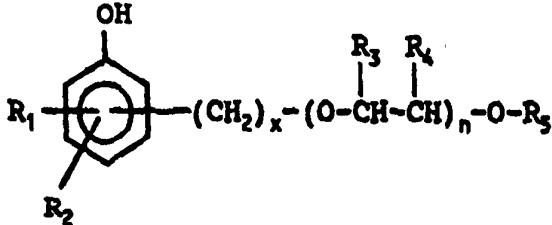





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C10L 1/18, 1/22</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/14927</b> <b>(43) International Publication Date:</b> 7 July 1994 (07.07.94)
<b>(21) International Application Number:</b> PCT/US93/12401 <b>(22) International Filing Date:</b> 17 December 1993 (17.12.93)  <b>(30) Priority Data:</b> 07/993,219                      18 December 1992 (18.12.92)      US  <b>(71) Applicant:</b> CHEVRON RESEARCH AND TECHNOLOGY COMPANY, a division of CHEVRON U.S.A. INC. [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).  <b>(72) Inventor:</b> CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US).  <b>(74) Agents:</b> CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FUEL ADDITIVE COMPOSITIONS CONTAINING POLY(OXYALKYLENE) HYDROXYAROMATIC ETHERS AND POLY(OXYALKYLENE) AMINES  <div style="text-align: center;">  <span style="margin-left: 20px;">(I)</span> </div> <div style="text-align: center; margin-top: 20px;">  <span style="margin-left: 20px;">(1)</span> </div> <b>(57) Abstract</b> <p>A fuel additive composition comprising: (a) a poly(oxyalkylene) hydroxyaromatic ether having formula (I) or a fuel-soluble salt thereof; where R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R<sub>3</sub> and R<sub>4</sub> are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R<sub>5</sub> is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of formula (1), where R<sub>6</sub> is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; n is an integer from 5 to 100; and x is an integer from 0 to 10; and (b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel fuel range.</p>		

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01 FUEL ADDITIVE COMPOSITIONS CONTAINING  
02 POLY(OXYALKYLENE) HYDROXYAROMATIC ETHERS  
03 AND POLY(OXYALKYLENE) AMINES  
04

05 BACKGROUND OF THE INVENTION  
06

07 Field of the Invention  
08

09 This invention relates to a fuel additive composition. More  
10 particularly, this invention relates to a fuel additive  
11 composition containing a poly(oxyalkylene) hydroxyaromatic  
12 ether and a poly(oxyalkylene) amine.  
13

14 Description of the Related Art  
15

16 It is well known that automobile engines tend to form  
17 deposits on the surface of engine components, such as  
18 carburetor ports, throttle bodies, fuel injectors, intake  
19 ports and intake valves, due to the oxidation and  
20 polymerization of hydrocarbon fuel. These deposits, even  
21 when present in relatively minor amounts, often cause  
22 noticeable driveability problems, such as stalling and poor  
23 acceleration. Moreover, engine deposits can significantly  
24 increase an automobile's fuel consumption and production of  
25 exhaust pollutants. Therefore, the development of effective  
26 fuel detergents or "deposit control" additives to prevent or  
27 control such deposits is of considerable importance and  
28 numerous such materials are known in the art.  
29

30 For example, aliphatic hydrocarbon-substituted phenols are  
31 known to reduce engine deposits when used in fuel  
32 compositions. U.S. Patent No. 3,849,085, issued November  
33 19, 1974 to Kreuz et al., discloses a motor fuel composition  
34 comprising a mixture of hydrocarbons in the gasoline boiling  
35 range containing about 0.01 to 0.25 volume percent of a high

-2-

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

12

13 Similarly, U.S. Patent No. 4,134,846, issued January 16,  
14 1979 to Machleder et al., discloses a fuel additive  
15 composition comprising a mixture of (1) the reaction product  
16 of an aliphatic hydrocarbon-substituted phenol,  
17 epichlorohydrin and a primary or secondary mono- or  
18 polyamine, and (2) a polyalkylene phenol. This patent  
19 teaches that such compositions show excellent carburetor,  
20 induction system and combustion chamber detergency and, in  
21 addition, provide effective rust inhibition when used in  
22 hydrocarbon fuels at low concentrations.

23

24 Poly(oxyalkylene) amines are also well known in the art as  
25 fuel additives for the prevention and control of engine  
26 deposits. For example, U.S. Patent No. 4,191,537, issued  
27 March 4, 1980 to R. A. Lewis et al., discloses a fuel  
28 composition comprising a major portion of hydrocarbons  
29 boiling in the gasoline range and from 30 to 2000 ppm of a  
30 hydrocarbyl poly(oxyalkylene) aminocarbamate having a  
31 molecular weight from about 600 to 10,000, and at least one  
32 basic nitrogen atom. The hydrocarbyl poly(oxyalkylene)  
33 moiety is composed of oxyalkylene units selected from 2 to 5  
34 carbon oxyalkylene units. These fuel compositions are  
35 taught to maintain the cleanliness of intake systems without

-3-

01 contributing to combustion chamber deposits.  
02  
03 Similar poly(oxyalkylene) amine fuel additives and fuel  
04 compositions containing such additives are described in U.S.  
05 Patent Nos. 4,160,648; 4,197,409; 4,233,168; 4,236,020;  
06 4,243,798; 4,247,301; 4,261,704; 4,270,930; 4,274,837;  
07 4,281,199; 4,288,612; 4,329,240; 4,332,595; 4,604,103;  
08 4,778,481; 4,881,945; 5,055,607; 5,094,667; and in PCT  
09 International Patent Application Publication No. WO  
10 90/07564, published July 12, 1990.

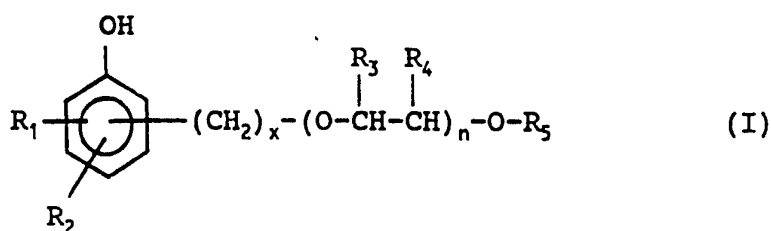
11  
12 It has now been discovered that the combination of a  
13 poly(oxyalkylene) amine and a novel poly(oxyalkylene)  
14 hydroxyaromatic ether affords a unique fuel additive  
15 composition that provides unexpectedly superior deposit  
16 control performance and fewer combustion chamber deposits  
17 than either component individually.

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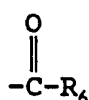
SUMMARY OF THE INVENTION

The present invention provides a novel fuel additive composition comprising:

- (a) a poly(oxyalkylene) hydroxyaromatic ether having the formula:



or a fuel-soluble salt thereof; wherein  $\text{R}_1$  and  $\text{R}_2$  are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;  $\text{R}_3$  and  $\text{R}_4$  are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;  $\text{R}_5$  is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



wherein  $\text{R}_6$  is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms;  $n$  is an integer from 5 to 100; and  $x$  is an integer from 0 to 10; and

- (b) a poly(oxyalkylene) amine having at least one basic nitrogen atom and a sufficient number of oxyalkylene

01 units to render the poly(oxyalkylene) amine soluble in  
02 hydrocarbons boiling in the gasoline or diesel fuel  
03 range.

04

05 The present invention further provides a fuel composition  
06 comprising a major amount of hydrocarbons boiling in the  
07 gasoline or diesel range and an effective deposit-  
08 controlling amount of the novel fuel additive composition of  
09 the present invention.

10

11 The present invention additionally provides a fuel  
12 concentrate comprising an inert stable oleophilic organic  
13 solvent boiling in the range of from about 150°F to 400°F  
14 and from about 10 to 70 weight percent of the fuel additive  
15 composition of the present invention.

16

17 Among other factors, the present invention is based on the  
18 surprising discovery that the unique combination of a  
19 poly(oxyalkylene) hydroxyaromatic ether and a  
20 poly(oxyalkylene) amine provides unexpectedly superior  
21 deposit control performance and fewer combustion chamber  
22 deposits than either component individually.

23

24

25 DETAILED DESCRIPTION OF THE INVENTION

26

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

29

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

32

33 The term "lower alkyl" refers to alkyl groups having 1 to  
34 about 6 carbon atoms and includes primary, secondary and  
35 tertiary alkyl groups. Typical lower alkyl groups include,

-6-

01 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,  
02 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

03

04 The term "lower alkoxy" refers to the group  $-OR_a$  wherein  $R_a$   
05 is lower alkyl. Typical lower alkoxy groups include  
06 methoxy, ethoxy, and the like.

07

08 The term "alkaryl" refers to the group:

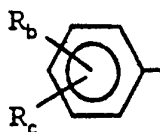
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14 wherein  $R_b$  and  $R_c$  are each independently hydrogen or an  
15 alkyl group, with the proviso that both  $R_b$  and  $R_c$  are not  
16 hydrogen. Typical alkaryl groups include, for example,  
17 tolyl, xylyl, cumenyl, ethylphenyl, butylphenyl,  
18 dibutylphenyl, hexylphenyl, octylphenyl, dioctylphenyl,  
19 nonylphenyl, decylphenyl, didecylphenyl, dodecylphenyl,  
20 hexadecylphenyl, octadecylphenyl, icosylphenyl,  
21 tricontylphenyl and the like. The term "alkylphenyl" refers  
22 to an alkaryl group of the above formula in which  $R_b$  is  
23 alkyl and  $R_c$  is hydrogen.

24

25 The term "aralkyl" refers to the group:

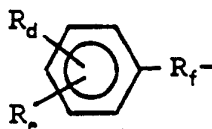
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31 wherein  $R_d$  and  $R_e$  are each independently hydrogen or an  
32 alkyl group; and  $R_f$  is an alkylene group. Typical alkaryl  
33 groups include, for example, benzyl, methylbenzyl,  
34 dimethylbenzyl, phenethyl, and the like.

35



-7-

01 The term "hydrocarbyl" refers to an organic radical composed  
02 primarily of carbon and hydrogen which may be aliphatic,  
03 alicyclic, aromatic or combinations thereof, e.g., aralkyl  
04 or alkaryl. Such hydrocarbyl groups are generally  
05 relatively free of aliphatic unsaturation, i.e., olefinic or  
06 acetylenic unsaturation.

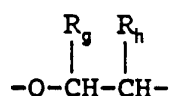
07

08 The term "oxyalkylene unit" refers to an ether moiety having  
09 the general formula:

10

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13

14 wherein  $R_g$  and  $R_h$  are each independently hydrogen or lower  
15 alkyl groups.

16

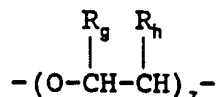
17 The term "poly(oxyalkylene)" refers to a polymer or oligomer  
18 having the general formula:

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23

24 wherein  $R_g$  and  $R_h$  are as defined above, and  $z$  is an integer  
25 greater than 1. When referring herein to the number of  
26 poly(oxyalkylene) units in a particular poly(oxyalkylene)  
27 compound, it is to be understood that this number refers to  
28 the average number of poly(oxyalkylene) units in such  
29 compounds unless expressly stated to the contrary.

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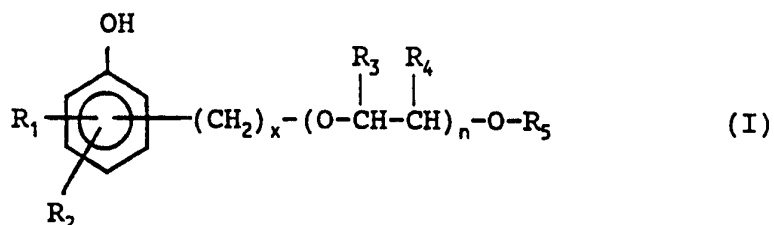
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The Poly(oxyalkylene) Hydroxyaromatic Ether

The poly(oxyalkylene) hydroxyaromatic ether component of the present invention has the general formula:



or a fuel-soluble salt thereof; wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_5$ ,  $n$  and  $x$  are as defined hereinabove.

Preferably,  $\text{R}_1$  is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms. More preferably,  $\text{R}_1$  is hydrogen or hydroxy. Most preferably,  $\text{R}_1$  is hydrogen.

$\text{R}_2$  is preferably hydrogen.

Preferably, one of  $\text{R}_3$  and  $\text{R}_4$  is lower alkyl having 1 to 3 carbon atoms and the other is hydrogen. More preferably, one of  $\text{R}_3$  and  $\text{R}_4$  is methyl or ethyl and the other is hydrogen. Most preferably, one of  $\text{R}_3$  and  $\text{R}_4$  is ethyl and the other is hydrogen.

$\text{R}_5$  is preferably hydrogen, alkyl having 2 to 22 carbon atoms, alkylphenyl having an alkyl group containing 4 to 24 carbon atoms, or an acyl group having the formula:  $-\text{C}(\text{O})\text{R}_7$ , wherein  $\text{R}_7$  is alkyl having 4 to 12 carbon atoms. More preferably,  $\text{R}_5$  is hydrogen, alkyl having 4 to 12 carbon atoms, or alkylphenyl having an alkyl group containing 4 to 12 carbon atoms. Most preferably,  $\text{R}_5$  is hydrogen.

01 Preferably, n is an integer from 10 to 50. More preferably,  
02 n is an integer from 15 to 30. Preferably, x is an integer  
03 from 0 to 2. More preferably, x is 0.

04

05 A preferred group of poly(oxyalkylene) hydroxyaromatic  
06 ethers for use in this invention are those of formula I  
07 wherein  $R_1$  is hydrogen, hydroxy, or lower alkyl having 1 to  
08 4 carbon atoms;  $R_2$  is hydrogen; one of  $R_3$  and  $R_4$  is hydrogen  
09 and the other is methyl or ethyl;  $R_5$  is hydrogen, alkyl  
10 having 4 to 12 carbon atoms, alkylphenyl having an alkyl  
11 group containing 4 to 12 carbon atoms, or an acyl group  
12 having the formula:  $-C(O)R_7$ , wherein  $R_7$  is alkyl having 4 to  
13 12 carbon atoms; n is 15 to 30 and x is 0.

14

15 Another preferred group of poly(oxyalkylene) hydroxyaromatic  
16 ethers for use in this invention are those of formula I  
17 wherein  $R_1$  is hydrogen, hydroxy, or lower alkyl having 1 to  
18 4 carbon atoms;  $R_2$  is hydrogen; one of  $R_3$  and  $R_4$  is hydrogen  
19 and the other is methyl or ethyl;  $R_5$  is hydrogen, alkyl  
20 having 4 to 12 carbon atoms, alkylphenyl having an alkyl  
21 group containing 4 to 12 carbon atoms, or an acyl group  
22 having the formula:  $-C(O)R_7$ , wherein  $R_7$  is alkyl having 4 to  
23 12 carbon atoms; n is 15 to 30 and x is 1 or 2.

24

25 A more preferred group of poly(oxyalkylene) hydroxyaromatic  
26 ethers for use in this invention are those of formula I  
27 wherein  $R_1$  is hydrogen or hydroxy;  $R_2$  is hydrogen; one of  $R_3$   
28 and  $R_4$  is hydrogen and the other is methyl or ethyl;  $R_5$  is  
29 hydrogen, alkyl having 4 to 12 carbon atoms, or alkylphenyl  
30 having an alkyl group containing 4 to 12 carbon atoms; n is  
31 15 to 30; and x is 0.

32

33 A particularly preferred group of poly(oxyalkylene)  
34 hydroxyaromatic ethers for use in this invention are those

35

01 having the formula:

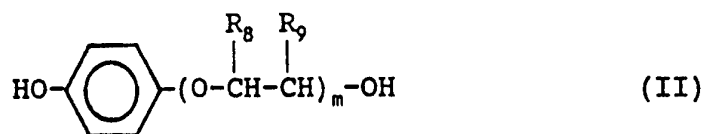
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wherein one of  $\text{R}_8$  and  $\text{R}_9$  is methyl or ethyl and the other is hydrogen; and  $m$  is an integer from 15 to 30.

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The poly(oxyalkylene) hydroxyaromatic ether component of the present fuel additive composition will generally have a sufficient molecular weight so as to be non-volatile at normal engine intake valve operating temperatures (about 200-250°C). Typically, the molecular weight of the poly(oxyalkylene) hydroxyaromatic ether component will range from about 600 to about 10,000, preferably from 1,000 to 3,000.

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Generally, the poly(oxyalkylene) hydroxyaromatic ethers employed in this invention will contain an average of about 5 to about 100 oxyalkylene units; preferably, 10 to 50 oxyalkylene units; more preferably, 15 to 30 oxyalkylene units.

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Fuel-soluble salts of poly(oxyalkylene) hydroxyaromatic ethers are also contemplated to be useful in the fuel additive composition of the present invention. Such salts include alkali metal, alkaline earth metal, ammonium, substituted ammonium and sulfonium salts. Preferred metal salts are the alkali metal salts, particularly the sodium and potassium salts, and the substituted ammonium salts, particularly tetraalkyl-substituted ammonium salts, such as the tetrabutylammonium salts.

-11-

01 General Synthetic Procedures

02

03 The poly(oxyalkylene) hydroxyaromatic ether component of the  
04 present fuel additive composition may be prepared by the  
05 following general methods and procedures. It should be  
06 appreciated that where typical or preferred process  
07 conditions (e.g. reaction temperatures, times, mole ratios  
08 of reactants, solvents, pressures, etc.) are given, other  
09 process conditions may also be used unless otherwise stated.  
10 Optimum reaction conditions may vary with the particular  
11 reactants or solvents used, but such conditions can be  
12 determined by one skilled in the art by routine optimization  
13 procedures.

14

15 The poly(oxyalkylene) hydroxyaromatic ethers employed in the  
16 present fuel additive composition may be prepared from a  
17 hydroxyaromatic compound having the formula:

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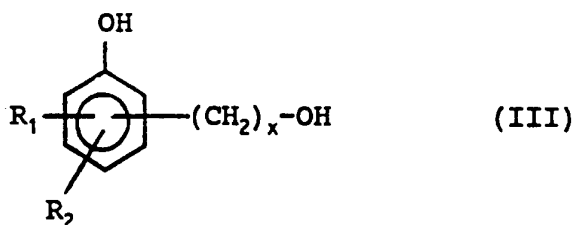
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wherein  $R_1$ ,  $R_2$ , and  $x$  are as defined above.

The hydroxyaromatic compounds of formula III are either known compounds or can be prepared from known compounds by conventional procedures. Suitable hydroxyaromatic compounds for use as starting materials in this invention include catechol, resorcinol, hydroquinone, 1,2,3-trihydroxybenzene (pyrogallol), 1,2,4-trihydroxybenzene (hydroquinol), 1,3,5-trihydroxybenzene (phloroglucinol), 1,4-dihydroxy-2-methylbenzene, 1,3-dihydroxy-5-methylbenzene, 2-t-butyl-1,4-

-12-

01 dihydroxybenzene, 2,6-di-*t*-butyl-1,4-dihydroxybenzene, 1,4-  
02 dihydroxy-2-methoxybenzene, 1,3-dihydroxy-5-methoxybenzene,  
03 4-hydroxybenzyl alcohol, 4-hydroxyphenethyl alcohol and the  
04 like.

05

06 In a preferred method of synthesizing the poly(oxyalkylene)  
07 hydroxyaromatic ether component of the present fuel additive  
08 composition, a hydroxyaromatic compound of formula III is  
09 first selectively protected to provide a compound having the  
10 formula:

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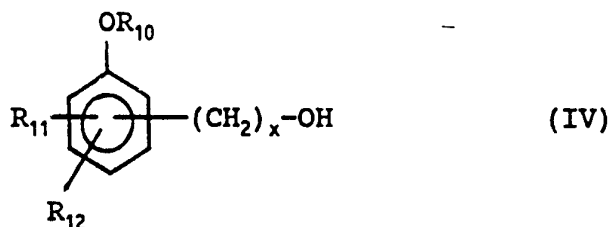
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19 wherein  $R_{10}$  is a suitable hydroxyl protecting group, such as  
20 benzyl, *tert*-butyldimethylsilyl, methoxymethyl, and the  
21 like;  $R_{11}$  and  $R_{12}$  are each independently hydrogen, lower  
22 alkyl, lower alkoxy, or the group  $-OR_{13}$ , wherein  $R_{13}$  is a  
23 suitable hydroxyl protecting group, such as benzyl, *tert*-  
24 butyldimethylsilyl, methoxymethyl, and the like.  
25 Preferably,  $R_{10}$  and  $R_{13}$  are benzyl; except in the case where  
26  $x$  is 1, then  $R_{10}$  and  $R_{13}$  are preferably a *tert*-butyl-  
27 dimethylsilyl group.

28

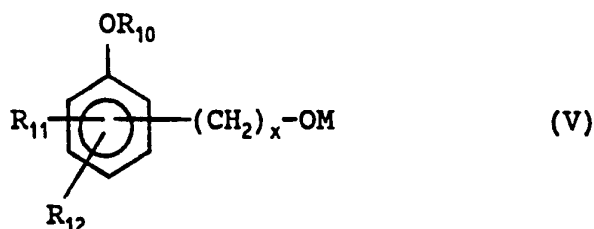
29 Selective protection of III may be accomplished using  
30 conventional procedures. The choice of a suitable  
31 protecting group for a particular hydroxyaromatic compound  
32 will be apparent to those skilled in the art. Various  
33 protecting groups, and their introduction and removal, are  
34 described, for example, in T. W. Greene and P. G. M. Wuts,  
35 *Protective Groups in Organic Synthesis*, Second Edition,



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01 Wiley, New York, 1991, and references cited therein.  
02 Alternatively, the protected derivatives IV can be prepared  
03 from known starting materials other than the hydroxyaromatic  
04 compounds of formula III by conventional procedures. In  
05 some cases, the protected derivatives IV are commercially  
06 available, e.g. 4-benzyloxyphenol is commercially available  
07 from Aldrich Chemical Co., Milwaukee, Wisconsin 53233.

08  
09 The protected hydroxyaromatic compound of formula IV is then  
10 deprotonated with a suitable base to provide a metal salt  
11 having the formula:



wherein R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub> and x are as defined above; and M is a metal cation, such as lithium, sodium or potassium.

Generally, this deprotonation reaction will be effected by contacting IV 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 about 0.25 to about 3 hours.

Metal salt V is generally not isolated, but is reacted *in situ* with about 5 to about 100 molar equivalents of an

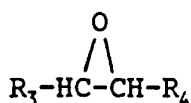
-14-

01 alkylene oxide (an epoxide) having the formula:

02

03

04



(VI)

05

06

07 wherein  $\text{R}_3$  and  $\text{R}_4$  are as defined above, to provide, after  
08 neutralization, a poly(oxyalkylene) polymer or oligomer  
09 having the formula:

10

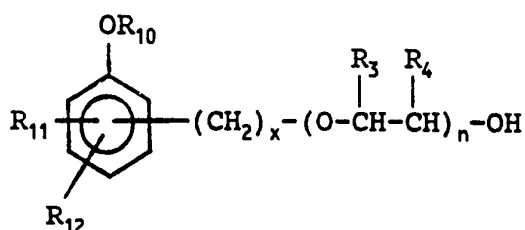
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(VII)

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17

18 wherein  $\text{R}_3$ ,  $\text{R}_4$ ,  $\text{R}_{10}$ ,  $\text{R}_{11}$ ,  $\text{R}_{12}$ ,  $n$  and  $x$  are as defined above.

19

20 Typically, this polymerization reaction is conducted in a  
21 substantially anhydrous inert solvent at a temperature of  
22 about 30°C to about 150°C for about 2 to about 120 hours.  
23 Suitable solvents for this reaction, include toluene, xylene  
24 and the like. The reaction will generally be conducted at a  
25 pressure sufficient to contain the reactants and the  
26 solvent, preferably at atmospheric or ambient pressure.  
27 More detailed reaction conditions for preparing  
28 poly(oxyalkylene) compounds may be found in U.S. Patent Nos.  
29 2,782,240 and 2,841,479, which are incorporated herein by  
30 reference.

31

32 The amount of alkylene oxide employed in this reaction will  
33 depend on the number of oxyalkylene units desired in the  
34 product. Typically, the molar ratio of alkylene oxide VI to  
35 metal salt V will range from about 5:1 to about 100:1;



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01 preferably, from 10:1 to 50:1, more preferably from 15:1 to  
02 30:1.

03

04 Suitable alkylene oxides for use in the polymerization  
05 reaction include, for example, ethylene oxide; propylene  
06 oxide; butylene oxides, such as 1,2-butylene oxide (1,2-  
07 epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane);  
08 pentylene oxides; hexylene oxides; octylene oxides and the  
09 like. Preferred alkylene oxides are propylene oxide and  
10 1,2-butylene oxide.

11

12 In the polymerization reaction, a single type of alkylene  
13 oxide may be employed, e.g. propylene oxide, in which case  
14 the product is a homopolymer, e.g. a poly(oxypropylene).  
15 However, copolymers are equally satisfactory and random  
16 copolymers are readily prepared by contacting the metal salt  
17 V with a mixture of alkylene oxides, such as a mixture of  
18 propylene oxide and 1,2-butylene oxide, under polymerization  
19 conditions. Copolymers containing blocks of oxyalkylene  
20 units are also suitable for use in the present invention.  
21 Block copolymers may be prepared by contacting the metal  
22 salt V with first one alkylene oxide, then others in any  
23 order, or repetitively, under polymerization conditions.

24

25 Poly(oxyalkylene) polymers of formula VII may also be  
26 prepared by living or immortal polymerization as described  
27 by S. Inoue and T. Aida in *Encyclopedia of Polymer Science*  
28 *and Engineering*, Second Edition, Supplemental Volume, J.  
29 Wiley and Sons, New York, pages 412-420 (1989). These  
30 procedures are especially useful for preparing  
31 poly(oxyalkylene) alcohols of formula V in which  $R_3$  and  $R_4$   
32 are both alkyl groups.

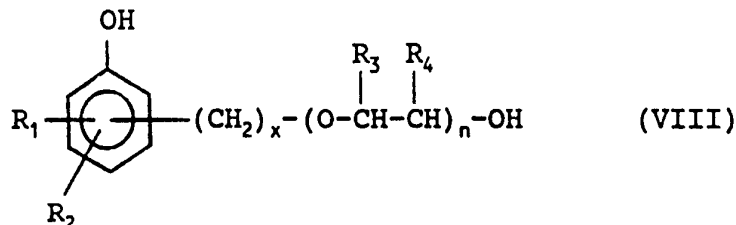
33

34 Deprotection of the aromatic hydroxyl group(s) of VII using

35

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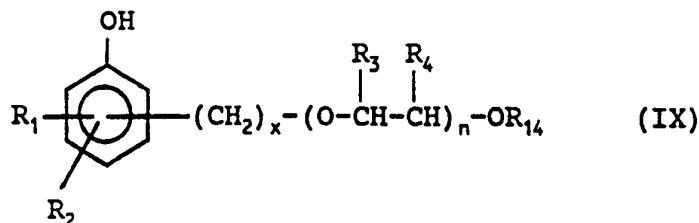
01 conventional procedures provides a poly(oxyalkylene)  
 02 hydroxyaromatic ether having the formula:



11 wherein  $\text{R}_1$ - $\text{R}_4$ ,  $n$  and  $x$  are as defined above.

12  
 13 Appropriate conditions for this deprotection step will  
 14 depend upon the protecting group(s) utilized in the  
 15 synthesis and will be readily apparent to those skilled in  
 16 the art. For example, benzyl protecting groups may be  
 17 removed by hydrogenolysis under 1 to about 4 atmospheres of  
 18 hydrogen in the presence of a catalyst, such as palladium on  
 19 carbon. Typically, this deprotection reaction will be  
 20 conducted in an inert solvent, preferably a mixture of ethyl  
 21 acetate and acetic acid, at a temperature of from about  $0^\circ\text{C}$   
 22 to about  $40^\circ\text{C}$  for about 1 to about 24 hours.

23  
 24 The poly(oxyalkylene) hydroxyaromatic ethers employed in the  
 25 present fuel additive composition that contain an alkyl or  
 26 alkaryl ether moiety, i.e. those having the formula:



33 wherein  $\text{R}_1$ - $\text{R}_4$ ,  $n$  and  $x$  are as defined above, and  $\text{R}_{14}$  is an  
 34 alkyl group or aralkyl group, may be conveniently prepared  
 35

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01 from a compound of formula VIII by selectively alkylating  
02 the hydroxyl group of the poly(oxyalkylene) moiety of VIII  
03 with a suitable alkylating agent.

04

05 Typically, this alkylation reaction will be conducted by  
06 first contacting VIII with a sufficient amount of a strong  
07 base capable of abstracting a proton from each the hydroxyl  
08 groups present in VIII, including the aromatic hydroxyl  
09 group(s) and the hydroxyl group of the poly(oxyalkylene)  
10 moiety. Suitable bases for this reaction include, for  
11 example, sodium hydride, potassium hydride, sodium amide and  
12 the like. Generally, this deprotonation reaction will be  
13 conducted in an inert solvent, such as toluene,  
14 tetrahydrofuran, and the like, under substantially anhydrous  
15 conditions at a temperature in the range from -10°C to 120°C  
16 for about 0.25 to about 3 hours. The resulting metal salt  
17 is then contacted with about 0.90 to about 1.1 molar  
18 equivalents of a suitable alkylating agent at a temperature  
19 in the range from 0°C to 120°C for about 1 to about 50 hours  
20 to afford, after neutralization, a poly(oxyalkylene)  
21 hydroxyaromatic ether of formula IX.

22

23 Suitable alkylating agents for use in this reaction include  
24 alkyl and aralkyl halides, such as alkyl chlorides, bromides  
25 and iodides and aralkyl chlorides, bromides and iodides; and  
26 alkyl and aralkyl sulfonates, such as alkyl mesylates and  
27 tosylates, and aralkyl mesylates and tosylates.

28

29 Preferred alkylating agents are primary and secondary alkyl  
30 halides having 1 to 30 carbon atoms, and primary and  
31 secondary aralkyl halides having 7 to 36 carbon atoms; more  
32 preferred alkylating agents are primary alkyl halides having  
33 4 to 12 carbon atoms.

34

35 Representative examples of alkylating agents include, but

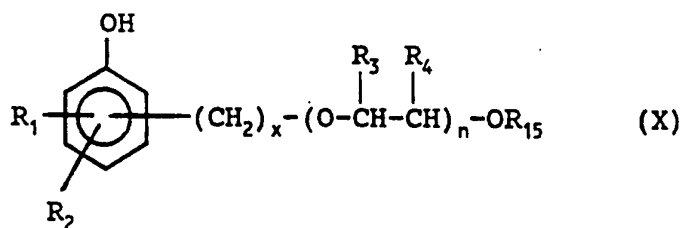
-18-

are not limited to, methyl iodide, ethyl iodide, n-propyl bromide, n-butyl bromide, n-pentyl bromide, n-hexyl chloride, n-octyl chloride, n-decyl chloride, benzyl chloride and phenethyl chloride. Particularly preferred alkylating agents are benzyl chloride, n-butyl bromide.

Alternatively, poly(oxyalkylene) hydroxyaromatic ethers of formula IX may be prepared by alkylating the hydroxyl group of the poly(oxyalkylene) moiety of protected intermediate VII, and then deprotecting the resulting product. The conditions for alkylating intermediate VII are essentially the same as those described above; however, a lesser amount of base will be required since the aromatic hydroxyl groups of VII are in a protected form.

Other suitable methods for preparing alkyl and alkaryl ethers from alcohols, and appropriate reaction conditions for such reactions, can be found, for example, in I.T. Harrison and S. Harrison, *Compendium of Organic Synthetic Methods*, Vol. 1, pp. 310-312, Wiley-Interscience, New York (1971) and references cited therein.

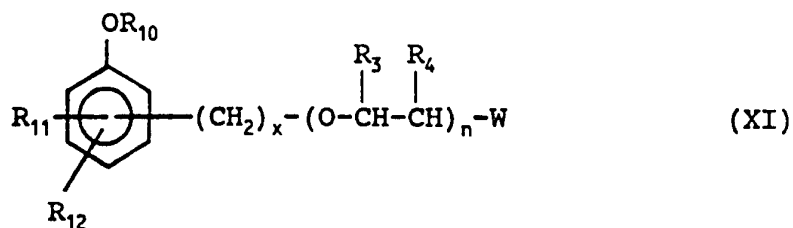
The poly(oxyalkylene) hydroxyaromatic ethers employed in the present fuel additive composition that contain an alkaryl ether moiety, i.e. those having the formula:



wherein  $\text{R}_1$ - $\text{R}_4$ ,  $n$  and  $x$  are as defined above, and  $\text{R}_{15}$  is a phenyl or alkaryl group, may be prepared from intermediate VII in several steps by first converting the hydroxyl group

-19-

01 present of the poly(oxyalkylene) moiety of VII into a  
 02 suitable leaving group, i.e. forming an intermediate having  
 03 the formula:



11  
 12 wherein  $R_3$ ,  $R_4$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$ ,  $n$  and  $x$  are as defined above,  
 13 and  $W$  is a suitable leaving group; and then displacing the  
 14 leaving group of XI with a metal salt of a phenol having the  
 15 formula:



21  
 22 wherein  $R_{16}$  and  $R_{17}$  are each independently hydrogen or an  
 23 alkyl group. Subsequent deprotection of the resulting  
 24 product affords poly(oxyalkylene) hydroxyaromatic ethers of  
 25 formula X.

26  
 27 The hydroxyl group of the poly(oxyalkylene) moiety of VII  
 28 may be converted into a suitable leaving group by contacting  
 29 VII with a sulfonyl chloride to form a sulfonate ester, such  
 30 as a methanesulfonate (mesylate) or a toluenesulfonate  
 31 (tosylate). Typically, this reaction is conducted in the  
 32 presence of a suitable amine, such as triethylamine or  
 33 pyridine, in an inert solvent, such as dichloromethane, at a  
 34 temperature in the range of about  $-10^{\circ}\text{C}$  to about  $30^{\circ}\text{C}$ .  
 35 Alternatively, the hydroxyl group of the poly(oxyalkylene)

-20-

01 moiety of VII can be exchanged for a halide, such chloride  
02 or bromide, by contacting VII with a halogenating agent,  
03 such as thionyl chloride, oxalyl chloride or phosphorus  
04 tribromide. Other suitable methods for preparing sulfonates  
05 and halides from alcohols, and appropriate reaction  
06 conditions for such reactions, can be found, for example, in  
07 I.T. Harrison and S. Harrison, *Compendium of Organic*  
08 *Synthetic Methods*, Vol. 1, pp. 331-337, Wiley-Interscience,  
09 New York (1971) and references cited therein.

10

11 After forming intermediate XI, the leaving group may be  
12 displaced therefrom by contacting XI with metal salt XII.  
13 Generally, this reaction will be conducted in an inert  
14 solvent, such as toluene, tetrahydrofuran and the like,  
15 under substantially anhydrous conditions at a temperature in  
16 the range of about 25°C to about 150°C for about 1 to about  
17 48 hours. The metal salt XII can be formed by contacting  
18 the corresponding phenol with a strong base capable of  
19 abstracting the proton from the phenolic hydroxyl group,  
20 such as sodium hydride, potassium hydride, sodium amide and  
21 the like, in an inert solvent.

22

23 Suitable phenolic compounds for use in this reaction include  
24 phenol, monoalkyl-substituted phenols and dialkyl-  
25 substituted phenols. Monoalkyl-substituted phenols are  
26 preferred, especially monoalkylphenols having an alkyl  
27 substituent in the para position. Representative examples  
28 of suitable phenolic compounds include, but are not limited  
29 to, phenol, methylphenol, dimethylphenol, ethylphenol,  
30 butylphenol, octylphenol, decylphenol, dodecylphenol,  
31 tetradecylphenol, hexadecylphenol, octadecylphenol,  
32 eicosylphenol, tetracosylphenol, hexacosylphenol,  
33 triacontylphenol and the like. Also, mixtures of  
34 alkylphenols may be employed, such as a mixture of C<sub>14</sub>-C<sub>18</sub>

35

-21-

01 alkylphenols, a mixture of C<sub>18</sub>-C<sub>24</sub> alkylphenols, a mixture of  
02 C<sub>20</sub>-C<sub>24</sub> alkylphenols, or a mixture of C<sub>16</sub>-C<sub>26</sub> alkylphenols.

03

04 Particularly preferred alkylphenols are those derived from  
05 alkylation of phenol with polymers or oligomers of C<sub>3</sub> to C<sub>6</sub>  
06 olefins, such as polypropylene or polybutene. These  
07 polymers preferably contain 10 to 30 carbon atoms. An  
08 especially preferred alkylphenol is prepared by alkylating  
09 phenol with a propylene polymer having an average of 4  
10 units. This polymer has the common name of propylene  
11 tetramer and is commercially available.

12

13 Alternatively, the poly(oxyalkylene) hydroxyaromatic ethers  
14 of formula X can be prepared by displacing a leaving group  
15 from an intermediate having the formula:

16

17

18

19

20



21

22 wherein R<sub>3</sub>, R<sub>4</sub>, R<sub>15</sub>, n and x are as defined above, and W is a  
23 suitable leaving group, with metal salt V; and then  
24 deprotecting the resulting product. Conditions for this  
25 reaction are essentially the same as those described above  
26 for reaction of XI with XII. Compounds of formula XIII may  
27 be prepared from XII and VI using the conditions described  
28 above for the preparation of VII, followed by conversion of  
29 the hydroxyl group of the poly(oxyalkylene) moiety of the  
30 resulting product into a suitable leaving using the  
31 procedures described above for the preparation of XI.

32

33 The poly(oxyalkylene) hydroxyaromatic ethers employed in the  
34 present fuel additive composition that contain an acyl

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-22-

01 moiety, i.e those having the formula:

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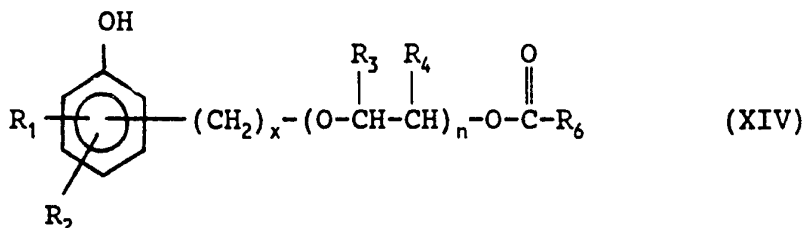
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35



wherein  $\text{R}_1$ - $\text{R}_4$ ,  $\text{R}_6$ ,  $n$  and  $x$  are as defined above; may be prepared from intermediate VII by first acylating the hydroxyl group of the poly(oxyalkylene) moiety of VII to form an ester. Subsequent deprotection of the aromatic hydroxyl group(s) of the resulting ester using conventional procedures then affords poly(oxyalkylene) hydroxyaromatic ethers of formula XIV.

Generally, the acylation reaction will be conducted by contacting intermediate VII with about 0.95 to about 1.2 molar equivalents of a suitable acylating agent. Suitable acylating agents for use in this reaction include acyl halides, such as acyl chlorides and bromides; and carboxylic acid anhydrides. Preferred acylating agents are those having the formula:  $\text{R}_6\text{C}(\text{O})-\text{X}$ , wherein  $\text{R}_6$  is alkyl having 1 to 30 carbon atom, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms, and  $\text{X}$  is chloro or bromo. More preferred acylating agents are those having the formula:  $\text{R}_7\text{C}(\text{O})-\text{X}$ , wherein  $\text{R}_7$  is alkyl having 4 to 12 carbon atoms.

Representative examples of suitable acylating agents include, but are not limited to, acetyl chloride, acetic anhydride, propionyl chloride, butanoyl chloride, pivaloyl chloride, octanoyl chloride, decanoyl chloride 4-*t*-butylbenzoyl chloride and the like.

Generally, this reaction is conducted in an inert solvent,



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01 such as toluene, dichloromethane, diethyl ether and the  
02 like, at a temperature in the range of about 25°C to about  
03 150°C, and is generally complete in about 0.5 to about 48  
04 hours. When an acyl halide is employed as the acylating  
05 agent, this reaction is preferably conducted in the presence  
06 of a sufficient amount of an amine capable of neutralizing  
07 the acid generated during the reaction, such as  
08 triethylamine, di(isopropyl)ethylamine, pyridine or 4-  
09 dimethylaminopyridine.

10

11 Additional methods for preparing esters from alcohols, and  
12 suitable reaction conditions for such reactions, can be  
13 found, for example, in I.T. Harrison and S. Harrison,  
14 *Compendium of Organic Synthetic Methods*, Vol. 1, pp. 273-276  
15 and 280-283, Wiley-Interscience, New York (1971) and  
16 references cited therein.

17

18

19 The Poly(oxyalkylene) Amine

20

21 The poly(oxyalkylene) amine component of the present fuel  
22 additive composition is a poly(oxyalkylene) amine having at  
23 least one basic nitrogen atom and a sufficient number of  
24 oxyalkylene units to render the poly(oxyalkylene) amine  
25 soluble in hydrocarbons boiling in the gasoline or diesel  
26 range.

27

28 Preferably, such poly(oxyalkylene) amines will also be of  
29 sufficient molecular weight so as to be nonvolatile at  
30 normal engine intake valve operating temperatures, which are  
31 generally in the range of about 200°C to 250°C.

32

33 Generally, the poly(oxyalkylene) amines suitable for use in  
34 the present invention will contain at least about 5

35

01 oxyalkylene units, preferably about 5 to 100, more  
02 preferably about 8 to 100, and even more preferably about 10  
03 to 100. Especially preferred poly(oxyalkylene) amines will  
04 contain about 10 to 25 oxyalkylene units.

05

06 The molecular weight of the presently employed  
07 poly(oxyalkylene) amines will generally range from about 500  
08 to about 10,000, preferably from about 500 to about 5,000.

09

10 Suitable poly(oxyalkylene) amine compounds for use in the  
11 present invention include hydrocarbyl poly(oxyalkylene)  
12 polyamines as disclosed, for example, in U.S. Patent No.  
13 4,247,301, issued January 27, 1981 to Honnen, the disclosure  
14 of which is incorporated herein by reference. These  
15 compounds are hydrocarbyl poly(oxyalkylene) polyamines  
16 wherein the poly(oxyalkylene) moiety comprises at least one  
17 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to 5  
18 carbon atom oxyalkylene units, and wherein the  
19 poly(oxyalkylene) chain is bonded through a terminal carbon  
20 atom to a nitrogen atom of a polyamine having from 2 to  
21 about 12 amine nitrogen atoms and from 2 to about 40 carbon  
22 atoms with a carbon-to-nitrogen ratio between about 1:1 and  
23 10:1. The hydrocarbyl group on these hydrocarbyl  
24 poly(oxyalkylene) polyamines will contain from about 1 to 30  
25 carbon atoms. These compounds generally have molecular  
26 weights in the range of about 500 to 10,000, preferably from  
27 about 500 to 5,000 and more preferably from about 800 to  
28 5,000.

29

30 The above-described hydrocarbyl poly(oxyalkylene) polyamines  
31 are prepared by conventional procedures known in the art, as  
32 taught, for example, in U.S. Patent No. 4,247,301.

33

34 Other poly(oxyalkylene) amines suitable for use in the  
35 present invention are the poly(oxyalkylene) polyamines

-25-

01 wherein the poly(oxyalkylene) moiety is connected to the  
02 polyamine moiety through an oxyalkylene hydroxy-type linkage  
03 derived from an epihalohydrin, such as epichlorohydrin or  
04 epibromohydrin. This type of poly(oxyalkylene) amine having  
05 an epihalohydrin-derived linkage is described, for example,  
06 in U.S. Patent No. 4,261,704, issued April 14, 1981 to  
07 Langdon, the disclosure of which is incorporated herein by  
08 reference.

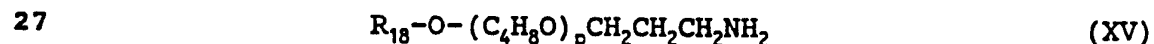
09

10 Useful polyamines for preparing the epihalohydrin-derived  
11 poly(oxyalkylene) polyamines include, for example, alkylene  
12 polyamines, polyalkylene polyamines, cyclic amines, such as  
13 piperazines, and amino-substituted amines. The  
14 poly(oxyalkylene) polyamines having an epihalohydrin-derived  
15 linkage between the poly(oxyalkylene) and polyamine moieties  
16 are prepared using known procedures as taught, for example,  
17 in U.S. Patent No. 4,261,704.

18

19 Another type of poly(oxyalkylene) amine useful in the  
20 present invention is a highly branched alkyl  
21 poly(oxyalkylene) monoamine as described, for example in  
22 U.S. Patent No. 5,094,667, issued March 10, 1992 to  
23 Schilowitz et al., the disclosure of which is incorporated  
24 herein by reference. These highly branched alkyl  
25 poly(oxyalkylene) monoamines have the general formula:

26



28

29 wherein  $R_{18}$  is a highly branched alkyl group containing from  
30 12 to 40 carbon atoms, preferably an alkyl group having 20  
31 carbon atoms which is derived from a Guerbet condensation  
32 reaction, and  $p$  is a number up to 30, preferably 4 to 8.  
33 The preferred alkyl group is derived from a Guerbet alcohol

34

35

-26-

01 containing 20 carbon atoms having the formula:

02

03

04

05

06

07 wherein R<sub>19</sub> is a hydrocarbyl chain.

08

09 The above highly branched alkyl poly(oxyalkylene) monoamines  
10 are prepared by using known methods as disclosed, for  
11 example, in U.S. Patent No. 5,094,667.

12

13 A particularly preferred class of poly(oxyalkylene) amine  
14 for use in the fuel additive composition of the present  
15 invention are the hydrocarbyl-substituted poly(oxyalkylene)  
16 aminocarbamates disclosed, for example, in U.S. Patent Nos.  
17 4,288,612; 4,236,020; 4,160,648; 4,191,537; 4,270,930;  
18 4,233,168; 4,197,409; 4,243,798 and 4,881,945, the  
19 disclosure of each of which are incorporated herein by  
20 reference.

21

22 These hydrocarbyl poly(oxyalkylene) aminocarbamates contain  
23 at least one basic nitrogen atom and have an average  
24 molecular weight of about 500 to 10,000, preferably about  
25 500 to 5,000, and more preferably about 1,000 to 3,000. As  
26 described more fully hereinbelow, these hydrocarbyl  
27 poly(oxyalkylene) aminocarbamates contain a (a)  
28 poly(oxyalkylene) moiety, (b) an amine moiety and (c) a  
29 carbamate connecting group.

30

31 A. The Poly(oxyalkylene) Moiety

32

33 The hydrocarbyl-terminated poly(oxyalkylene) polymers which  
34 are utilized in preparing the hydrocarbyl poly(oxyalkylene)  
35 aminocarbamates employed in the present invention are

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01 monohydroxy compounds, e.g., alcohols, often termed  
02 monohydroxy polyethers, or polyalkylene glycol monocarbyl  
03 ethers, or "capped" poly(oxyalkylene) glycols, and are to be  
04 distinguished from the poly(oxyalkylene) glycols (diols), or  
05 polyols, which are not hydrocarbyl-terminated, i.e., are not  
06 capped. These hydrocarbyl poly(oxyalkylene) alcohols may be  
07 produced under conditions essentially the same as those  
08 described above for the preparation of VII, i.e. by the  
09 addition of lower alkylene oxides, such as ethylene oxide,  
10 propylene oxide, butylene oxide, etc. to a hydroxy compound,  
11  $R_{20}OH$ , under polymerization conditions, wherein  $R_{20}$  is the  
12 hydrocarbyl group which caps the poly(oxyalkylene) chain.

13

14 In the hydrocarbyl poly(oxyalkylene) aminocarbamates  
15 employed in the present invention, the group  $R_{20}$  will  
16 generally contain from 1 to about 30 carbon atoms,  
17 preferably from 2 to about 20 carbon atoms and is preferably  
18 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl  
19 wherein the alkyl is a straight or branched-chain of from  
20 1 to about 24 carbon atoms. More preferably,  $R_{20}$  is  
21 alkylphenyl wherein the alkyl group is a branched-chain of  
22 12 carbon atoms, derived from propylene tetramer, and  
23 commonly referred to as tetrapropenyl.

24

25 The oxyalkylene units in the poly(oxyalkylene) moiety  
26 preferably contain from 2 to about 5 carbon atoms but one or  
27 more units of a larger carbon number may also be present.  
28 Generally, each poly(oxyalkylene) polymer contains at least  
29 about 5 oxyalkylene units, preferably about 5 to about 100  
30 oxyalkylene units, more preferably about 8 to about 100  
31 units, even more preferably about 10 to 100 units, and most  
32 preferably 10 to about 25 such units. The poly(oxyalkylene)  
33 moiety of the hydrocarbyl poly(oxyalkylene) aminocarbamates  
34 employed in the present invention is more fully described  
35 and exemplified in U.S. Patent No. 4,191,537, issued March

-28-

01 4, 1980 to Lewis, the disclosure of which is incorporated  
02 herein by reference.

03

04 Although the hydrocarbyl group on the hydrocarbyl  
05 poly(oxyalkylene) moiety will preferably contain from 1 to  
06 about 30 carbon atoms, longer hydrocarbyl groups,  
07 particularly longer chain alkyl phenyl groups, may also be  
08 employed. For example, alkylphenyl poly(oxyalkylene)  
09 aminocarbamates wherein the alkyl group contains at least 40  
10 carbon atoms, as described in U.S. Patent No. 4,881,945,  
11 issued November 21, 1989 to Buckley, are also contemplated  
12 for use in the present invention. The alkyl phenyl group on  
13 the aminocarbamates of U.S. Patent No. 4,881,945 will  
14 preferably contain an alkyl group of 50 to 200 carbon atoms,  
15 and more preferably, an alkyl group of 60 to 100 carbon  
16 atoms. The disclosure of U.S. Patent No. 4,881,945 is  
17 incorporated herein by reference.

18

19 Also contemplated for use in the present invention are  
20 alkylphenyl poly(oxypropylene) aminocarbamates wherein the  
21 alkyl group is a substantially straight-chain alkyl group  
22 of about 25 to 50 carbon atoms derived from an alpha olefin  
23 oligomer of C<sub>8</sub> to C<sub>20</sub> alpha olefins, as described in  
24 PCT International Patent Application Publication No. WO  
25 90/07564, published July 12, 1990, the disclosure of which  
26 is incorporated herein by reference.

27

28 B. The Amine Moiety

29

30 The amine moiety of the hydrocarbyl poly(oxyalkylene)  
31 aminocarbamate is preferably derived from a polyamine having  
32 from 2 to about 12 amine nitrogen atoms and from 2 to about  
33 40 carbon atoms.

34

35 The polyamine is preferably reacted with a hydrocarbyl

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01 poly(oxyalkylene) chloroformate to produce the hydrocarbyl  
02 poly(oxyalkylene) aminocarbamate fuel additive finding use  
03 within the scope of the present invention. The  
04 chloroformate is itself derived from hydrocarbyl  
05 poly(oxyalkylene) alcohol by reaction with phosgene.

06

07 The polyamine provides the hydrocarbyl poly(oxyalkylene)  
08 aminocarbamate with, on the average, at least about one  
09 basic nitrogen atom per carbamate molecule, i.e., a nitrogen  
10 atom titratable by strong acid. The polyamine preferably  
11 has a carbon-to-nitrogen ratio of from about 1:1 to about  
12 10:1. The polyamine may be substituted with substituents  
13 selected from hydrogen, hydrocarbyl groups of from 1 to  
14 about 10 carbon atoms, acyl groups of from 2 to about 10  
15 carbon atoms, and monoketone, monohydroxy, mononitro,  
16 monocyano, alkyl and alkoxy derivatives of hydrocarbyl  
17 groups of from 1 to 10 carbon atoms. It is preferred that  
18 at least one of the basic nitrogen atoms of the polyamine is  
19 a primary or secondary amino nitrogen. The amine moiety of  
20 the hydrocarbyl poly(oxyalkylene) aminocarbamates employed  
21 in the present invention has been described and exemplified  
22 more fully in U.S. Patent No. 4,191,537.

23

24 A more preferred polyamine for use in preparing the  
25 hydrocarbyl poly(oxyalkylene) aminocarbamates finding use  
26 within the scope of the present invention is a polyalkylene  
27 polyamine, including alkylenediamine, and including  
28 substituted polyamines, e.g., alkyl and hydroxyalkyl-  
29 substituted polyalkylene polyamine. Preferably, the  
30 alkylene group contains from 2 to 6 carbon atoms, there  
31 being preferably from 2 to 3 carbon atoms between the  
32 nitrogen atoms. Examples of such polyamines include  
33 ethylenediamine, diethylenetriamine, triethylenetetramine,  
34 di(trimethylene)triamine, dipropylenetriamine,  
35 tetraethylenepentamine, etc.

01 Among the polyalkylene polyamines, polyethylene polyamine  
02 and polypropylene polyamine containing 2 to about 12 amine  
03 nitrogen atoms and 2 to about 24 carbon atoms are especially  
04 preferred and in particular, the lower polyalkylene  
05 polyamines, e.g., ethylenediamine, diethylenetriamine,  
06 propylenediamine, dipropylenetriamine, etc., are most  
07 preferred.

08

09 C. The Aminocarbamate Connecting Group

10

11 The hydrocarbyl poly(oxyalkylene) aminocarbamate employed as  
12 the poly(oxyalkylene) amine component of the fuel additive  
13 composition of the present invention is obtained by linking  
14 the polyamine and the hydrocarbyl poly(oxyalkylene) alcohol  
15 together through a carbamate linkage, i.e.,

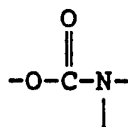
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17

18

19

20



21 wherein the oxygen may be regarded as the terminal hydroxyl  
22 oxygen of the poly(oxyalkylene) alcohol, the nitrogen is  
23 derived from the polyamine and the carbonyl group  $-\text{C}(\text{O})-$ , is  
24 preferably provided by a coupling agent, such as phosgene.

25

26 In a preferred method of preparation, the hydrocarbyl  
27 poly(oxyalkylene) alcohol is reacted with phosgene to  
28 produce a chloroformate and the chloroformate is reacted  
29 with the polyamine. Since there may be more than one  
30 nitrogen atom of the polyamine which is capable of reacting  
31 with the chloroformate, the carbamate product may contain  
32 more than one hydrocarbyl poly(oxyalkylene) moiety. It is  
33 preferred that the hydrocarbyl poly(oxyalkylene)  
34 aminocarbamate product contains on the average, about  
35 one poly(oxyalkylene) moiety per molecule (i.e., is a



-31-

01 monocarbamate), although it is understood that this reaction  
02 route may lead to mixtures containing appreciable amounts of  
03 di- or higher poly(oxyalkylene) chain substitution on a  
04 polyamine containing several reactive nitrogen atoms.

05

06 A particularly preferred aminocarbamate is alkylphenyl  
07 poly(oxybutylene) aminocarbamate, wherein the amine moiety  
08 is derived from ethylene diamine or diethylene triamine.  
09 Synthetic methods to avoid higher degrees of substitution,  
10 methods of preparation, and other characteristics of the  
11 aminocarbamates used in the present invention are more fully  
12 described and exemplified in U.S. Patent No. 4,191,537.

13

14

15 Fuel Compositions

16

17 The fuel additive composition of the present invention will  
18 generally be employed in hydrocarbon fuels to prevent and  
19 control engine deposits, particularly intake valve deposits.  
20 The proper concentration of the additive composition  
21 necessary to achieve the desired level of deposit control  
22 varies depending upon the type of fuel employed, the type of  
23 engine, and the presence of other fuel additives.

24

25 Generally, the present fuel additive composition will be  
26 employed in hydrocarbon fuel in a concentration ranging from  
27 about 75 to about 5,000 parts per million (ppm) by weight,  
28 preferably from 200 to 2,500 ppm.

29

30 In terms of individual components, hydrocarbon fuel  
31 containing the fuel additive composition of this invention  
32 will generally contain about 50 to 2,500 ppm of the  
33 poly(oxyalkylene) hydroxyaromatic ether component and about  
34 25 to 1,000 ppm of the poly(oxyalkylene) amine component.  
35 The ratio of the poly(oxyalkylene) hydroxyaromatic ether to

-32-

01 poly(oxyalkylene) amine will generally range from about  
02 0.5:1 to about 10:1, and will preferably be about 1:1 or  
03 greater.

04

05 The fuel additive composition of the present invention may  
06 be formulated as a concentrate using an inert stable  
07 oleophilic (i.e., dissolves in gasoline) organic solvent  
08 boiling in the range of about 150°F to 400°F (about 65°C to  
09 205°C). Preferably, an aliphatic or an aromatic hydrocarbon  
10 solvent is used, such as benzene, toluene, xylene or higher-  
11 boiling aromatics or aromatic thinners. Aliphatic alcohols  
12 containing about 3 to 8 carbon atoms, such as isopropanol,  
13 isobutylcarbinol, n-butanol and the like, in combination  
14 with hydrocarbon solvents are also suitable for use with the  
15 present additives. In the concentrate, the amount of the  
16 additive composition will generally range from about 10 to  
17 about 70 weight percent, preferably 10 to 50 weight percent,  
18 more preferably from 20 to 40 weight percent.

19

20 In gasoline fuels, other fuel additives may be employed with  
21 the additives of the present invention, including, for  
22 example, oxygenates, such as t-butyl methyl ether, antiknock  
23 agents, such as methylcyclopentadienyl manganese  
24 tricarbonyl, and other dispersants/detergents, such as  
25 hydrocarbyl amines or succinimides. Additionally,  
26 antioxidants, metal deactivators and demulsifiers may be  
27 present.

28

29 In diesel fuels, other well-known additives can be employed,  
30 such as pour point depressants, flow improvers, cetane  
31 improvers, and the like.

32

33 A fuel-soluble, nonvolatile carrier fluid or oil may also be  
34 used with the fuel additive composition of this invention.

35 The carrier fluid is a chemically inert hydrocarbon-soluble

-33-

01 liquid vehicle which substantially increases the nonvolatile  
02 residue (NVR), or solvent-free liquid fraction of the fuel  
03 additive composition while not overwhelmingly contributing  
04 to octane requirement increase. The carrier fluid may be a  
05 natural or synthetic oil, such as mineral oil, refined  
06 petroleum oils, synthetic polyalkanes and alkenes, including  
07 hydrogenated and unhydrogenated polyalphaolefins, and  
08 synthetic poly(oxyalkylene)-derived oils, such as those  
09 described, for example, in U.S. Patent No. 4,191,537 to  
10 Lewis.

11

12 These carrier fluids are believed to act as a carrier for  
13 the fuel additive composition of the present invention and  
14 to assist in removing and retarding deposits. The carrier  
15 fluid may also exhibit synergistic deposit control  
16 properties when used in combination with the fuel additive  
17 composition of this invention.

18

19 The carrier fluids are typically employed in amounts ranging  
20 from about 100 to about 5000 ppm by weight of the  
21 hydrocarbon fuel, preferably from 400 to 3000 ppm of the  
22 fuel. Preferably, the ratio of carrier fluid to deposit  
23 control additive will range from about 0.5:1 to about 10:1,  
24 more preferably from 1:1 to 4:1, most preferably about 2:1.

25

26 When employed in a fuel concentrate, carrier fluids will  
27 generally be present in amounts ranging from about 20 to  
28 about 60 weight percent, preferably from 30 to 50 weight  
29 percent.

30

31

### EXAMPLES

32

33 The following examples are presented to illustrate specific  
34 embodiments of the present invention and synthetic  
35 preparations thereof; and should not be interpreted as

-34-

01 limitations upon the scope of the invention.

02

03

Example 1

04

05

Preparation of

06

$\alpha$ -(4-Benzyloxyphenyl)- $\omega$ -hydroxypoly(oxybutylene)

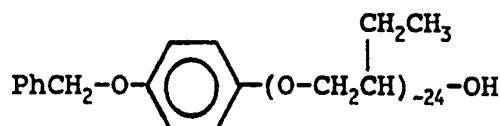
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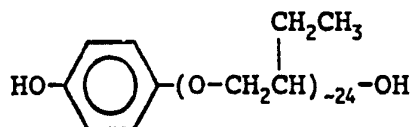
35

To a flask equipped with a magnetic stirrer, thermometer, addition funnel, reflux condenser and nitrogen inlet was added 6.88 grams of a 35 wt % dispersion of potassium hydride in mineral oil. Forty grams of 4-benzyloxyphenol dissolved in 500 mL of anhydrous toluene was added dropwise and the resulting mixture was stirred at room temperature for ten minutes. The temperature of the reaction mixture, a thick white suspension, was raised to 90°C and 430.8 mL of 1,2-epoxybutane was added dropwise. The reaction mixture was refluxed until the pot temperature reached 110°C (approximately 48 hours) at which time the reaction mixture was a light brown clear solution. The reaction was cooled to room temperature, quenched with 50 mL of methanol and diluted with 1 liter of diethyl ether. The resulting mixture was washed with saturated aqueous ammonium chloride, followed by water and saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo* to yield 390 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane: diethyl ether (1:1), to yield 339.3 grams of the desired product as a colorless oil.

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Example 2

## Preparation of

 $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene)

A solution of 54.10 grams of the product from Example 1 in 100 mL of ethyl acetate and 100 mL of acetic acid containing 5.86 grams 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 solvent in vacuo followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 48.1 grams of the desired product as a colorless oil. The product had an average of 24 oxybutylene units.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.2 (broad s, 2H), 6.7 (s, 4H), 3.1-4.0 (m, 72H), 1.2-1.8 (m, 48H), 0.8 (t, 72H).

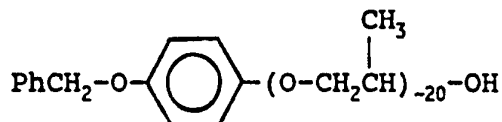
Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- $\alpha$ -(2-hydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene);
- $\alpha$ -(3-hydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene);
- $\alpha$ -(3-*t*-butyl-4-hydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene);
- $\alpha$ -(4-hydroxy-3-methoxyphenyl)- $\omega$ -hydroxypoly(oxybutylene);
- $\alpha$ -(3,4-dihydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene);
- $\alpha$ -(3,4-hydroxy-5-methylphenyl)- $\omega$ -hydroxypoly(oxybutylene);
- $\alpha$ -(3,5-di-*t*-butyl-4-hydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene); and
- $\alpha$ -(3,4,5-trihydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene).

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Example 3

## Preparation of

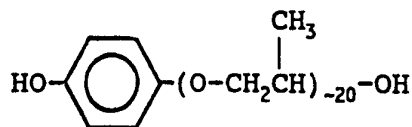
 $\alpha$ -(4-Benzyloxyphenyl)- $\omega$ -hydroxypoly(oxypropylene)

To a flask equipped with magnetic stirrer, thermometer, addition funnel, reflux condenser and nitrogen inlet was added 6.88 grams of a 35 wt % dispersion of potassium hydride in mineral oil. 4-Benzyloxyphenol (40 grams) dissolved in 500 mL of anhydrous toluene was added dropwise and then stirred at room temperature for ten minutes. The temperature of the reaction mixture, a thick white suspension, was raised to 110°C and stirred for 3 hours. The reaction was cooled to room temperature and 349.9 mL of 1,2-epoxypropane was added dropwise. The reaction mixture was refluxed until the pot temperature reached 110°C (approximately 96 hours) at which time the reaction mixture was a light brown clear solution. The reaction was cooled to room temperature, quenched with 50 mL of methanol and diluted with 1 liter of diethyl ether. The reaction was washed with saturated aqueous ammonium chloride, followed by water and saturated aqueous sodium chloride. The organic layer was dried over anhydrous sulfate, filtered and the solvents removed under vacuum to yield 212.2 grams of the desired product as a light yellow oil.

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Example 4

## Preparation of

 $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene)

A solution of 60.0 grams of the product from Example 3 in 100 mL of ethyl acetate and 100 mL of acetic acid containing 7.0 grams 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 solvent in vacuo followed by azeotropic removal of the residual acetic acid with toluene under vacuum yielded 31.7 grams of the desired product as a brown oil. The product had an average of 20 oxypropylene units.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.7 (s, 4H), 5.4-6.0 (broad s, 2H), 3.0-4.0 (m, 60H), 0.8-1.4 (m, 60H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- $\alpha$ -(2-hydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene);
- $\alpha$ -(3-hydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene);
- $\alpha$ -(4-hydroxy-3-methylphenyl)- $\omega$ -hydroxypoly(oxypropylene);
- $\alpha$ -(3,5-dimethoxy-4-hydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene);
- $\alpha$ -(3,4-dihydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene);
- $\alpha$ -(3,5-di-*t*-butyl-4-hydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene); and
- $\alpha$ -(3,4,5-trihydroxyphenyl)- $\omega$ -hydroxypoly(oxypropylene).

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01 Example 5

02

03 Preparation of 2-(4-Benzyloxyphenyl)ethanol

04

05 To a flask equipped with a magnetic stirrer, reflux  
 06 condenser and nitrogen inlet was added 13.8 grams of 2-(4-  
 07 hydroxyphenyl)ethanol, 14.5 grams of anhydrous potassium  
 08 carbonate, 33.0 grams of tetrabutylammonium bromide, 12 mL  
 09 of benzyl chloride and 200 mL of acetone. The reaction  
 10 mixture was heated at reflux for 3 days, and then cooled to  
 11 room temperature and filtered. The filtrate was  
 12 concentrated *in vacuo*, diluted with 500 mL of  
 13 dichloromethane, and washed with 2% aqueous sodium hydroxide  
 14 and then with saturated brine. The organic layer was dried  
 15 over anhydrous magnesium sulfate, filtered, and concentrated  
 16 *in vacuo*. The resulting product was purified by  
 17 chromatography on silica gel, eluting with dichloromethane,  
 18 to yield 20.0 grams of the desired product as a white solid.

19

20 Example 6

21

## 22 Preparation of

23  $\alpha$ -[2-(4-Benzyloxyphenyl)ethyl]- $\omega$ -hydroxypoly(oxybutylene)

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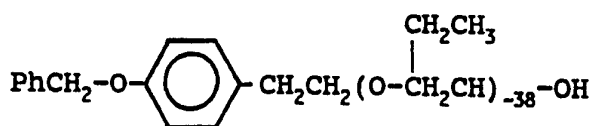
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To a flask equipped with a magnetic stirrer, thermometer,  
 addition funnel, reflux condenser and nitrogen inlet was  
 added 1.05 grams of a 35 weight percent dispersion of  
 potassium hydride in mineral oil and 50 mL of toluene.  
 2-(4-Benzyloxyphenyl)ethanol (6.8 grams) from Example 5,  
 dissolved in 7.5 mL of toluene, was added dropwise and the



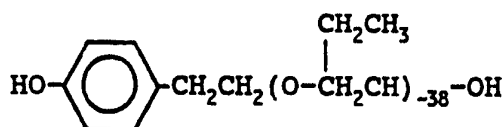
-39-

01 mixture was heated at reflux for two hours. The reaction  
 02 was cooled to room temperature and 65 mL of 1,2-epoxybutane  
 03 were added dropwise. The reaction mixture was then refluxed  
 04 until the pot temperature reached 110°C (approximately 16  
 05 hours). The reaction was then cooled to room temperature,  
 06 quenched with 50 mL of methanol and diluted with diethyl  
 07 ether (300 mL). The organic layer was washed with water (2  
 08 times), saturated aqueous ammonium chloride (2 times), dried  
 09 over anhydrous magnesium sulfate, filtered and concentrated  
 10 *in vacuo*. The resulting product was chromatographed on  
 11 silica gel, eluting with hexane/diethyl ether, followed by  
 12 hexane/diethyl ether/ethanol (7.5:2.5:0.5) to yield 26.0  
 13 grams of the desired product as a colorless oil.

#### 14 Example 7

#### 15 Preparation of

16  $\alpha$ -[2-(4-Hydroxyphenyl)ethyl]- $\omega$ -hydroxypoly(oxybutylene)



25 A solution of 26.0 grams of the product from Example 6 in 50  
 26 mL of ethyl acetate and 50 mL of acetic acid containing 3.0  
 27 grams of 10% palladium on charcoal was hydrogenolyzed at 35-  
 28 40 psi for 16 hours on a Parr low-pressure hydrogenator.  
 29 Catalyst filtration and removal of solvent *in vacuo* followed  
 30 by azeotropic removal of residual acetic acid with toluene  
 31 under vacuum yielded 21.0 grams of the desired product as a  
 32 light yellow oil. The product had an average of 38  
 33 oxybutylene units. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.7, 6.9 (AB quartet,  
 34 4H), 3.0-3.8 (m, 116H), 2.75 (t, 2H), 0.6-1.8 (m, 190H).  
 35

-40-

01 Similarly, by using the above procedures and the appropriate  
 02 starting materials and reagents, the following compounds can  
 03 be prepared:

04

05  $\alpha$ -[2-(2-hydroxyphenyl)ethyl]- $\omega$ -hydroxypoly(oxybutylene);

06  $\alpha$ -[2-(3-hydroxyphenyl)ethyl]- $\omega$ -hydroxypoly(oxybutylene);

07  $\alpha$ -[3-(4-hydroxyphenyl)propyl]- $\omega$ -hydroxypoly(oxybutylene);

08  $\alpha$ -[2-(3,4-dihydroxyphenyl)ethyl]- $\omega$ -hydroxypoly(oxybutylene);

09  $\alpha$ -[3-(3,4-dihydroxyphenyl)propyl]- $\omega$ -hydroxy-

10 poly(oxybutylene);

11  $\alpha$ -[2-(3,5-di-*t*-butyl-4-hydroxyphenyl)ethyl]- $\omega$ -hydroxy-

12 poly(oxybutylene); and

13  $\alpha$ -[2-(3,4,5-trihydroxyphenyl)ethyl]- $\omega$ -hydroxy-

14 poly(oxybutylene).

15

#### 16 Example 8

17

#### 18 Preparation of

#### 19 $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -benzyloxypoly(oxybutylene)

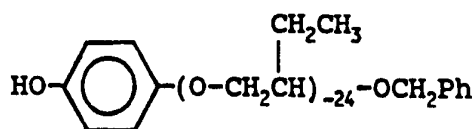
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26 To a flask equipped with a magnetic stirrer, thermometer,  
 27 reflux condenser and nitrogen inlet was added 0.8 grams of a  
 28 35 wt % dispersion of potassium hydride in mineral oil. The  
 29 oil was removed by trituration with anhydrous toluene. The  
 30 product from Example 2 (6.0 grams) was dissolved in 50 mL of  
 31 anhydrous tetrahydrofuran and added dropwise to the  
 32 potassium hydride. The reaction mixture was heated to  
 33 reflux for 45 minutes and then cooled to room temperature.  
 34 Benzyl chloride (0.36 mL) was added dropwise and the  
 35 reaction was then heated to reflux for 12 hours, cooled to

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01 room temperature and quenched with 2 mL of isopropanol. The  
02 solvent was removed in vacuo and the residue dissolved in  
03 200 mL of diethyl ether, washed with 5% aqueous hydrochloric  
04 acid followed by saturated aqueous sodium chloride. The  
05 organic layer was dried over anhydrous magnesium sulfate,  
06 filtered and the solvents removed under vacuum. The oil was  
07 chromatographed on silica gel, eluting with hexane/ ethyl  
08 acetate (7:3), to yield 3.8 grams of the desired product as  
09 a colorless oil. The product had an average of 24  
10 oxybutylene units. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.2-7.4 (m, 6H), 6.7  
11 (s, 4H), 4.4-4.7 (m, 2H), 3.1-4.0 (m, 72H), 1.2-1.8 (m,  
12 48H), 0.8 (t, 72H).

13

14 Similarly, by using the above procedures and the appropriate  
15 starting materials and reagents, the following compounds can  
16 be prepared:

17

18 α-(2-hydroxyphenyl)-ω-benzyloxypoly(oxybutylene);

19 α-(3-hydroxyphenyl)-ω-benzyloxypoly(oxybutylene);

20 α-(3,4-dihydroxyphenyl)-ω-benzyloxypoly(oxybutylene);

21 α-(3,5-di-t-butyl-4-hydroxyphenyl)-ω-benzyloxy-  
22 poly(oxybutylene);

23 α-(4-hydroxy-3-methoxyphenyl)-ω-benzyloxy-  
24 poly(oxybutylene); and

25 α-[2-(4-hydroxyphenyl)ethyl]-ω-benzyloxypoly(oxybutylene).

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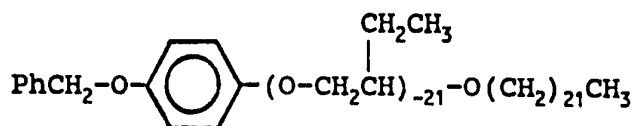
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Example 9

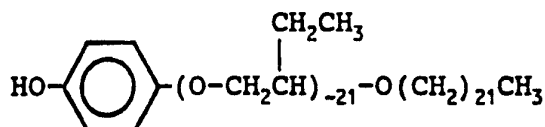
Preparation of  
 $\alpha$ -(4-Benzoxypyphenyl)- $\omega$ -docosanoxypoly(oxybutylene)



To a flask equipped with a magnetic stirrer, addition funnel, reflux condenser and nitrogen inlet was added 7.26 grams of a 35 wt % dispersion of potassium hydride in mineral oil. The oil was removed by trituration with anhydrous hexane, and 500 milliliters of anhydrous tetrahydrofuran were added.  $\alpha$ -(4-Benzoyloxyphenyl)- $\omega$ -hydroxypoly(oxybutylene) (104.0 grams) containing an average of 21 oxybutylene units (prepared essentially as described in Example 1), dissolved in 100 milliliters of anhydrous tetrahydrofuran, was added dropwise and the resulting mixture was heated to reflux for two hours. The reaction was then cooled to room temperature and 24.0 grams of 1-bromodocosane were added. The reaction was refluxed for sixteen hours, cooled to room temperature, diluted with 1200 mL of diethyl ether, and washed with 5% aqueous hydrochloric acid, followed by brine. The organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to give an oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (7:3) to yield 11.0 grams of the desired product as a yellow oil.

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## Example 10

Preparation of  
 $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -docosanoxypoly(oxybutylene)

A solution of 11.0 grams of the product from Example 9 in 50 mL of ethyl acetate and 50 mL of acetic acid containing 1.5 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 14 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of solvent *in vacuo* followed by azeotropic removal of the residual acetic acid with toluene under vacuum yielded 10.2 grams of the desired product. The product had an average of 21 oxybutylene units.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.7 (s, 4H), 3.1-4.0 (m, 62H), 0.6-1.8 (m, 148H).

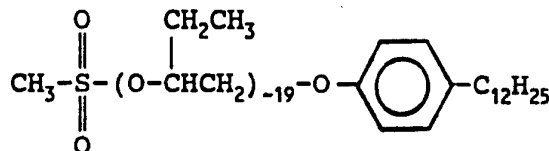
Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- $\alpha$ -(4-hydroxyphenyl)- $\omega$ -n-butoxypoly(oxybutylene);
- $\alpha$ -(4-hydroxyphenyl)- $\omega$ -n-octyloxypoly(oxybutylene);
- $\alpha$ -(4-hydroxyphenyl)- $\omega$ -n-dodecyloxypoly(oxybutylene);
- $\alpha$ -(3,5-di-t-butyl-4-hydroxyphenyl)- $\omega$ -n-pentyloxy-poly(oxybutylene);
- $\alpha$ -(4-hydroxy-3-methoxyphenyl)- $\omega$ -n-hexyloxypoly(oxybutylene);
- $\alpha$ -(3,4-hydroxyphenyl)- $\omega$ -nonyloxypoly(oxybutylene); and
- $\alpha$ -[2-(4-hydroxyphenyl)ethyl]- $\omega$ -octyloxypoly(oxybutylene).

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Example 11

Preparation of  
 $\alpha$ -(Methanesulfonyl)- $\omega$ -4-dodecylphenoxypoly(oxybutylene)

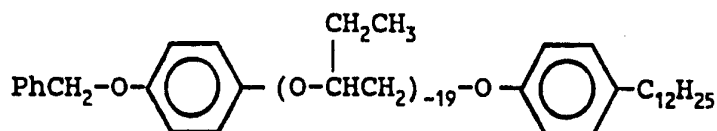


To a flask equipped with a magnetic stirrer, septa and a nitrogen inlet was added 35.0 grams of  $\alpha$ -hydroxy- $\omega$ -4-dodecylphenoxypoly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648), 440 mL of dichloromethane and 3.6 mL of triethylamine. The flask was cooled in an ice bath and 1.8 mL of methanesulfonyl chloride were added dropwise. The ice bath was removed and the reaction was stirred at room temperature for 16 hours. Dichloromethane (800 mL) was added and the organic phase was washed two times with saturated aqueous sodium bicarbonate, and then once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 35.04 grams of the desired product as a yellow oil.

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Example 12

## Preparation of

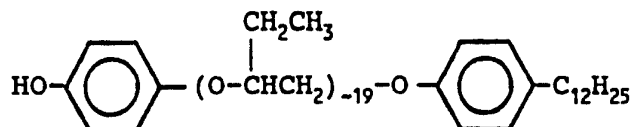
 $\alpha$ -(4-Benzoyloxyphenyl)- $\omega$ -4-dodecylphenoxy poly(oxybutylene)

To a flask equipped magnetic stirrer, reflux condenser, nitrogen inlet and septa was added 2.59 grams of a 35 wt % dispersion of potassium hydride in mineral oil. The mineral oil was removed by trituration with hexane and the flask was cooled in an ice bath. 4-Benzoyloxyphenol (4.11 grams) dissolved in 150 mL of tetrahydrofuran was added dropwise. The ice bath was removed and the reaction was allowed to stir for 45 minutes at room temperature. The mesylate from Example 11 was dissolved in 275 mL of anhydrous tetrahydrofuran and added to the reaction mixture. The resulting solution was refluxed for 16 hours, cooled to room temperature and 10 mL of methanol were added. The reaction was diluted with 1 liter of diethyl ether, washed with water (1 time), brine (1 time), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to 36.04 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (8:1.8:0.2) to yield 18.88 grams of the desired product as a light yellow oil.

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Example 13

## Preparation of

 $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -4-dodecylphenoxypoly(oxybutylene)

A solution of 18.88 grams of the product from Example 12 in 80 mL of ethyl acetate and 80 mL of acetic acid containing 2.08 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 6 hours on a Parr low-pressure hydrogenator. Filtration of the catalyst and removal of solvent in vacuo, followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 17.63 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene units. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.0-7.3 (M, 2H), 6.6-6.9 (m, 6H), 4.0-4.2 (m, 1H), 3.8-4.0 (m, 2H), 3.0-3.8 (m, 54H), 0.5-1.8 (m, 120H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

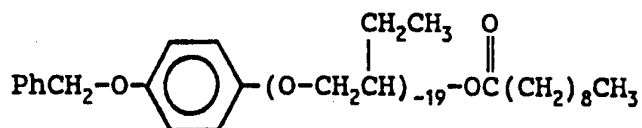
$\alpha$ -(2-hydroxyphenyl)- $\omega$ -4-dodecylphenoxypoly(oxybutylene);  
 $\alpha$ -(3-hydroxyphenyl)- $\omega$ -4-dodecylphenoxypoly(oxybutylene);  
 $\alpha$ -(3,4-dihydroxyphenyl)- $\omega$ -4-dodecylphenoxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -phenoxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -4-*t*-butylphenoxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -4-decylphenoxypoly(oxybutylene); and  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -4-octadecylphenoxypoly(oxybutylene).



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Example 14

## Preparation of

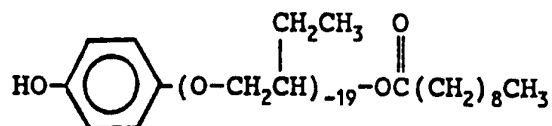
 $\alpha$ -(4-Benzoxyphehyl)- $\omega$ -decanoyloxypoly(oxybutylene)

$\alpha$ -(4-Benzoxyphehyl)- $\omega$ -hydroxypoly(oxybutylene) (40.75 grams) containing an average of 19 oxybutylene units (prepared essentially as described in Example 1) was combined with 200 mL of toluene, 3.9 mL of triethylamine, 1.5 grams of 4-dimethylamine pyridine and 5.2 mL of n-decanoyl chloride in a flask equipped with a thermometer, magnetic stirrer, reflux condenser and nitrogen inlet. The contents were refluxed for 16 hours, cooled to room temperature and diluted with 400 mL of hexane. The organic layers were washed with water (2 times), saturated aqueous sodium bicarbonate (2 times), saturated aqueous sodium chloride (2 times), dried over anhydrous magnesium sulfate, filtered and concentrated to yield 40 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether (1:1) to yield 23.3 grams of the product as a yellow oil.

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Example 15

Preparation of  
 $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -decanoyloxypoly(oxybutylene)



A solution of the ester from Example 14 (23.3 grams) in 50 mL of ethyl acetate and 50 mL of acetic acid containing 2.5 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Filtration of the catalyst and removal of solvent *in vacuo* followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 16.0 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene units. IR (neat) 1735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.7 (s, 4H), 4.8-4.9 (m, 1H), 3.1-4.0 (m, 56H), 2.3 (t, 2H), 0.7-1.8 (m, 112H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

$\alpha$ -(2-hydroxyphenyl)- $\omega$ -decanoyloxypoly(oxybutylene);  
 $\alpha$ -(3-hydroxyphenyl)- $\omega$ -decanoyloxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -dodecanoyloxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -octanoyloxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -butanoyloxypoly(oxybutylene);  
 $\alpha$ -(4-hydroxyphenyl)- $\omega$ -benzoyloxypoly(oxybutylene);  
 $\alpha$ -(3,4-dihydroxyphenyl)- $\omega$ -hexanoyloxypoly(oxybutylene);  
 $\alpha$ -(3,4-hydroxyphenyl)- $\omega$ -2-ethylhexanoyloxy-  
poly(oxybutylene);

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01  $\alpha$ -(3,5-di-t-butyl-4-hydroxyphenyl)- $\omega$ -nonanoyloxy-  
02 poly(oxybutylene);  
03  $\alpha$ -(3,4,5-trihydroxyphenyl)- $\omega$ -decanoyloxy-  
04 poly(oxybutylene); and  
05  $\alpha$ -[2-(4-hydroxyphenyl)ethyl]- $\omega$ -decanoyloxypoly(oxybutylene).  
06  
07

08 Example 16

09  
10 Single-Cylinder Engine Test

11  
12 The test compounds were blended in gasoline and their  
13 deposit reducing capacity determined in an ASTM/CFR single-  
14 cylinder engine test.

15  
16 A Waukesha CFR single-cylinder engine was used. Each run  
17 was carried out for 15 hours, at the end of which time the  
18 intake valve was removed, washed with hexane and weighed.  
19 The previously determined weight of the clean valve was  
20 subtracted from the weight of the valve at the end of the  
21 run. The differences between the two weights is the weight  
22 of the deposit. A lesser amount of deposit indicates a  
23 superior additive. The operating conditions of the test  
24 were as follows: water jacket temperature 200°F; vacuum of  
25 12 in Hg, air-fuel ratio of 12, ignition spark timing of 40°  
26 BTC; engine speed is 1800 rpm; the crankcase oil is a  
27 commercial 30W oil.

28  
29 The amount of carbonaceous deposit in milligrams on the  
30 intake valves is reported for each of the test compounds in  
31 Table I.

32  
33  
34  
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-50-

01

Table I

02

Single-Cylinder Engine Test Results

03

04

Intake Valve Deposit Weight  
(in milligrams)

05

Sample <sup>1</sup>	Run 1	Run 2	Average
Base Fuel	214.7	193.7	204.2
Example 2	12.7	26.5	19.6
Example 4	59.6	73.8	66.7
Example 7	44.3	54.0	42.9
Example 8	52.8	75.9	64.4
Example 10	53.9	47.9	50.9
Example 13	32.2	32.3	32.3
Example 15	32.5	31.1	31.8

15

16

<sup>1</sup> At 200 parts per million actives (ppma).

17

18

19

20

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22

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

23

24

25

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28

The data in Table I illustrates the significant reduction in intake valve deposits provided by the poly(oxyalkylene) hydroxyaromatic ether component of the present fuel additive composition (Examples 2, 4, 7, 8, 10, 13, 15) compared to the base fuel.

29

30

Example 17

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32

Multicylinder Engine Test

33

34

35

The fuel additive composition of the present invention was tested in a laboratory multicylinder engine to evaluate its

-51-

01 intake valve and combustion chamber deposit control  
02 performance. The test engine was a 4.3 liter, TBI (throttle  
03 body injected), V6 engine manufactured by General Motors  
04 Corporation. The major engine dimensions are set forth in  
05 Table II:

Table II

Engine Dimensions

Bore	10.16 cm
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

14  
15 The test engine was operated for 40 hours (24 hours a day)  
16 on a prescribed load and speed schedule representative of  
17 typical driving conditions. The cycle for engine operation  
18 during the test is set forth in Table III.

Table III

Engine Driving Cycle

Step	Mode	Time in Mode, [Sec] <sup>1</sup>	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

33 <sup>1</sup> All steps, except step number 3, include a 15 second  
34 transition ramp. Step 3 includes a 20 second  
35 transition ramp.

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01 All of the test runs were made with the same base gasoline,  
 02 which was representative of commercial unleaded fuel. The  
 03 results are set forth in Table IV.

04  
 05 Table IV  
 06  
 07 Multicylinder Engine Test Results

08				
09	Sample	Conc. (ppma)	Intake Valve Deposits	Combustion Chamber, Deposits <sup>1</sup>
10				
11	Base Fuel	---	972	1902
12				
13	Poly(oxyalkylene) Hydroxyaromatic			
14	Ether <sup>2</sup>	400	283	2547
15				
16	Poly(oxyalkylene) Amine <sup>3</sup>	200	340	2282
17				
18	Poly(oxyalkylene) Hydroxyaromatic			
19	Ether/ Poly(oxyalkylene)	400/200	75	2177
20	Amine <sup>4</sup>			
21				
22				

23 <sup>1</sup> Average of two runs, in milligrams (mg).

24 <sup>2</sup>  $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -hydroxypoly(oxybutylene) prepared  
 25 as described in Example 2.

26 <sup>3</sup> Dodecylphenyl poly(oxyalkylene) ethylene diamine  
 27 carbamate prepared essentially as described in Examples  
 6-8 of U.S. Patent No. 4,160,648.

28 <sup>4</sup> Mixture of 400 ppm of  $\alpha$ -(4-Hydroxyphenyl)- $\omega$ -  
 29 hydroxypoly(oxybutylene) and 200 ppm of dodecylphenyl  
 30 poly(oxyalkylene) ethylene diamine carbamate.

31 The base fuel employed in the above multicylinder engine  
 32 tests contained no fuel detergent. The test compounds were  
 33 admixed with the base fuel at the indicated concentrations.  
 34

35

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01 The data in Table IV demonstrates that the combination of a  
02 poly(oxyalkylene) hydroxyaromatic ether and a  
03 poly(oxyalkylene) amine has a synergistic effect and gives  
04 significantly better intake valve deposit control than  
05 either component individually. Moreover, the data in Table  
06 IV further demonstrates that the combination produces fewer  
07 combustion chamber deposits than each individual component.

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01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

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05 (a) a poly(oxyalkylene) hydroxyaromatic ether having  
06 the formula:

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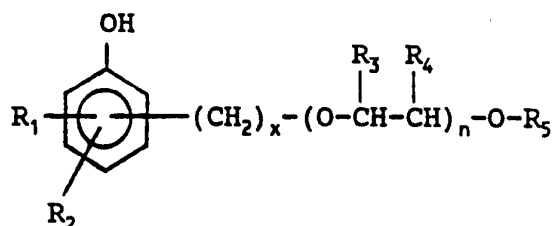
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35



or a fuel-soluble salt thereof; wherein

$R_1$  and  $R_2$  are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

$R_3$  and  $R_4$  are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

$R_5$  is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



wherein  $R_6$  is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms;



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- 01           n is an integer from 5 to 100; and x is an integer  
02           from 0 to 10; and  
03
- 04           (b) a poly(oxyalkylene) amine having at least one  
05           basic nitrogen atom and a sufficient number of  
06           oxyalkylene units to render the poly(oxyalkylene)  
07           amine soluble in hydrocarbons boiling in the  
08           gasoline or diesel range.  
09
- 10    2.    The fuel additive composition according to Claim 1,  
11           wherein n of said poly(oxyalkylene) hydroxyaromatic  
12           ether is an integer ranging from 10 to 50.  
13
- 14    3.    The fuel additive composition according to Claim 2,  
15           wherein n of said poly(oxyalkylene) hydroxyaromatic  
16           ether is an integer ranging from 15 to 30.  
17
- 18    4.    The fuel additive composition according to Claim 2,  
19           wherein R<sub>1</sub> of said poly(oxyalkylene) hydroxyaromatic  
20           ether is hydrogen, hydroxy, or lower alkyl having 1 to  
21           4 carbon atoms; and R<sub>2</sub> is hydrogen.  
22
- 23    5.    The fuel additive composition according to Claim 4,  
24           wherein R<sub>5</sub> of said poly(oxyalkylene) hydroxyaromatic  
25           ether is hydrogen, alkyl having 2 to 22 carbon atoms,  
26           alkylphenyl having an alkyl group containing 4 to 24  
27           carbon atoms, or an acyl group having the formula:  
28           -C(O)R<sub>7</sub>, wherein R<sub>7</sub> is alkyl having 4 to 12 carbon  
29           atoms.  
30
- 31    6.    The fuel additive composition according to Claim 5,  
32           wherein R<sub>1</sub> of said poly(oxyalkylene) hydroxyaromatic  
33           ether is hydrogen or hydroxy.  
34
- 35    7.    The fuel additive composition according to Claim 6,

-56-

01        wherein  $R_5$  of said poly(oxyalkylene) hydroxyaromatic  
02        ether is hydrogen, alkyl having 4 to 12 carbon atoms,  
03        or alkylphenyl having an alkyl group containing 4 to 12  
04        carbon atoms.

05

06        8.    The fuel additive composition according to Claim 7,  
07        wherein one of  $R_3$  and  $R_4$  of said poly(oxyalkylene)  
08        hydroxyaromatic ether is lower alkyl having 1 to 3  
09        carbon atoms and the other is hydrogen.

10

11        9.    The fuel additive composition according to Claim 8,  
12        wherein one of  $R_3$  and  $R_4$  of said poly(oxyalkylene)  
13        hydroxyaromatic ether is methyl or ethyl and the other  
14        is hydrogen.

15

16        10.   The fuel additive composition according to Claim 9,  
17        wherein  $x$  of said poly(oxyalkylene) hydroxyaromatic  
18        ether is 0, 1 or 2.

19

20        11.   The fuel additive composition according to Claim 10,  
21        wherein  $R_1$  and  $R_5$  of said poly(oxyalkylene)  
22        hydroxyaromatic ether are both hydrogen, and  $x$  is 0.

23

24        12.   The fuel additive composition according to Claim 1,  
25        wherein said poly(oxyalkylene) amine has a molecular  
26        weight in the range of about 500 to about 10,000.

27

28        13.   The fuel additive composition according to Claim 1,  
29        wherein said poly(oxyalkylene) amine contains at least  
30        about 5 oxyalkylene units.

31

32        14.   The fuel additive composition according to Claim 1,  
33        wherein said poly(oxyalkylene) amine is a hydrocarbyl  
34        poly(oxyalkylene) polyamine.

35

- 01 15. The fuel additive composition according to Claim 1,  
02 wherein said poly(oxyalkylene) amine is a  
03 poly(oxyalkylene) polyamine, wherein the  
04 poly(oxyalkylene) moiety is connected to the polyamine  
05 moiety through an oxyalkylene hydroxy linkage derived  
06 from an epihalohydrin.  
07
- 08 16. The fuel additive composition according to Claim 1,  
09 wherein said poly(oxyalkylene) amine is a branched  
10 alkyl poly(oxyalkylene) monoamine, wherein the branched  
11 alkyl group is derived from the product of a Guerbet  
12 condensation reaction.  
13
- 14 17. The fuel additive composition according to Claim 1,  
15 wherein said poly(oxyalkylene) amine is a hydrocarbyl  
16 poly(oxyalkylene) aminocarbamate.  
17
- 18 18. The fuel additive composition according to Claim 17,  
19 wherein the hydrocarbyl group of said hydrocarbyl  
20 poly(oxyalkylene) aminocarbamate contains from 1 to  
21 about 30 carbon atoms.  
22
- 23 19. The fuel additive composition according to Claim 18,  
24 wherein said hydrocarbyl group of said hydrocarbyl  
25 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
26 group.  
27
- 28 20. The fuel additive composition according to Claim 19,  
29 wherein the alkyl moiety of said alkylphenyl group is  
30 tetrapropenyl.  
31
- 32 21. The fuel additive composition according to Claim 17,  
33 wherein the amine moiety of said hydrocarbyl  
34 poly(oxyalkylene) aminocarbamate is derived from a  
35 polyamine having from 2 to 12 amine nitrogen atoms and

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01 from 2 to 40 carbon atoms.

02

03 22. The fuel additive composition according to Claim 21,  
04 wherein said polyamine is a polyalkylene polyamine  
05 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon  
06 atoms.

07

08 23. The fuel additive composition according to Claim 22,  
09 wherein said polyalkylene polyamine is selected from  
10 the group consisting of ethylenediamine,  
11 propylenediamine, diethylenetriamine and  
12 dipropylenetriamine.

13

14 24. The fuel additive composition according to Claim 17,  
15 wherein the poly(oxyalkylene) moiety of said  
16 hydrocarbyl poly(oxyalkylene) aminocarbamate is derived  
17 from C<sub>2</sub> to C<sub>5</sub> oxyalkylene units.

18

19 25. The fuel additive composition according to Claim 17,  
20 wherein said hydrocarbyl poly(oxyalkylene)  
21 aminocarbamate is an alkylphenyl poly(oxybutylene)  
22 aminocarbamate, wherein the amine moiety is derived  
23 from ethylenediamine or diethylenetriamine.

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01 26. A fuel composition comprising a major amount of  
 02 hydrocarbons boiling in the gasoline or diesel range  
 03 and an effective detergent amount of a fuel additive  
 04 composition comprising:

05

06 (a) a poly(oxyalkylene) hydroxyaromatic ether having  
 07 the formula:

08

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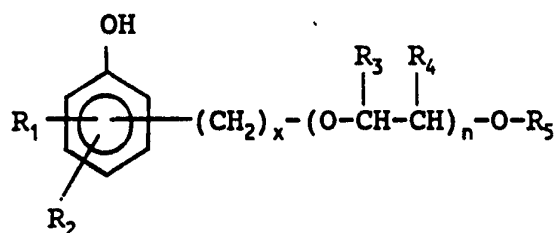
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16

or a fuel-soluble salt thereof; wherein

17

18 R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen,  
 19 hydroxy, lower alkyl having 1 to 6 carbon atoms,  
 20 or lower alkoxy having 1 to 6 carbon atoms;

21

22 R<sub>3</sub> and R<sub>4</sub> are each independently hydrogen or lower  
 23 alkyl having 1 to 6 carbon atoms;

24

25 R<sub>5</sub> is hydrogen, alkyl having 1 to 30 carbon atoms,  
 26 phenyl, aralkyl or alkaryl having 7 to 36 carbon  
 27 atoms, or an acyl group of the formula:

28

29

30

31

32



33 wherein R<sub>6</sub> is alkyl having 1 to 30 carbon atoms,  
 34 phenyl, or aralkyl or alkaryl having 7 to 36  
 35 carbon atoms;

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- 01           n is an integer from 5 to 100; and x is an integer  
02           from 0 to 10; and  
03
- 04           (b) a poly(oxyalkylene) amine having at least one  
05           basic nitrogen atom and a sufficient number of  
06           oxyalkylene units to render the poly(oxyalkylene)  
07           amine soluble in hydrocarbons boiling in the  
08           gasoline or diesel range.  
09
- 10   27. The fuel composition according to Claim 26, wherein R<sub>1</sub>  
11       of said poly(oxyalkylene) hydroxyaromatic ether is  
12       hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon  
13       atoms; R<sub>2</sub> is hydrogen; one of R<sub>3</sub> and R<sub>4</sub> is hydrogen and  
14       the other is methyl or ethyl; R<sub>5</sub> is hydrogen, alkyl  
15       having 2 to 22 carbon atoms, alkylphenyl having an  
16       alkyl group containing 4 to 24 carbon atoms, or an acyl  
17       group having the formula: -C(O)R<sub>7</sub>, wherein R<sub>7</sub> is alkyl  
18       having 4 to 12 carbon atoms; n is 15 to 30; and x is 0,  
19       1 or 2.  
20
- 21   28. The fuel composition according to Claim 27, wherein R<sub>1</sub>  
22       of said poly(oxyalkylene) hydroxyaromatic ether is  
23       hydrogen or hydroxy; R<sub>5</sub> is hydrogen, alkyl having 4 to  
24       12 carbon atoms, or alkylphenyl having an alkyl group  
25       containing 4 to 12 carbon atoms; and x is 0.  
26
- 27   29. The fuel composition according to Claim 28, wherein R<sub>1</sub>  
28       and R<sub>5</sub> of said poly(oxyalkylene) hydroxyaromatic ether  
29       are both hydrogen.  
30
- 31   30. The fuel composition according to Claim 26, wherein  
32       said poly(oxyalkylene) amine is a hydrocarbyl  
33       poly(oxyalkylene) aminocarbamate.  
34
- 35   31. The fuel composition according to Claim 30, wherein the

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01 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)  
02 aminocarbamate contains from 1 to about 30 carbon  
03 atoms; and wherein the amine moiety of said hydrocarbyl  
04 poly(oxyalkylene) aminocarbamate is derived from a  
05 polyamine having from 2 to 12 amine nitrogen atoms and  
06 from 2 to 40 carbon atoms.

07

08 32. The fuel composition according to Claim 31, wherein  
09 said hydrocarbyl group of said hydrocarbyl  
10 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
11 group; and wherein said polyalkylene polyamine is  
12 selected from the group consisting of ethylenediamine,  
13 propylenediamine, diethylenetriamine and  
14 dipropylenetriamine.

15

16 33. The fuel composition according to Claim 32, wherein the  
17 alkyl moiety of said alkylphenyl group is  
18 tetrapropenyl.

19

20 34. The fuel composition according to Claim 30, wherein  
21 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an  
22 alkylphenyl poly(oxybutylene) aminocarbamate, wherein  
23 the amine moiety is derived from ethylenediamine or  
24 diethylenetriamine.

25

26 35. The fuel composition according to Claim 26, wherein  
27 said composition contains about 50 to about 2,500 parts  
28 per million by weight of said poly(oxyalkylene)  
29 hydroxyaromatic ether and about 25 to about 1,000 parts  
30 per million of said poly(oxyalkylene) amine.

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-62-

01 36. A fuel concentrate comprising an inert stable  
 02 oleophilic organic solvent boiling in the range of from  
 03 about 150°F to 400°F and from about 10 to about 70  
 04 weight percent of a fuel additive composition  
 05 comprising:

06  
 07 (a) a poly(oxyalkylene) hydroxyaromatic ether having  
 08 the formula:

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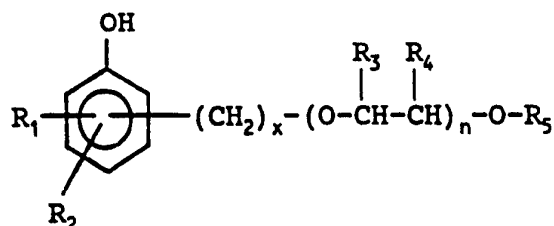
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or a fuel-soluble salt thereof; wherein

R<sub>1</sub> and R<sub>2</sub> are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R<sub>3</sub> and R<sub>4</sub> are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R<sub>5</sub> is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



wherein R<sub>6</sub> is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36



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- 01 carbon atoms;  
02  
03 n is an integer from 5 to 100; and x is an integer  
04 from 0 to 10; and  
05  
06 (b) a poly(oxyalkylene) amine having at least one  
07 basic nitrogen atom and a sufficient number of  
08 oxyalkylene units to render the poly(oxyalkylene)  
09 amine soluble in hydrocarbons boiling in the  
10 gasoline or diesel range.  
11  
12
- 13 37. The fuel concentrate according to Claim 36, wherein R<sub>1</sub>  
14 of said poly(oxyalkylene) hydroxyaromatic ether is  
15 hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon  
16 atoms; R<sub>2</sub> is hydrogen; one of R<sub>3</sub> and R<sub>4</sub> is hydrogen and  
17 the other is methyl or ethyl; R<sub>5</sub> is hydrogen, alkyl  
18 having 2 to 22 carbon atoms, alkylphenyl having an  
19 alkyl group containing 4 to 24 carbon atoms, or an acyl  
20 group having the formula: -C(O)R<sub>7</sub>, wherein R<sub>7</sub> is alkyl  
21 having 4 to 12 carbon atoms; n is 15 to 30; and x is 0,  
22 1 or 2.  
23
- 24 38. The fuel concentrate according to Claim 37, wherein R<sub>1</sub>  
25 of said poly(oxyalkylene) hydroxyaromatic ether is  
26 hydrogen or hydroxy; R<sub>5</sub> is hydrogen, alkyl having 4 to  
27 12 carbon atoms, or alkylphenyl having an alkyl group  
28 containing 4 to 12 carbon atoms; and x is 0.  
29
- 30 39. The fuel concentrate according to Claim 38, wherein R<sub>1</sub>  
31 and R<sub>5</sub> of said poly(oxyalkylene) hydroxyaromatic ether  
32 are both hydrogen.  
33
- 34 40. The fuel composition according to Claim 36, wherein  
35 said poly(oxyalkylene) amine is a hydrocarbyl

01 poly(oxyalkylene) aminocarbamate.

02

03 41. The fuel composition according to Claim 40, wherein the  
04 hydrocarbyl group of said hydrocarbyl poly(oxyalkylene)  
05 aminocarbamate contains from 1 to about 30 carbon  
06 atoms; and wherein the amine moiety of said hydrocarbyl  
07 poly(oxyalkylene) aminocarbamate is derived from a  
08 polyamine having from 2 to 12 amine nitrogen atoms and  
09 from 2 to 40 carbon atoms.

10

11 42. The fuel composition according to Claim 41, wherein  
12 said hydrocarbyl group of said hydrocarbyl  
13 poly(oxyalkylene) aminocarbamate is an alkylphenyl  
14 group; and wherein said polyalkylene polyamine is  
15 selected from the group consisting of ethylenediamine,  
16 propylenediamine, diethylenetriamine and  
17 dipropylenetriamine.

18

19 43. The fuel composition according to Claim 42, wherein the  
20 alkyl moiety of said alkylphenyl group is  
21 tetrapropenyl.

22

23 44. The fuel composition according to Claim 40, wherein  
24 said hydrocarbyl poly(oxyalkylene) aminocarbamate is an  
25 alkylphenyl poly(oxybutylene) aminocarbamate, wherein  
26 the amine moiety is derived from ethylenediamine or  
27 diethylenetriamine.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/12401

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C10L 1/18, 1/22

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/400, 442, 443, 448, 450; 560/103, 129, 144; 568/607, 608, 609, 610, 611, 606

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 5,094,667 (Schilowitz et al), 10 March 1992, see entire document.	1-16,26-29,36-39
Y	US,A, 4,881,945 (Buckley, III), 21 November 1989, see entire document.	1-15, 17-44
Y	US,A, 4,261,704 (Langdon), 14 April 1981, see entire document.	1-15,26-29,36-39
Y	US,A, 4,247,301 (Honnen) 27 January 1981, see entire document	1-15,26-29,36-39
E	US,A, 5,298,039 (Mohr et al) 29 March 1994, see entire document.	1-44
A,P	US,A, 5,192,335 (Cherpeck) 09 March 1993, see entire document.	1-44



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

06 MAY 1994

Date of mailing of the international search report

MAY 31 1994

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/12401

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 5,024,678 (Mertens-Gottselig et al) 18 June 1991, see entire document.	1-44
A	US,A, 5,006,130 (Aiello et al) 09 April 1991, see entire document.	1-44
A	US,A, 3,927,994 (Romans) 23 December 1975, see entire document.	1-44
A	US,A, 3,615,295 (Manary, Jr) 26 October 1971, see entire document.	1-44
A	US,A, 2,807,525 (Foreman) 24 September 1957, see entire document.	1-44

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/12401

## A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

44/387, 400, 434, 442, 443, 448, 450; 560/103, 129, 144; 568/607, 608, 609, 610, 611, 606