phase, the engine was disassembled and intake valve deposit weights were once again measured and recorded. The before and after intake valve deposit weights were used to calculate percent clean up. Data from these experiments are shown in Table 2.

Table 2- Intake Valve Clean Up Data from 2.4 L PFI Engine

| Fuel Composition         | Intake Valve Deposit<br>Clean up Percentage |
|--------------------------|---------------------------------------------|
| Comparative<br>Example A | 23%                                         |
| Example 2                | 48%                                         |
| Example 3                | 50%                                         |

5 Example 5

Approximately 30 gallons of a fuel composition was prepared employing 3,000 ppma of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1 and 4,700 ppm of 2-(2-hexyloxy-ethoxy)-ethanol [or diethylene glycol hexyl ether] in a base fuel.

10 Example 6

Approximately 30 gallons of a fuel composition was prepared employing 3,000 ppma of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1; 2,759 ppm of 1-phenoxy-propan-2-ol [or propylene phenyl glycol ether]; 566 ppm of 2-butoxy-ethanol; 652 ppm propylene carbonate and 724 ppm benzyl alcohol in a base fuel.

15

Comparative Example B

Approximately 30 gallons of a comparative fuel composition was prepared employing 3,000 ppma of a of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1 and 4,700 ppm of an aromatic C<sub>9</sub> carrier fluid in a base fuel.

20

Example 7

Performance Example 4.6 L Port Fuel Injected Engine Dynamometer Test:

A 1991 eight cylinder engine, having displacement volume of 4.6 liter was used in these experiments. Clean up procedures were similar to the above experiments.

25

Deposit accumulation phase was set at 100 hours, followed by one tank full (20 gallons) clean up. It is noted that due to the nature of these dynamometer experiments, 30 gallons of fuel had been additized, however, ten gallons were used to purge the fuel lines, leaving 20 gallons of fuel for the clean up purposes. Upon completion of the clean up phase, the engine was disassembled and intake valve

deposit weights were measured and recorded. The before and after intake valve deposit weights were used to calculate percent clean up. Experimental data are shown in Table 3.

5 Table 3 - Intake Valve Clean Up Data from 4.6 L PFI Engine

| Fuel Composition         | Intake Valve Deposit<br>Clean up Percentage |
|--------------------------|---------------------------------------------|
| Comparative<br>Example B | 19.7 %                                      |
| Example 5                | 57.2 %                                      |
| Example 6                | 49.6 %                                      |

#### Example 8

Approximately 20 gallons of a fuel composition was prepared employing 2,200 ppma  
10 of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1; 3,000 ppm of 2-  
phenoxy-ethanol; 220 ppma of 4-polyisobutyl phenoxyethyl para-amino benzoate and  
620 ppm of a C<sub>9</sub> aromatic carrier fluid in base fuel. The 4-polyisobutyl phenoxyethyl  
para-amino benzoate was prepared in accordance with Example C-1.

#### 15 Comparative Example C

Approximately 20 gallons of a fuel composition was prepared employing 2,200 ppma  
of the dodecylphenoxy poly(oxybutylene)amine employed in Ex. 1; 220 ppma of 4-  
polyisobutyl phenoxyethyl para-amino benzoate (as employed in Ex. 8) and 3620 ppm  
of a C<sub>9</sub> aromatic carrier fluid in base fuel.

20

#### Example 9

Performance Example using a 1.8 L Direct Injection Spark Ignition Engine Test:  
A 1998 vehicle equipped with a four cylinder DISI engine, having displacement  
volume of 1.8 liter was also used to evaluate fuel additives of Example 8 and  
25 Comparative Example C. In these experiments, both injector flow restriction and  
combustion chamber deposit data were measured and recorded. The test procedure  
used here consisted of a 5,000 mile deposit build-up phase followed by a tank full  
(20 gallons) deposit clean up phase, all performed on a mileage accumulator lane. In  
order to obtain injector flow values, clean injectors and injectors after the dirty up

phase were flow tested in a special high pressure flow rig. These injectors were also flow tested after the one tank clean up to establish percent improvement in fuel flow values. Combustion chamber deposit data (piston top, cylinder head, and piston bowl) are based on deposit thickness and were acquired using similar procedure described above. Clean up data from these experiments are shown in Table 4.

Table 4 – Injector and Combustion Chamber Clean Up Data from 1.8 L DISI Vehicle

| Fuel Composition      | Increase in Injector Flow (%) | Piston Top Clean up (%) | Cylinder Head Clean up (%) | Piston Bowl Clean up (%) |
|-----------------------|-------------------------------|-------------------------|----------------------------|--------------------------|
| Comparative Example C | 55                            | 40.5                    | -8.5                       | 68                       |
| Example 8             | 100                           | 46                      | -8                         | 100                      |

10

It is well known in the scientific community, that intake system deposits, combustion chamber deposits, piston deposits and injector deposits have an adverse affect on engine performance and emissions. Furthermore, deposit buildup inside the combustion chamber can lead to combustion chamber deposit interference (CCDI). CCDI results in audible knocking noise, produced by physical contact between piston and cylinder head, particularly during cold starts. Example 1 and the data in Table 1, demonstrate that the fuel compositions of this invention are highly effective in removing unwanted deposits from a wide variety of engine components in just one tank full of gasoline. Of particular interest is the fact that the additives of this invention have the ability to penetrate deep into the engine, thus removing deposits and varnish buildup from piston ring land areas. Such a successful clean up mechanism, as demonstrated by the data in Table 1, will have a significant positive impact on freeing up partially stuck piston rings, thus reducing engine oil consumption. Reduced engine oil consumption will lower combustion chamber deposit formation and CCDI. Tables 2 and 3 demonstrate a synergistic effect and improved performance when employing a hydrocarbyl-substituted polyoxyalkylene amine with the glycol component and further with the cyclic carbonate of the present invention for removal of intake valve deposits. This is a dramatic improvement over the same type and concentration of the hydrocarbyl-substituted polyoxyalkylene

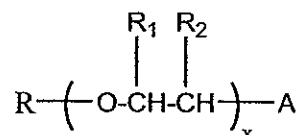
30

amine employed by itself in a carrier. Furthermore, this same kind of dramatic improvement is illustrated in Table 4, evaluating the performance in intake valve, piston top and piston bowl clean-up.

CLAIMS:

1. A fuel composition comprising a major amount of hydrocarbons boiling in the gasoline range and

a) 2,200 to 30,000 parts per million by weight of a hydrocarbyl-substituted polyoxyalkylene amine of the formula:



wherein:

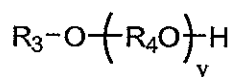
R is a hydrocarbyl group having from about 1 to about 30 carbon atoms;

R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen or lower alkyl having from about 1 to about 6 carbon atoms and each R<sub>1</sub> and R<sub>2</sub> is independently selected in each -O-CHR<sub>1</sub>-CHR<sub>2</sub>- unit;

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

x is an integer from about 5 to about 100; and

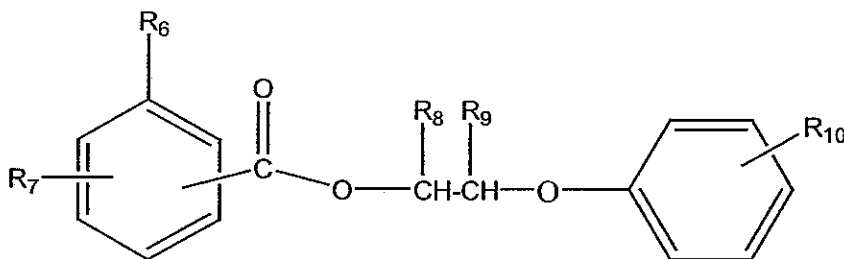
b) 1,000 to 60,000 parts per million by weight of at least one glycol ether component of the formula:



wherein:

$R_3$  is a hydrocarbonyl group having from about 1 to about 30 carbon atoms;  $R_4$  is a  $C_2$  to  $C_5$  alkylene group; and  $y$  is an integer from 1 to 50.

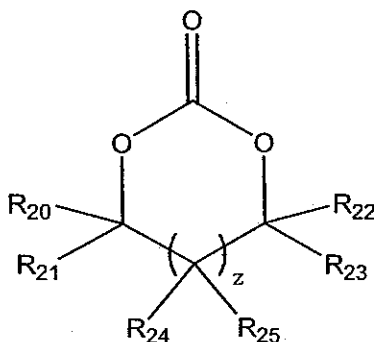
2. The fuel composition of claim 1, further comprising 100 to 10,000 parts per million by weight of an aromatic ester compound of the formula:



wherein:

- $R_6$  is nitro or  $-(CH_2)_n-NR_{11}R_{12}$ , wherein  $R_{11}$  and  $R_{12}$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and  $n$  is 0 or 1;
- $R_7$  is hydrogen, hydroxy, nitro or  $-NR_{13}R_{14}$ , wherein  $R_{13}$  and  $R_{14}$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms;
- $R_8$  and  $R_9$  are independently hydrogen or lower alkyl having 1 to 6 carbon atoms; and
- $R_{10}$  is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000.

3. The fuel composition of any one of the preceding claims, further comprising 100 to 15,000 parts per million by weight of an cyclic carbonate of the formula



wherein:

R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub>, and R<sub>25</sub> are independently selected from hydrogen, hydroxy, hydroxymethyl, hydroxyethyl, hydrocarbyl group from about 1 to 6 carbon atoms; and z is an integer from zero to one.

- 5     4.     The fuel composition according to any one of the preceding claims, wherein R is alkyl or alkylphenyl.
5.     The fuel composition according to any one of the preceding claims, wherein one of R<sub>1</sub> and R<sub>2</sub> is lower alkyl of 1 to 4 carbon atoms, and the other is  
10     hydrogen.
6.     The fuel composition according to claim 5, wherein one of R<sub>1</sub> and R<sub>2</sub> is methyl or ethyl, and the other is hydrogen.
- 15     7.     The fuel composition according to any one of the preceding claims, wherein x is an integer from about 5 to 50.
8.     The fuel composition according to claim 7, wherein x is an integer from about 8 to 30.  
20
9.     The fuel composition according to claim 8, wherein x is an integer from about 10 to 25.
10.     The fuel composition according to any one of the preceding claims, wherein  
25     A is amino or N-alkyl amino having from 1 to 4 carbon atoms.
11.     The fuel composition according to any one of claims 1 to 9, wherein A is a polyamine selected from the group consisting of ethylene diamine and diethylene triamine.  
30
12.     The fuel composition according to any one of the preceding claims, wherein the composition contains from 3,000 to 20,000 parts per million by weight of the hydrocarbyl-substituted polyoxyalkylene amine.

13. The fuel composition according to claim 12, wherein the composition contains from 6,000 to 15,000 parts per million by weight of the hydrocarbyl-substituted polyoxyalkylene amine.
- 5
14. The fuel composition according to claim 12, wherein the composition contains from 12,000 to 20,000 parts per million by weight of the hydrocarbyl-substituted polyoxyalkylene amine.
- 10
15. The fuel composition according to any one of claims 1 to 11, wherein the composition contains greater than 12,000 parts per million by weight of a hydrocarbyl-substituted polyoxyalkylene amine.
- 15
16. The fuel composition according to any one of the preceding claims, wherein  $R_3$  is alkyl, alkylphenyl, or phenyl.
17. The fuel composition according to any one of the preceding claims, wherein  $R_4$  is a  $C_2$  to  $C_4$  alkylene group.
- 20
18. The fuel composition according to any one of the preceding claims, wherein  $y$  is an integer from about 8 to 30.
19. The fuel composition according to claim 18, wherein  $y$  is an integer from about 10 to 25.
- 25
20. The fuel composition according to any one of claims 1 to 17, wherein  $y$  is an integer from 1 to 4.
21. The fuel composition according to claim 20, wherein  $R_4$  is ethylene or propylene.
- 30

22. The fuel composition according to claim 21, wherein  $R_3$  is selected so that the molecular weight of each of the at least one glycol ether is from about 100 to 450.
- 5 23. The fuel composition according to claim 22, wherein the molecular weight is less than 350.
24. The fuel composition according to any one of the preceding claims, wherein the composition contains from 1,500 to 40,000 parts per million by weight of the at least glycol ether.
- 10 25. The fuel composition according to claim 24, wherein the composition contains from 3,000 to 30,000 parts per million by weight of the glycol ether.
- 15 26. The fuel composition according to claim 22, wherein the composition contains from 3,000 to 15,000 parts per million by weight of a mixture of glycol ethers.
- 20 27. The fuel composition according to any one of claims 2 to 26, wherein  $R_6$  is amino or  $-\text{CH}_2\text{NH}_2$ .
28. The fuel composition according to any one of claims 2 to 27, wherein  $R_7$  is hydrogen or hydroxyl.
- 25 29. The fuel composition according to any one of claims 2 to 28, wherein one of  $R_8$  and  $R_9$  is hydrogen, methyl or ethyl and the other is hydrogen.
30. The fuel composition according to claim 29, wherein  $R_9$  is hydrogen.
- 30 31. The fuel composition according to any one of claims 2 to 30, wherein  $R_{10}$  is a polyalkyl group having an average molecular in the range of about 900 to 2,500.

32. The fuel composition according to any one of claims 2 to 31, wherein R<sub>6</sub> is amino, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are hydrogen and R<sub>10</sub> is a polyalkyl group derived from polyisobutene.
- 5 33. The fuel composition according to any one of claims 2 to 32, wherein the composition contains from 150 to 10,000 parts per million by weight of the aromatic ester.
34. The fuel composition according to claim 33, wherein the composition  
10 contains from 150 to 5,000 parts per million by weight of the aromatic ester.
35. The fuel composition according to claim 34, wherein the composition contains from 200 to 3,000 parts per million by weight of the aromatic ester.
- 15 36. The fuel composition according to any one of claims 3 to 35, wherein z is zero and R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub> are hydrogen.
37. The fuel composition according to any one of claims 3 to 35, wherein the  
cyclic carbonate is selected from the group consisting of 1,3-dioxolan-2-one;  
20 4-methyl-1,3-dioxolan-2-one; 4-hydroxymethyl-1,3-dioxolan-2-one; 4,5-  
dimethyl-1,3-dioxolan-2-one; 4-ethyl-1,3-dioxolan-2-one; 4,4-dimethyl-1,3-  
dioxolan-2-one (previous three also referred to as butylenes carbonates); 4-  
methyl-5-ethyl-1,3-dioxolan-2-one; 4,5-diethyl-1,3-dioxolan-2-one; 4,4-  
diethyl-1,3-dioxolan-2-one; 1,3-dioxan-2-one; 4,4-dimethyl-1,3-dioxan-2-  
25 one; 5,5-dimethyl-1,3-dioxan-2-one; 5,5-dihydroxymethyl-1,3-dioxan-2-one;  
5-methyl-1,3-dioxan-2-one; 4-methyl-1,3-dioxan-2-one; 5-hydroxy-1,3-  
dioxan-2-one; 5-hydroxymethyl-5-methyl-1,3-dioxan-2-one; 5,5-diethyl-1,3-  
dioxan-2-one; 5-methyl-5-propyl-1,3-dioxan-2-one; 4,6-dimethyl-1,3-  
dioxan-2-one; and 4,4,6-trimethyl-1,3-dioxan-2-one.
- 30 38. The fuel composition according to claim 37, wherein the cyclic carbonate is selected from 1,3-dioxolan-2-one and 4-methyl-1,3-dioxolan-2-one.

39. The fuel composition according to any one of claims 3 to 38, wherein the composition contains from 200 to 7,000 parts per million by weight of the cyclic carbonate.
- 5 40. The fuel composition according to claim 33, wherein the composition contains from 150 to 5,000 parts per million by weight of the cyclic carbonate.
- 10 41. The fuel composition according to claim 34, wherein the composition contains from 200 to 3,000 parts per million by weight of the cyclic carbonate.
42. The fuel composition according to claim 1, wherein:  
the composition contains greater than 15,000 parts per million by  
15 weight of the hydrocarbyl-substituted polyoxyalkylene amine, wherein R is alkylphenyl having from 12 to 24 carbon atoms, R<sub>1</sub> is hydrogen, R<sub>2</sub> is methyl or ethyl, x is an integer from 10 to 25, and A is amino; and  
the composition contains 3,000 to 15,000 parts per million by weight  
of the at least one glycol ether, wherein R<sub>3</sub> is alkyl from 1 to 6 carbon atoms  
20 or phenyl, R<sub>4</sub> is ethylene or 1,2-propylene and y is an integer from 1 to 3.
43. The composition according to claim 42, wherein the at least one glycol ether is a mixture of glycol ethers.
- 25 44. The composition according to claim 43 wherein the hydrocarbyl-substituted polyoxyalkylene amine is a dodecylphenoxy poly(oxybutylene) amine and wherein the at least one glycol ether is a mixture of 2-butoxy-ethanol and of 2-phenoxy-ethanol.
- 30