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(54) **Middle distillate hydrocarbon foam control agents from alkylmethylsiloxanes.**

(57) Organosilicone materials that are "density-matched" to hydrocarbon media also act as defoamers in hydrocarbon fuel, such as diesel fuel. Specifically, our defoamers are described as cross-linked organopolysiloxane-polyoxyalkylenes. They are characteristized by being slightly soluble or insoluble in water and hydrocarbon fuels. By changing the solvent and the method of dispersion, different particle size distributions are obtained.

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This invention relates to foam control and is particularly concerned with controlling foaming in hydrocarbon liquids.

There are a number of patents which disclose specific compositions which reduce or eliminate foam. For example, U.S. Patent 5,192,336 discloses that bis-strearamides act as defoamers by remaining dispersed within hydrocarbon fuels. This is in contrast to silicone polyether defoamers of U.S. Patent 4,690,668 and U.S. Patent 3,233,986, which settle out over time because of their higher density relative to hydrocarbon fuel, often necessitating periodic agitation to re-disperse them. Silicone polyethers also tend to be more soluble or dispersible in water, which is a constant component of hydrocarbon fuels. In storage tanks, water tends to coalesce and forms a layer at the bottom of the tank. As the silicone polyether settles due to gravity effects and its hydrocarbon insolubility, eventual contact with the water layer can result in its ultimate absorbtion into that phase. Thus, it can be irreversibly removed from the fuel in its entirety.

Presently, middle distillate fuels exhibit foaming during transfer operations, such as filling a vehicle's fuel tank at a service station. In the processing, transportation and storage of hydrocarbon liquids, it is frequently observed that foaming occurs as the liquid is passed from one vessel to another. For example, as hydrocarbon fuel is passed into a storage tank, foam may develop at the surface of the fuel. In many cases, the extent of foaming is sufficiently significant and persistent to require a reduction in the passage rate of the liquid fuel into the vessel. It is therefore desirable to provide means for controlling such foaming to permit sustained or higher rates of passage.

Various proposals have been made as solutions for this problem. One proposal uses silicone additives to control foaming of various grades of hydrocarbon liquids. However, a solution for diesel fuels has not been satisfactorily found.

U.S. Patent 3,233,986 deals with siloxane polyoxyalkylene block copolymers as antifoam agents and discloses a wide variety of such copolymers to reduce foaming of organic liquids. Organic liquids mentioned are various hydrocarbon fuels, e.g., kerosene, gasoline and diesel fuel. One copolymer therein comprises groups represented by the formula:

$$G^3(OG'')_nOG'Si\begin{matrix}G_c\\|\\O\end{matrix}_{\frac{3-c}{2}}$$

wherein G^3 is a member selected from hydrogen atom and monovalent hydrocarbon groups, G'' is an alkylene radical containing at least two carbon atoms, G' is a divalent hydrocarbon radical, G is a monovalent hydrocarbon radical, n has a value of at least two and c has a value from 0 to 2 inclusive.

At least 60% by weight of the groups OG'' must be oxyethylene or oxypropylene groups, and other oxyalkylene groups may also be present. Each oxyalkylene block preferably contains from four to thirty OG'' groups. However, the number of oxyalkylene groups (OG'') and the average molecular weight of the copolymer attributable to the oxyalkylene blocks is not described therein as critical. Moreover, useful copolymers can contain siloxane blocks and oxyalkylene blocks in any relative amount.

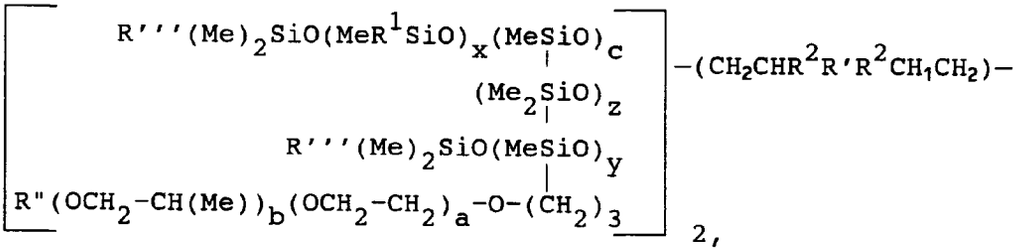
Finally, while the amount of the copolymers used with a liquid hydrocarbon is not critical (ranges from 5 to 2000 parts by weight of the copolymer per million parts of the liquid), some copolymers in U.S. Patent 3,233,986, when employed in certain hydrocarbon fuels in amounts of less than 100 parts copolymer per million parts hydrocarbon, do not act to reduce the tendency of the hydrocarbon to foam. Rather, the tendency of the hydrocarbon to foam is actually increased.

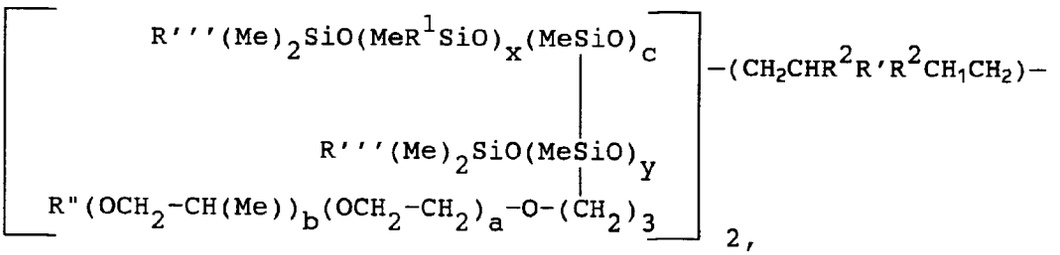
Organosilicone materials "density-matched" to the hydrocarbon medium act as defoamers in hydrocarbon fuel as described herein. Specifically our defoamers can be described as alkylmethylsiloxanes or crosslinked organopolysiloxane-polyoxyalkylenes. They are characterized by being slightly soluble or insoluble in water and hydrocarbon fuels. By changing the solvent and the method of dispersion, different particle size distributions of our alkylmethylsiloxanes or organopolysiloxane-polyoxyalkylenes are obtained.

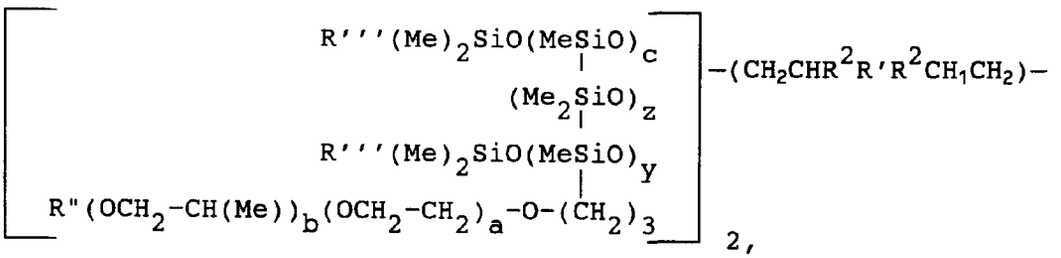
By using materials that do not readily settle from the hydrocarbon, and which are sparingly soluble or only dispersible in water, our defoamers do not lose their defoaming capability during storage as readily as conventional silicone polyethers which rapidly settle from the fuel and which are more soluble in water.

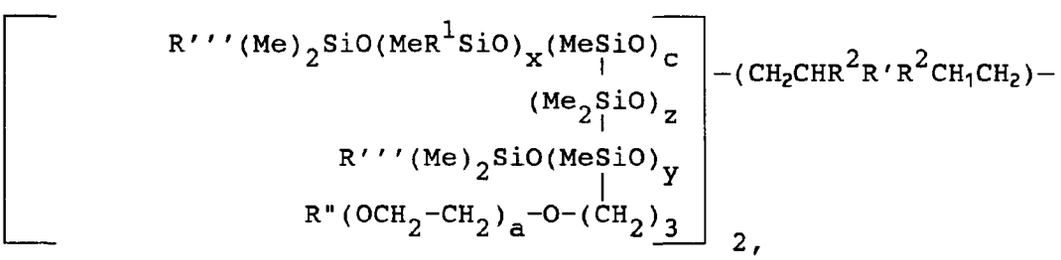
In one aspect, the present invention is directed to such formulations to reduce the tendency of hydrocarbon liquids to foam. Alkylmethylsiloxane mixtures comprising an alkylmethylsiloxane of the structure $R^{II}Me_2SiO(Me_2SiO)_m(MeR^{I}SiO)_ySiMe_2R^{II}$ or $R^{II}Me_2SiO(MeR^{I}SiO)_nSiMe_2R^{II}$, wherein R^{I} is the same or different alkyl of 2 to 100 carbon atoms, R^{II} is methyl or R^{I}, m is 1-499, $n \geqq 1$ and $m + n \leqq 500$. Our invention may also comprise mixtures of the aforesaid compositions.

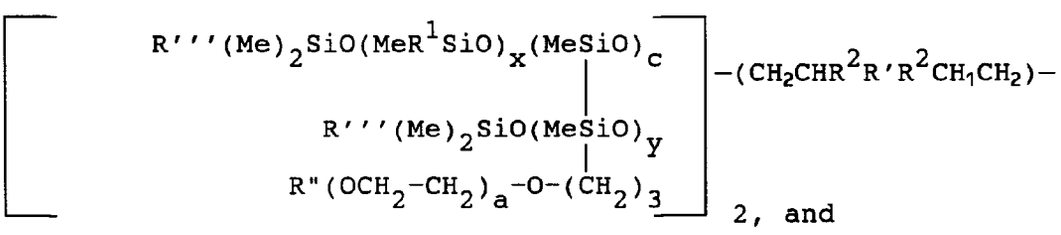
In a second aspect of the invention, the crosslinked organopolysiloxane-polyoxyalkylenes are selected from the group of:

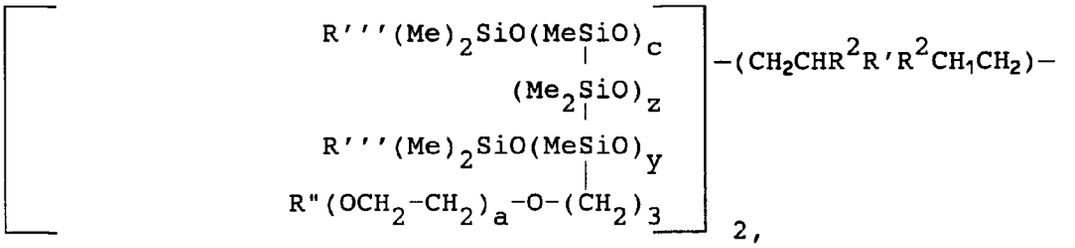












where:

Me is CH_3-;

R^1 is 2 to 25 aliphatic carbon radicals;

R' is selected from

(i) divalent organic radicals, and

(ii) divalent organosiloxane groups, wherein (i) and (ii) do not contain hydrolyzable groups;

R" is a terminal group;

R"' is independently selected from

(i) hydrogen, and

(ii) aliphatic carbon radicals having 1 to 25 carbon atoms;

R^2 is independently selected from

(i) hydrogen, and

(ii) aliphatic carbon radicals having 1 to 3 carbon atoms;

where

each $\underline{x}$ = 1-200;

each $\underline{c}$ = 1-5;

each $\underline{z}$ = 1-600;

each $\underline{y}$ = 1-40;

$\underline{x}+\underline{y}+\underline{z} \geqq 10$;

each $\underline{a}$ = 4-40; and

each $\underline{b}$ = 1-40.

This general class of cross-linked organopolysiloxane-polyoxyalkylenes are disclosed in U.S. Patent 4,853,474 which shows the general materials as well as their preparation.

The aliphatic radicals represented by R^1 include the C_2 to C_{25} paraffin, olefin and acetylenic hydrocarbons. The paraffinic hydrocarbons are preferred, such as ethyl, propyl, hexyl, decyl, dodecyl, octadecyl and eicosyl.

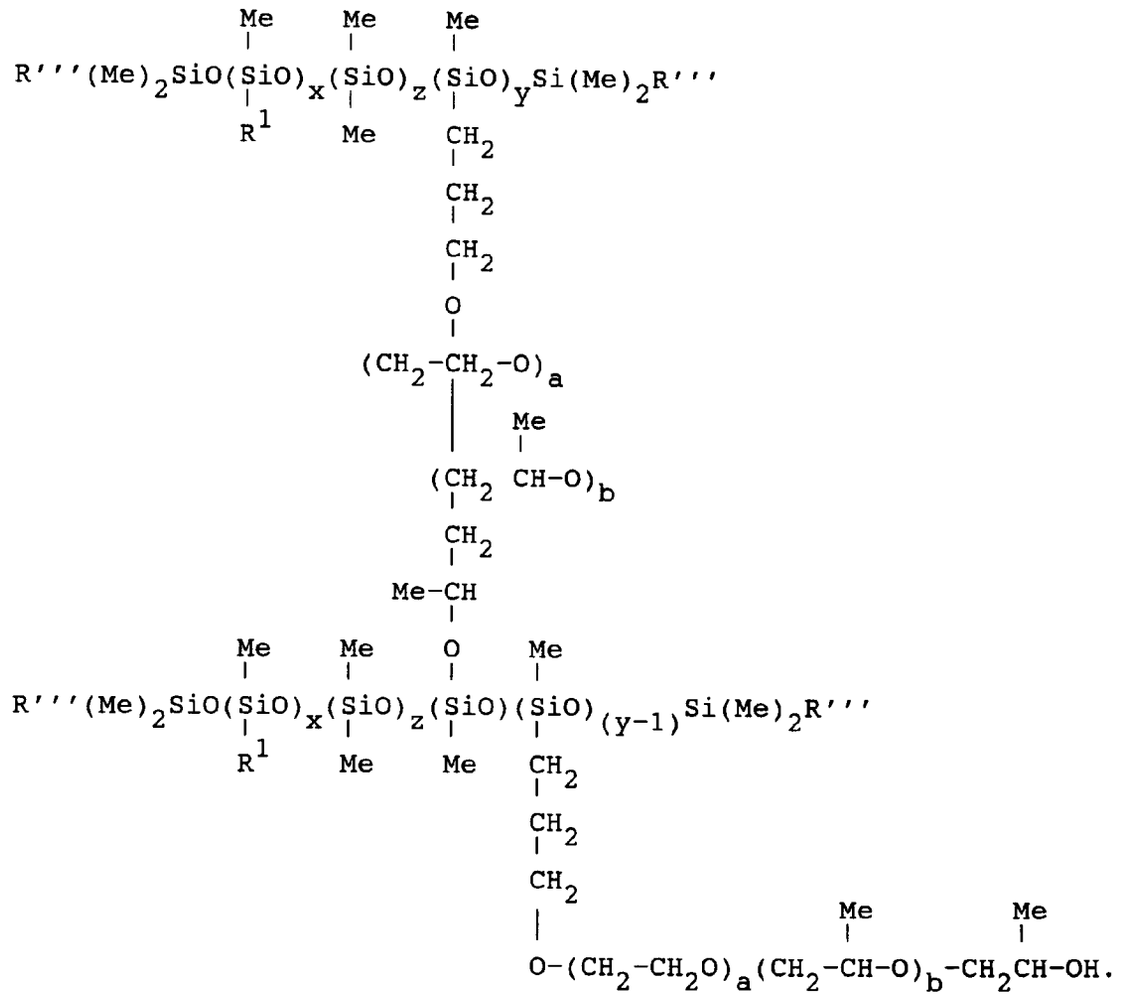
The organic groups represented by R' include C_1 to C_{10} alkylene radicals such as methylene, dimethylene, trimethylene, pentamethylene and decamethylene; cycloalkylene radicals such as cyclohexylene; divalent aromatic radicals such as p-phenylene or o-phenylene; and oxygen containing radicals such as -$COOCH_2CH_2OOC$- and -CH_2OCH_2-.

The terminal group represented by R" includes radicals of C_1 to C_{20}, like acetyl, propionyl, butyryl, isobutyryl, lauroyl, myristoyl, and stearoyl 3-carboxypentadecanoyl; alkyl radicals of C_1 to C_{10}, such as methyl, ethyl, propyl, butyl, and decyl; and the hydrogen atom.

The aliphatic radical represented by R"' includes any of the radicals illustrated for R and also includes the methyl radical.

The cross-linking radical R^2 represents the hydrogen atom and monovalent C_1 to C_3 aliphatic radicals such as methyl, ethyl and propyl.

It is preferred that the cross-linking bond is not hydrolyzable, and that R' contains no hydrolyzable bonds. In conventional organosiloxane-polyoxyalkylenes, some cross-linking may accidentally occur where the polyoxyalkylene is hydroxy terminated at one end. The hydroxy group may react with a silicon hydride creating a polyoxyalkylene bridge between two silicon backbone molecules as shown below:



However, the degree to which this cross-linking may occur in the reaction process is not readily predictable. Further, the SiOC bond formed at the hydroxy end of the bridge is subject to hydrolysis, under the operating conditions described above.

In contrast, the preferred bridge bond of the organopolysiloxane-polyoxyalkylenes of the second aspect of the present invention is a saturated carbon-silicon bond which is not hydrolyzable and is highly stable. Further, the organic or organosiloxane body R' of the cross-linking bridge is free of hydrolyzable bonds. Further, R' should not interfere with the organopolysiloxane-polyoxyalkylene formation in any way.

Hydrocarbon fuels of particular interest in the present invention are diesel fuel and jet fuel. The hydrocarbon fuel is preferably a diesel fuel used in motor vehicles, e.g. cars, heavy vehicles, marine applications or aviation. The expression "diesel fuel" means gas oil and fuel oil including those materials which are light domestic, heating oils and diesel fuel irrespective of whether they are intended for vehicular, heating or other uses. These materials are characterized as having a viscosity of not more than 115" Redwood 1 at 38°C. and a boiling point in the range of 200°C. to 380°C. Particularly included are those hydrocarbon liquids having a viscosity of 30" to 40" Redwood at 38°C., including those having a viscosity at 20°C. of 2.9 to 10.2 mm^2/s [centistokes (cS)] and at 38°C. of 1.6 to 6.0 mm^2/s (cS). Further, these materials have a carbon residue (Conradson) of <0.2% by weight, a water content of <0.05% by weight, a sulphur content of <1.0% by weight and a net calorific value within the range of 10100 to 10300 Kcal/Kg.

The expression "jet fuel" means kerosene and light oils or medium oils for example known as AVTUR fuel. AVTUR fuel is a medium oil distilling between 150° and 300°C. that distills at least 65% in volume at 250°C., has a flash point above 38°C., has a maximum aromatic content of 20% by volume, has been treated to have a kinematic viscosity of less than 15 mm^2/s (cS) at -34°C. and has a freezing point not greater than -50°C.

The present invention may also find limited use for controlling foaming of other hydrocarbon liquids; for

example, residual fuel oils having a viscosity at 38°C. of greater than 115" Redwood, light medium and heavy naphtha, vaporizing oils, motor oils and motor spirits. Our invention is particularly beneficial in the control of foaming of hydrocarbon liquids and especially diesel fuels, as they are pumped rapidly from one vessel to another in the presence of air and possibly in the presence of water. Such circumstances exist during transfer of materials though a supply pipe from one vessel to another, during separation of various grades of hydrocarbon liquids from crude oil or selected feedstocks, and during transfer from transportation tankers to fixed storage tanks.

Frequently, hydrocarbon liquids have dispersed therein various "additive packages" which contain corrosion inhibitors, anti-scaling agents, octane improvers, emulsifiers, detergents and their mixtures. These additives are known to improve overall engine performance. The types and quantities of these additives are well known to those skilled in the art.

The organopolysiloxane-polyoxyalkylene polymers of this aspect are used in any desired quantity and are incorporated into the hydrocarbon liquid in any suitable manner. Typically, our copolymers are added to the hydrocarbon liquid in the form of a solution or dispersion. The preferred polymers are effective to reduce the tendency of hydrocarbon liquids to foam when used in quantities of 100 parts per million or less, for example in the range of 1 to 50 ppm by volume. Surprisingly, the most preferred polymers are effective when used in quantities of from 1 to 29 ppm by volume.

Our invention also includes alkylmethylsiloxanes selected from: $R^{II}Me_2SiO(Me_2SiO)_m(MeR^{I}SiO)_nSiMe_2R^{II}$ and $R^{II}Me_2SiO(MeR^{I}SiO)_nSiMe_2R^{II}$, wherein $\underline{m}$ is 1-499, $\underline{n} \geqq 1$, with $\underline{m} + \underline{n} \leqq 500$, R^{I} is the same or different alkyl group of 2-100 carbon atoms, and R^{II} is methyl or R^{I}. Exemplary alkylmethylsiloxanes include $Me_3SiO[Me(CH_3(CH_2)_v)SiO]SiMe_3$, where $\underline{v}$ averages between 24 and 28, or $\underline{v}$ averages between 30 and 50.

These alkylmethylsiloxanes are density matched to the hydrocarbon liquid. By "density matched", it is meant that the alkylmethylsiloxanes have a density roughly approximating the density of the hydrocarbon liquid. The density of most alkylmethylsiloxanes is within the range of the described hydrogen liquids, generally 0.8 to 0.9 g/cm^3.

The above alkylmethylsiloxanes are known in the art and are produced by known methods. For example, cyclic alkylmethylsiloxane polymers can be produced by the reaction of a cyclic siloxane having Si-H functional units thereon (eg., $[MeHSiO]_a$) with a slight stoichiometric excess of an alkene in the presence of a platinum supported catalyst on carbon. Likewise, linear alkylmethyl copolymers can be produced by the reaction of a linear siloxane having Si-H functionality in the chain such as $(Me_3SiO_{0.5})_2(MeHSiO)_{z1}$, in which $\underline{z1}$ is 4-100, and a cyclic siloxane having $(Me_2SiO)_{z2}$ units, in which $\underline{z2}$ is 3-6. The reaction product (generally 10% cyclic and 90% linear) is then contacted with a slight stoichiometric excess of an alkene in the presence of a platinum catalyst.

Batch production of the alkylmethylsiloxanes is conducted by adding the reaction product to a non-agitated suspension of the catalyst in the alkene at 60°C. Continuous production of the alkylmethylsiloxanes is conducted by pumping a preheated solution of a stoichiometric excess of an alkene CH_2=CHR and the reaction product through a packed column containing platinum catalyst supported on carbon chips. The column will require provision for the removal of heat because of the exothermic nature of the reaction.

For antifoam applications, the preferred alkylmethylsiloxane is $Me_3SiO[Me(CH_3(CH_2)_v)SiO]SiMe_3$, where v averages between 24 and 28, or $\underline{v}$ averages between 30 and 50.

In the second aspect of this invention, the preferred organopolysiloxane-polyoxyalkylene is $Me_3SiO[(C_{12}H_{25})CH_3SiO]_{38.5}[R_3CH_3SiO]_{1.5}SiMe_3$, where $R_3 = (CH_2)_3(CH_2CH_2O)_{18}(CH_2CH(CH_3)O)_{18}H$. These antifoaming agents may be added directly to the hydrocarbon fuel, or may be predispersed in a predispersent liquid, such as the hydrocarbon fuel, xylene, toluene, naphtha or other aromatics; various ketones; ethers and other commonly used organic solvents.

Example 1

Four samples of the first aspect of the invention were prepared. For Sample A, 90 g. of diesel fuel was weighed into a 473.2 ml (16 oz.) glass bottle. To this was added 10 ppm of $Me_3SiO[Me(CH_3(CH_2)_v)SiO]SiMe_3$, where $\underline{v}$ averages between 30 and 50 (the "first antifoam agent"), predispersed as a 1% wt. solution in xylene. For Sample B, 90 g. of diesel fuel was weighed into a 473.2 ml (16 oz.) glass bottle, and to this was added 10 ppm of the first antifoam agent, predispersed as a 1% wt. solution in diesel fuel.

For Sample C, 90 g. of diesel fuel was weighed into a 473.2 ml (16 oz.) glass bottle. To this was added 10 ppm of $Me_3SiO[Me(CH_3(CH_2)_v)SiO]SiMe_3$, where $\underline{v}$ averages between 24 and 28 (the "second antifoam agent"), predispersed as a 1% wt. solution in xylene. For Sample D, 90 g. of diesel fuel was weighed into a 473.2 ml (16 oz.) glass bottle, and to this was added 10 ppm of the first antifoam agent, predispersed as a 1% wt. solution in diesel fuel.

The mixtures were then gently swirled to disperse the antifoam solution. Then, 10 g. of deionized (DI) water was added to each bottle, and the contents of each were again gently swirled to provide limited contact between phases.

50cm^3 of the fuel phase from each of the above samples were pipetted into separate 100cm^3 graduated cylinders. The cylinders were then stopped with a glass stopper and the contents shaken 60-65 times during a one minute period. After the foam shaking had stopped, the foam volume was immediately recorded and the amount of time required for the foam to break and expose a clear section of liquid was measured. The foam height was then converted to a "Percent Foam Volume" using the following formula, which is relative to the original liquid volume of 50cm^3:

100 x {(recorded foam volume - 50)cm^3 / 50cm^3 }= "Percent Foam Volume".

Table I has the results of the trials:

TABLE I

	DAY 1		DAY 7	
	%Foam Volume	Break Time	%Foam Volume	Break Time
Sample A sec.	+ 18%	23 sec.	+ 23%	31
Sample B sec.	+ 18%	25 sec.	+ 21%	34
Sample C sec.	+ 26%	60 sec.	+ 19%	43
Sample D sec.	+ 28%	57 sec.	+ 21%	49
Control sec. (No Antifoam)	+ 27%	57 sec.	+ 25%	47

The first antifoam additive of Samples A and B reduce the break time by as much as 50% over the control (untreated diesel fuel). Samples A and B also showed a significant decrease in overall foam volume when compared to the control. Samples C and D also had improvement over the control.

Example 2

Two samples of the second aspect of the invention were prepared. For Sample A, 90 g. of diesel fuel was weighed into a 473.2 ml (16 oz.) glass bottle. To this was added 10 ppm of $Me_3SiO[(C_{12}H_{25})CH_3SiO]_{38.5}[R_3CH_3SiO]_{1.5}SiMe_3$ where $R_3 = (CH_2)_3(CH_2CH_2O)_{18}(CH_2CH(CH_3)O)_{18}H$ (the "antifoam agent"), predispersed as a 1% wt. solution in xylene. For Sample B, 90 g. of diesel fuel was weighed into a 473.2 ml (16 oz.) glass bottle, and to this was added 10 ppm of the antifoam agent, predispersed as a 1% wt. solution in diesel fuel. The mixtures were then gently swirled to disperse the antifoam solution. Then 10 gm. of DI water was added to each bottle, and the contents of each were again gently swirled to provide limited contact between phases.

Fifty cm^3 of the fuel phase from each of the above samples were pipetted into separate 100cm^3 graduated cylinders. The cylinders were then stopped with a glass stopper and the contents shaken 60-65 times during a one minute period. The foam volume after shaking was recorded and the amount of time required for the foam to break and expose a clear section of liquid was measured. The foam height was then converted to a "Percent Foam Volume" using the above formula.

Table II shows the results of the trials:

TABLE II

	DAY 1		DAY 7	
	%Foam Volume	Break Time	%Foam Volume	Break Time
Sample A	+ 25%	34 sec.	+ 24%	41 sec.
Sample B	+ 23%	43 sec.	+ 24%	48 sec.
No Antifoam (control)	+ 27%	57 sec.	+ 25%	47 sec.

Table II shows that the antifoam additive of Samples A and B reduce the break time by as much as 50% over untreated diesel fuel.

Claims

1. An antifoam composition comprising a hydrocarbon liquid and a density matched organopolysiloxane-polyoxyalkylene selected from:

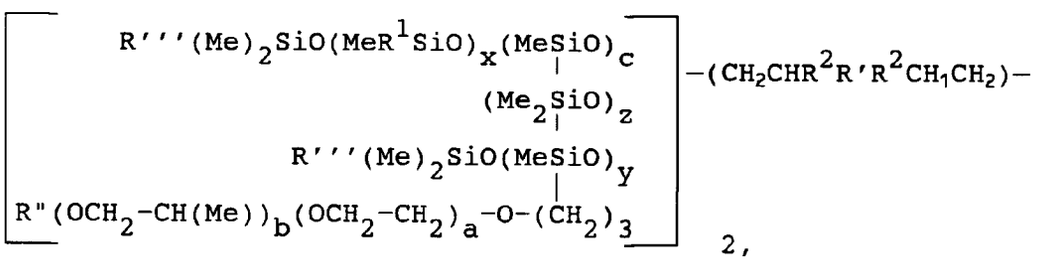
(I) $R^{II}Me_2SiO(Me_2SiO)_m(MeR^{I}SiO)_ySiMe_2R^{II}$;

(II) $R^{II}Me_2SiO(MeR^{I}SiO)_nSiMe_2R^{II}$;

wherein m is 1-499, $n \geqq 1$ and $m + n \leqq 500$, R^{I} is the same or different alkyl of 2 to 100 atoms, R^{II} is methyl or R^{I}, and

(III)

(a)



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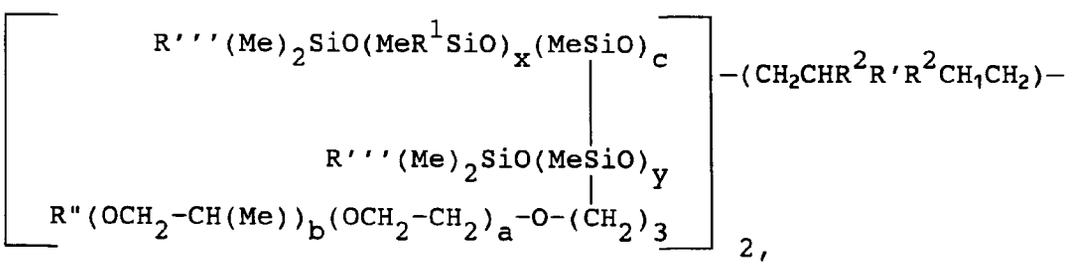

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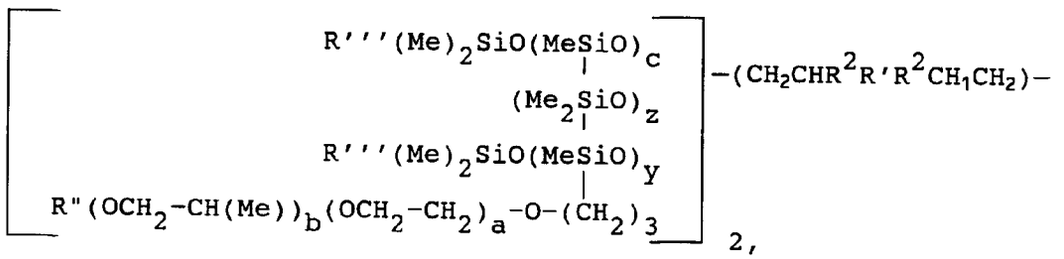

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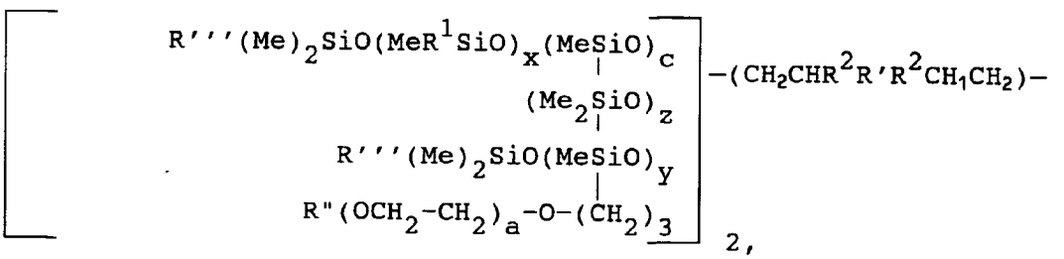

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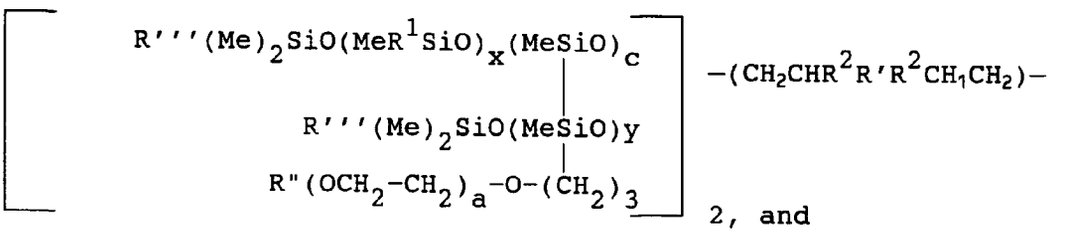

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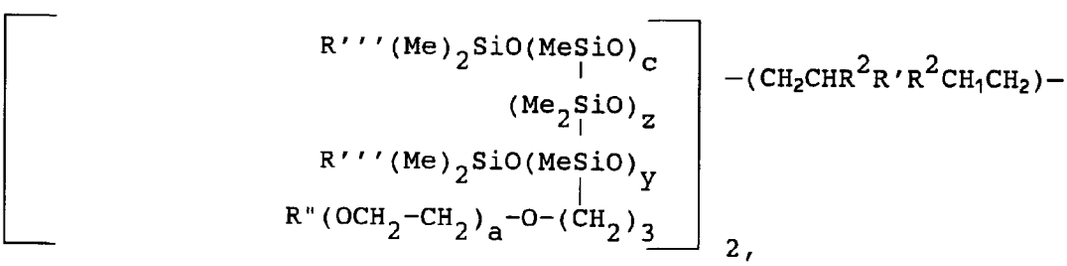

where:

Me is CH_3-;

R^1 is 2 to 25 aliphatic carbon radicals;

R' is selected from

(i) divalent organic radicals, and

(ii) divalent organosiloxane groups, wherein (i) and (ii) do not contain hydrolyzable groups;

R" is a terminal group;

R"' is independently selected from

(i) hydrogen, and

(ii) aliphatic carbon radicals having 1 to 25 carbon atoms;

R^2 is independently selected from

(i) hydrogen, and

(ii) aliphatic carbon radicals having 1 to 3 carbon atoms; where

each x = 1-200;

each c = 1-5;

each z = 1-600;

each y = 1-40;

$x+y+z \geqq 10$;

each a = 4-40; and

each b = 1-40; and

wherein said density matched organopolysiloxane-polyoxyalkylene is present in an amount of less than 100 parts per million by volume of said hydrocarbon liquid.

2. The composition of claim 1 selected from group (III) wherein c is greater than 1 and there are up to six organopolysiloxane-polyoxyalkylene molecules cross-linked together.

3. The composition of claim 2 in which said cross-linker is linked to the siloxane backbone of said organopolysiloxane-polyoxyalkylene molecules through a saturated silicon to carbon bond.

4. The composition of claim 3 in which said cross-linker is an organosiloxane radical.

5. The composition of claim 4 in which said cross-linker comprises diethyltetramethyldisiloxane.

6. The composition of claim 1 using group (II) wherein, n = 1, R^{II} is methyl and R^{I} is the same or different alkyl groups of between 30 and 50 carbon atoms.

7. The composition of claim 1 using group (II) wherein n = 1, R^{II} is methyl and R^{I} is the same or different alkyl groups of between 24 and 28 carbon atoms.

8. The composition of claim 1 in which said hydrocarbon liquid is diesel fuel.

9. The composition of claim 1 in which said hydrocarbon liquid is jet fuel.

10. The composition of claims 8 or 9 in which said hydrocarbon liquid includes an additive package comprising corrosion inhibitors, anti-scaling agents, octane improvers, emulsifiers, detergents and their mixtures.

11. A method for reducing the amount of foam in a hydrocarbon liquid, comprising the step of adding to a hydrocarbon liquid a density matched organopolysiloxane-polyoxyalkylene of claim 1.

12. The method of claim 11 wherein said organopolysiloxane-polyoxyalkylene is predispersed in a predispersent prior to addition to the hydrocarbon liquid.

13. The method of claim 12 wherein said antifoaming agent is dispersed in a dispersent selected from:

(a) hydrocarbon liquid;

(b) xylene;

(c) toluene;

(d) ketones;

(e) esters; or

(f) ethers.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 8392

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	EP-A-0 167 361 (THE BRITISH PETROLEUM) * page 4, line 6 - line 8 *	1,11-13 8,10	C10L1/28 B01D19/04 C08G77/50
P,Y	WO-A-94 19430 (EXXON) * page 3, line 10 - line 25 * * page 6, line 10 - page 10, line 21 *	8,10	C08G77/46
P,X	EP-A-0 578 423 (DOW CORNING) * page 3, line 35 - line 44 * * page 4, line 40 - line 45 *	1,6,7,9	
X	FR-A-2 579 481 (DOW CORNING) * the whole document *	1,11-13	
X	EP-A-0 121 210 (UNION CARBIDE) * page 12, line 11 - line 25; claims 1,2 *	1,9	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 March 1995	De La Morinerie, B

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