



(86) Date de dépôt PCT/PCT Filing Date: 2003/11/03
(87) Date publication PCT/PCT Publication Date: 2004/05/21
(85) Entrée phase nationale/National Entry: 2005/05/03
(86) N° demande PCT/PCT Application No.: EP 2003/012275
(87) N° publication PCT/PCT Publication No.: 2004/041975
(30) Priorité/Priority: 2002/11/04 (102 51 312.0) DE

(51) Cl.Int.⁷/Int.Cl.⁷ C10L 1/14, B01D 19/04

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(54) Titre : CARBURANTS CONTENANT UN ADDITIF A EFFET AMELIORE
(54) Title: IMPROVER CONTAINING FUEL

(57) Abrégé/Abstract:

The invention relates to an improver in the form of a mixture of at least polysiloxane antifoaming agent and at least partially or totally neutralised fat acid. The inventive fuel and additive containing said mixture are also disclosed.



Abstract

The present invention relates to an additive mixture comprising
5 at least one polysiloxane antifoam and at least one partially or
completely neutralized fatty acid, and also to a fuel composition
and an additive concentrate, each of which comprise this
composition.

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Improver containing fuel

5 Description

The present invention relates to an additive mixture comprising at least one polysiloxane antifoam and at least one partially or completely neutralized fatty acid.

10 An important component of fuel additive packages is antifoams which are intended to dampen the natural foaming behavior of fuels, in particular on filling, for example during the filling procedure at the gas pump. Polysiloxanes, in particular
15 polysiloxane alkoxylates, are frequently used antifoams.

For instance, US 6,093,222 describes antifoam compositions for diesel fuels which comprise various polysiloxanes. The polysiloxanes are substituted by long-chain polyether groups, organic polyols, hydrocarbon radicals and/or phenol radicals.
20 However, as a consequence of the high costs for the production of polysiloxane antifoams, these, in the amount in which they are required to achieve an antifoam performance, represent a not insignificant cost factor.

25 WO 95/04117 describes an additive composition which comprises an antifoam and a nitrogen-containing dispersant which burns ashlessly. The nitrogen-containing dispersant which burns ashlessly is intended to increase the long-term storage stability of the antifoam. However, the dispersant does not reduce the
30 amount of antifoam required for damping the foam formation of a fuel.

It is an object of the present invention to provide an additive mixture which exhibits an improved antifoam action in comparison
35 to prior art antifoams.

We have found that this object is achieved by an additive mixture comprising,

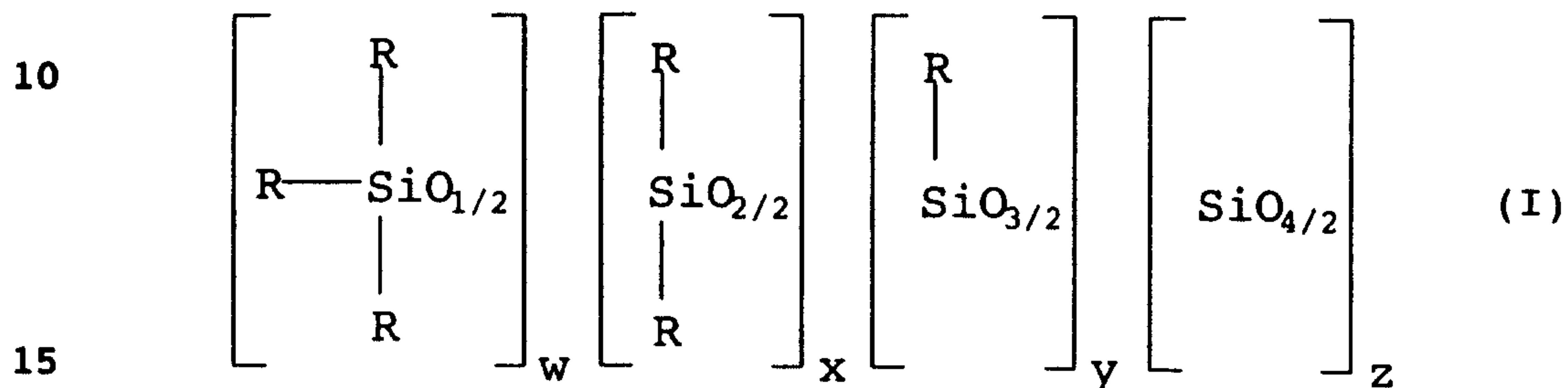
- 40 i) as component A, at least one polysiloxane antifoam and
- ii) as component B, at least one partially or completely neutralized fatty acid, a long-chain carboxylic acid, an ester of such a carboxylic acid or a mixture comprising
45 at least one of these compounds.

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Suitable polysiloxane antifoams are any common antifoams based on polysiloxane and known to those skilled in the art. Such antifoams are described, for example, in ATC Doc. 52 "Fuel Additives and the Environment".

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A preferred antifoam is a polysiloxane of the general formula I



where

20 the R radicals are each independently an R¹, R², R³, R⁴ or R⁵ radical where

R¹ is an aromatic or saturated aliphatic hydrocarbon radical,

25 R² is an organic polyol,

R³ is a polyether radical,

R⁴ is a phenol radical,

R⁵ is an R² radical, except that some or all of the hydroxyl groups have been converted to diesters, diethers, acetals and/or ketals,

30

w = 2 + y + 2 z,

y and z are each independently a number from 0 to 2 where the sum of y and z corresponds to a number from 0 to 2 and

w + x + y + z = from 20 to 60.

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In R¹, the aromatic or saturated aliphatic hydrocarbon radical is preferably C₁-C₂₄-alkyl, in particular methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl or stearyl; C₃-C₂₄-cycloalkyl, in particular cyclopropyl, cyclopentyl, cyclohexyl, cyclooctyl or cyclodecyl; C₄-C₂₄-alkylcycloalkyl, in particular methylcyclohexyl, dimethylcyclohexyl or ethylcyclohexyl; C₆-C₁₀-aryl, in particular phenyl; or C₇-C₁₈-arylalkyl, in particular methylphenyl, dimethylphenyl or phenylethyl. R¹ is more preferably C₁-C₂₄-alkyl, 45 in particular methyl.

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In R², the organic polyol is preferably a saturated or unsaturated, branched or unbranched, aliphatic hydrocarbon radical having at least two hydroxyl groups which is optionally interrupted by one or more oxygen atoms. Preference is given to
5 the hydrocarbon radical being saturated. The R² radical preferably has a molecular weight of from 100 to 700, more preferably from 130 to 650 and in particular of about 400.

The R² radicals are introduced into the polysiloxane framework,
10 for example, by reacting an unsaturated polyol with a polysiloxane which contains hydrogen atoms bonded to silicon. Examples of polyols suitable for preparing saturated R² radicals include trimethylolpropane monoallyl ether, ethoxylated pentaerythritol allyl ether, propoxylated pentaerythritol allyl
15 ether, triisopropanolamine allyl ether, ethoxylated allylsorbitol and 1,3-allyloxypropanediol. An example of a polyol suitable for preparing an unsaturated R² radical is 2-butyne-1,4-diol.

R³ is preferably a polyether radical which comprises at least 50%
20 by weight, more preferably at least 75% by weight and in particular 100% by weight, of copolymerized ethylene oxide units. The molecular weight of R³ is preferably up to 1500, more preferably from 100 to 350.

25 R⁴ is preferably a phenol radical which is substituted by mono- or polyunsaturated alkene and/or alkyne radicals. Suitable examples thereof include eugenol, vinylphenol, vinylguaiacol and 4-allylphenol.

30 In the case of preferred polysiloxanes of the formula I, the quotient of the number of R¹ groups to the number of R² groups (R¹/R²) is from 3 to 19.

Also, in preferred polysiloxanes I, the quotient of the sum of
35 the number of R³, R⁴ and R⁵ groups to the number of R² groups [(R³+R⁴+R⁵)/R²] is from 0 to 2.

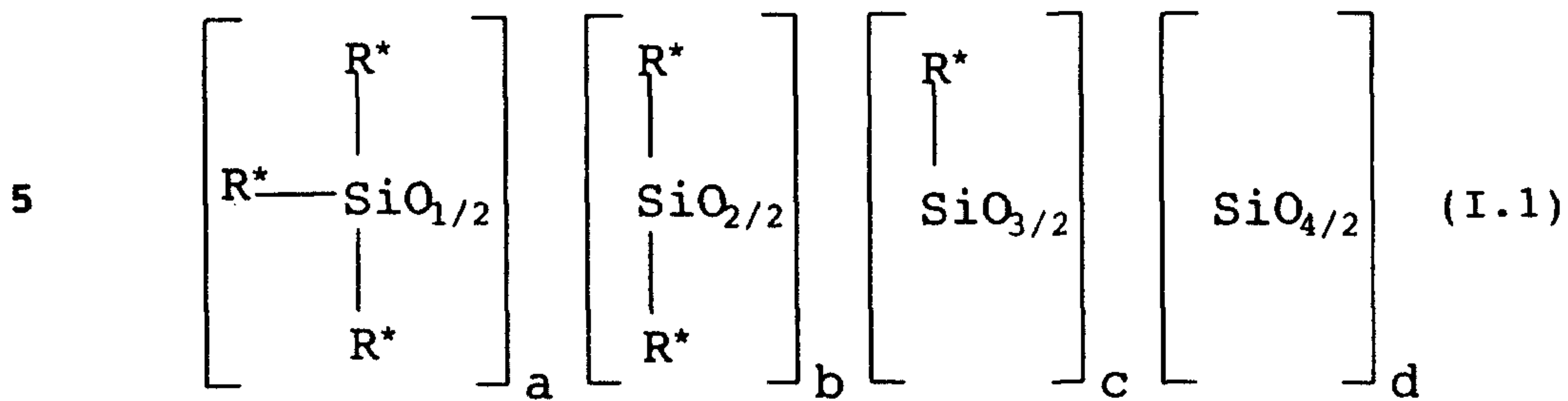
In a preferred embodiment, component A contains a plurality of different polysiloxanes I.

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In a particularly preferred embodiment, a polysiloxane I as defined above is used with a polysiloxane of the general formula I.1

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where

the R^* radicals are each independently an R^1 or R^3 radical where R^1 and R^3 are each as defined for polysiloxane I;

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$$a = 2 + c + 2d;$$

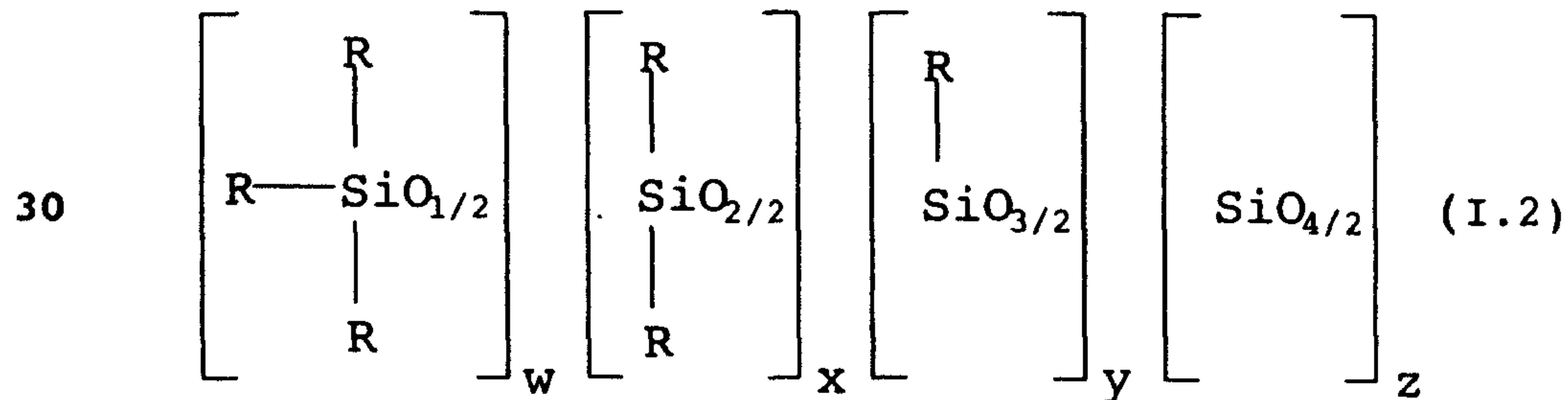
c and d are each independently a number from 0 to 2 and

20 $a + b + c + d =$ from 15 to 50,

and/or

with a polysiloxane of the general formula I.2

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where

R , w , x , y and z are each as defined for polysiloxane I, R^2 is a saturated polyol and

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the quotient of the number of R^3 groups to the number of R^2 groups (R^3/R^2) and the quotient of the number of R^4 groups to the number of R^2 groups (R^4/R^2) are each greater than 0.

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Such polysiloxane combinations are known, for example, from US 6,093,222, which is fully incorporated herein by way of reference.

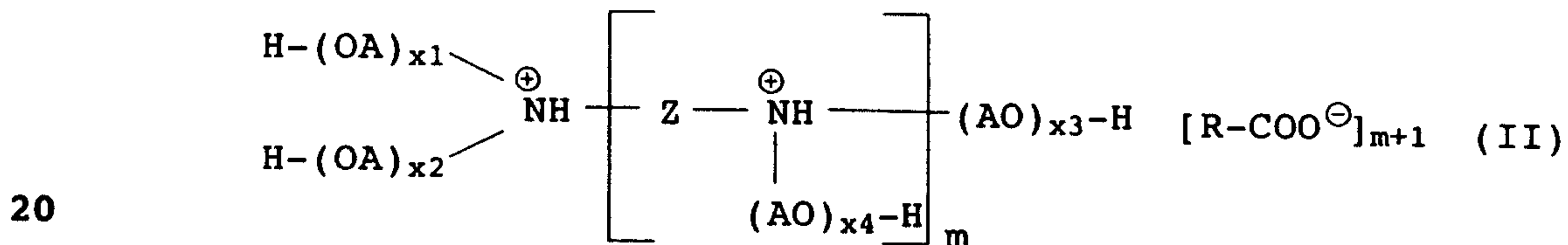
5 In preferred polysiloxanes I.1, the quotient of the number of R¹ groups to the number of R³ groups (R¹/R³) is from 3 to 19.

In preferred polysiloxanes I.2, the quotient (R³/R²) is from 0.25 to 5.

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Component B is preferably a fatty acid which has been partially or completely neutralized by amines.

Particular preference is given to component B comprising at least 15 one fatty acid salt of the formula II



where

25 R is C₇-C₂₃-alkyl or mono- or polyunsaturated C₇-C₂₃-alkenyl, each of which are optionally substituted by one or more hydroxyl groups;

A is C₂-C₈-alkylene;

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Z is C₁-C₈-alkylene, C₃-C₈-cycloalkylene, C₆-C₁₂-arylene or C₇-C₂₀-arylalkylene;

m is a number from 0 to 5; and

35

x¹, x², x³ and x⁴ are each independently a number from 0 to 24, at least one x not being 0,

and optionally at least one further fatty acid RCOOH where R is 40 as defined above.

Such fatty acid salts II are described, for example, in WO 01/38463, which is fully incorporated herein by way of reference.

45 The relatively long-chain radical R occurring in the carboxylate anion RCOO⁻ or in the fatty acid RCOOH is, for example, a branched or preferably linear C₇-C₂₃-, preferably C₁₁-C₂₁-, in particular

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C₁₅- to C₁₉-alkyl group which may additionally bear hydroxyl groups. Examples of parent carboxylic acids include octanoic acid, 2-ethylhexanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid (lauric acid), tridecanoic acid, isotridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid) and eicosanoic acid. The acids mentioned may be of natural or synthetic origin. The parent acids of the carboxylate anions may also be mixtures of the acids mentioned.

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However, preference is given to the relatively long chain radical R occurring in the carboxylate anion RCOO⁻ or in the fatty acid RCOOH being a mono- or polyunsaturated C₇- to C₂₃ radical, in particular a mono- or polyunsaturated C₁₁- to C₂₁-, in particular C₁₅- to C₁₉-alkenyl group which may additionally bear hydroxyl groups. These unsaturated radicals are preferably linear. Examples of monounsaturated fatty acids include palmitoleic acid, oleic acid and erucic acid. In the case of polyunsaturated alkenyl groups, these preferably contain two or three double bonds. Examples of parent carboxylic acids include elaidic acid, ricinoleic acid, linoleic acid and linolenic acid. Particularly good results are obtained with oleic acid. The parent carboxylic acids of the carboxylate anions may also be mixtures of such unsaturated carboxylic acids with each other and also with the abovementioned saturated carboxylic acids. Examples of such mixtures include tall oil, tall oil fatty acid and rapeseed oil fatty acid. The unsaturated carboxylic acids mentioned and the mixtures mentioned are generally of natural origin.

The alkylene group A in compounds of the formula II is preferably derived from appropriate alkylene oxides such as ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide and cis- or trans-2,3-butylene oxide. However, it may also be 1,3-propylene, 1,4-butylene, 1,6-hexylene or 1,8-octylene. A may likewise be a mixture of different groups mentioned. Particular preference for A is given to ethylene, 1,2-propylene or 1,2-butylene groups.

The variable Z is in particular C₁- to C₄-alkylene groups such as methylene, 1,2-propylene, 1,2-butylene, 1,3-butylene or 2,3-butylene, C₅- to C₆-cycloalkylene groups such as 1,3-cyclopentylidene or 1,3- or 1,4-cyclohexylidene, or C₆- to C₈-arylene or -arylalkylene groups such as 1,3- or 1,4-phenylene, 2-methyl-1,4-phenylene or 1,3- or 1,4-bismethylenephenylene.

However, the variable Z preferably represents polymethylene groups of the formula -(CH₂)_n- where n = 2 to 8, in particular where n = 2 to 6, i.e. in particular 1,2-ethylene, 1,3-propylene,

1,4-butylene, 1,5-pentylene and 1,6-hexylene, but in addition also 1,7-heptylene and 1,8-octylene.

When the variable m is 0, the parent cationic components of the
 5 fatty acid salts used according to the invention are generally, depending on the sum (Σ) of all variables x^1 , x^2 and x^3 , mixtures of mono-, di- and/or trialkanolamines or pure trialkanolamines. Examples of such alkanolamines include monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine,
 10 diisopropanolamine, triisopropanolamine and also their corresponding mixtures. Within this group, the oleic acid salt of triethanolamine [$(x^1+x^2+x^3) = 3$; A = ethylene] is of particular interest.

15 However, preference is given to the variable m being the number 1 or 2. When $m = 1$, the parent molecules are partially and/or completely alkoxyated alkylenediamines such as 1,2-ethylenediamine, 1,3-propylenediamine or 1,4-butylenediamine. When $m = 2$, the parent molecules are usually partially and/or
 20 completely alkoxyated dialkylenetriamines such as di(1,2-ethylene)triamine, di(1,3-propylene)triamine or di(1,4-butylene)triamine. Within this group, the bis-oleic acid salts of N,N,N',N'-tetrakis(2'-hydroxyethyl)-1,2-ethylenediamine ($\Sigma x = 4$) and
 25 N,N,N',N'-tetrakis(2'-hydroxypropyl)-1,2-ethylene-diamine ($\Sigma x = 4$) and also the tris-oleic acid salts of di(1,2-ethylene)triamine reacted with from 4 to 5 mol of ethylene oxide or 1,2-propylene oxide are of particular interest.

30 However, it is also possible that higher homologs of the alkylenediamines and dialkylenetriamines mentioned, for example triethylenetetramine ($m = 3$), tetraethylenepentamine ($m = 4$) or pentaethylenehexamine ($m = 5$), may be the parent amine components for the fatty acid salts used according to the invention.

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In a preferred embodiment, the number x , i.e. the sum of x^1 , x^2 , x^3 and x^4 (Σx), of alkylene oxide units (OA) introduced per amine molecule is dependent upon the number of N-H bonds in the parent amine and may correspond to the number of N-H bonds ($\Sigma x = m+3$).
 40 However, it is also possible for more or fewer OA units to be incorporated. In the case of greater than stoichiometric incorporation, a preferred upper limit is a threefold alkoxylation per N-H bond [300% of $(m+3)$] with regard to the properties of the resulting fatty acid salts. In the case of less
 45 than stoichiometric incorporation, a preferred lower limit is an average 50% alkoxylation [50% of $(m+3)$]; in this case, there are

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usually mixtures of species having differing degrees of alkoxylation.

In a particularly preferred embodiment, the sum (Σ) of all 5 variables x has a value of from 75% to 125% of $(m+3)$.

The fatty acid salts of the general formula II can typically be prepared easily by alkoxyating the parent amines by customary methods and subsequently neutralizing with the fatty acids of the 10 formula RCOOH.

When C₂- to C₄-alkylene oxides are used, the alkoxylation for the introduction of the first alkylene oxide unit into the N-H bond is advantageously carried out in the presence of small amounts of 15 water (usually from 0.5 to 5% by weight, based on the amount of amine used) without catalyst at temperatures of from 80 to 140°C and, for the introduction of further alkylene oxide units, with the exclusion of water in the presence of basic catalysts such as alkali metal hydroxides, e.g. sodium or potassium hydroxide, at 20 temperatures of from 100 to 150°C.

The neutralization is generally effected by heating the alkoxyated amine obtained in this way with the appropriate stoichiometric or slightly less than stoichiometric amount (i.e. 25 from 90 to 100%, in particular from 95 to 100%, of theory) of fatty acid to temperatures of from 30 to 100°C, in particular from 40 to 80°C, for a period of from 15 minutes to 10 hours, in particular from 30 minutes to 5 hours. The neutralization reaction should be conducted in such a way that no carboxylic 30 ester fractions occur in the product. In many cases, both the alkoxyated amine and the fatty acid may be used as liquids, which makes the reaction to the corresponding fatty acid salt particularly simple. The sequence of addition of alkoxyated amine and fatty acid is uncritical, i.e. either the alkoxyated 35 amine may be initially charged and the fatty acid added or the fatty acid may be initially charged and the alkoxyated amine added.

However, it is also possible in principle to add the alkoxyated 40 amine and the fatty acid as individual components to the additive concentrates or to the mineral oil products and to allow the salt formation to take place there.

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Other useful components B for the additive mixtures according to the invention are long-chain carboxylic acids, esters thereof or mixtures of substances which comprise at least one of these components.

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For the purpose of the present invention, long-chain carboxylic acids encompass saturated and unsaturated mono- or polycarboxylic acids having from 4 to 50 carbon atoms, preferably from 8 to 24 carbon atoms. When the carboxylic acids are present in dimerized

10 form, the carbon number is correspondingly doubled.

Polycarboxylic acids according to the invention preferably comprise from 2 to 4 carboxyl groups. Unsaturated carboxylic acids according to the invention comprise one or more, preferably one, two or three, in particular noncumulated, double bonds.

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Preferred examples of saturated or unsaturated long-chain monocarboxylic acids are the saturated or unsaturated C₈-C₂₄-monocarboxylic acids specified in connection with the above definition for the compound of the formula II.

20

Examples of suitable polycarboxylic acids include saturated and unsaturated dicarboxylic acids, for example the dimerized variant of oleic acid.

25 The carboxylic acids used may be of natural or synthetic origin. They may be used as a pure substance or as a substance mixture which comprises one or more of these carboxylic acids, optionally together with further substances. A nonlimiting example is that of tall oil fatty acid mixtures. These typically comprise a

30 mixture of saturated, monounsaturated and polyunsaturated C₁₈-carboxylic acids and varying proportions of a hydrolyzable resin. Suitable products are described, for example, in WO-A-98/04656, which is incorporated herein by way of reference.

35 The long-chain carboxylic esters which can be used according to the invention can be prepared in a conventional manner by reacting the above long-chain carboxylic acids with mono- or polyhydric alcohols.

40 The alcohols present in the esters according to the invention are preferably derived from straight-chain or branched C₁- to C₂₀-alkanes and bear from 1 to 8, for example from 1 to 4, hydroxyl groups. Cyclic alcohols having from 6 to 12 carbon atoms can likewise be used.

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Preferred acyclic mono- or polyhydric alcohols comprise from 2 to 12, for example from 2 to 5, carbon atoms, are straight-chain or branched and have from 1 to 4 hydroxyl groups. Nonlimiting examples are monohydric alcohols such as methanol, ethanol and n-
5 and isopropanol, and polyhydric alcohols such as glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, mannitol, inositol, glucose and fructose. The hydrocarbyl radical of the alcohols which can be used according to the invention may optionally contain one or more heteroatoms such as oxygen,
10 sulfur, nitrogen or phosphorus, in the carbon chain.

When polyhydric alcohols are used, these may be present in the esters according to the invention in partly or fully esterified form. Preference is given to mono- and diester esters.

15

Nonlimiting examples of esters which can be used are methyl esters of the above saturated or unsaturated monocarboxylic acids, and also the corresponding esterification products of naturally occurring fatty acids or fatty acid mixtures.

20 Particular examples include mono- or diesters, for example glycerol monooleate, glycerol dioleate and glycerol monostearate.

In the additive mixture according to the invention, component A and component B are used in a weight ratio of preferably from
25 1:200 to 1:10, more preferably from 1:100 to 1:10 and in particular from 1:50 to 1:10.

The present invention further provides the use of the additive mixture according to the invention for additizing fuel
30 compositions, in particular for improving the antifoam performance of a fuel composition.

Useful fuels are gasoline fuels and middle distillates, such as diesel fuels, heating oil or kerosene, although preference is
35 given to diesel fuels.

The diesel fuels are, for example, crude oil raffinates which typically have a boiling range of from 100 to 400°C. These are usually distillates having a 95% point of up to 360°C or even
40 higher. However, these may also be "Ultra Low sulfur Diesel" or "City Diesel", characterized by a maximum 95% point of, for example, 345°C and a maximum sulfur content of, for example, 0.005% by weight or by 95% point of, for example, 285°C and a maximum sulfur content of 0.001% by weight. In addition to the
45 diesel fuels obtainable by refining, those obtainable by coal gasification or gas liquefaction ("gas to liquid" (GTL) fuels)

are also suitable. Mixtures of the abovementioned diesel fuels with renewable fuels, such as biodiesel, are also suitable.

Particular preference is given to using the additive mixture
5 according to the invention for additizing diesel fuels having low sulfur contents, i.e. having a sulfur content of less than 0.05% by weight, preferably of less than 0.02% by weight, in particular of less than 0.005% by weight and especially of less than 0.001% by weight, of sulfur.

10

The present invention also provides a fuel composition comprising a majority of a hydrocarbon fuel and an effective amount of the additive mixture according to the invention and optionally at least one further additive. With regard to suitable fuels, the
15 same applies as was stated previously.

The additive mixture according to the invention is preferably present in the fuel in an amount of from 1 to 1000 ppm by weight, more preferably from 20 to 300 ppm by weight and in particular
20 from 50 to 150 ppm by weight, based on the total amount of the additized fuel.

The present invention further provides an additive concentrate comprising the additive mixture according to the invention, at
25 least one diluent and also optionally at least one further additive.

Examples of useful diluents include the fractions obtained in crude oil processing, such as kerosene, naphtha or brightstock.
30 In addition, aromatic and aliphatic hydrocarbons and alkoxyalkanols are suitable. In the case of middle distillates, in particular in the case of diesel fuels, preferably used diluents are naphtha, kerosene, diesel fuels, aromatic hydrocarbons such as Solvent Naphtha heavy, Solvesso® or
35 Shellsol®, and also mixtures of these solvents and diluents.

The additive mixture according to the invention is present in the concentrate in a concentration of from 0.1 to 80% by weight, more preferably from 0.1 to 60% by weight and in particular from 15 to
40 50% by weight, based on the total weight of the concentrate.

Useful additives which may be present in the fuel or concentrate according to the invention in addition to the additive mixtures according to the invention, in particular for diesel fuels,
45 include detergents, corrosion inhibitors, dehazers, demulsifiers, other customary antifoams, antioxidants, metal deactivators, multifunctional stabilizers, cetane number improvers, combustion

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improvers, dyes, markers, solubilizers, antistats, lubricity improvers, additives which improve the cold properties such as flow improvers ("MDFI"), paraffin dispersants ("WASA") and the combination of the two last-mentioned additives ("WAFI"). Useful
 5 additives are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry (1990) Vol. A 16, p. 719 ff., which is incorporated herein by way of reference.

The customary antifoams include the polysiloxanes mentioned at
 10 the outset, acylated polyamines and their mixtures with different N-acyl compounds such as polyalkenylsuccinamides.

The synergistically effective combination of components A and B in the additive mixture according to the invention leads to a
 15 distinct improvement in the antifoam performance of fuels additized by it compared to prior art additives.

The examples which follow are intended to illustrate the invention, without restricting it.

20

Examples

The tests described hereinbelow were carried out with the following fuels:

- diesel fuel to DIN EN 590 having a sulfur content of 48 ppm:

25 Diesel I

- diesel fuel to DIN EN 590 having a sulfur content of 15 ppm (ULSD): diesel II

- diesel fuel to DIN EN 590 having a sulfur content of 4 ppm (MK1): diesel III

30 - blend of 5% of biodiesel in 95% of diesel I: blend I

- blend of 8% of ethanol in 91% of diesel I (1% stabilizer package): blend II

- gas to liquid fuel: GTL

- blend of 20% of GTL in 80% of diesel I: blend III

35

The lubricity improvers used were the following products:

Lubricity I: Product prepared according to Example 1

40 Lubricity II: Tall oil fatty acid mixture obtainable under the trade name Kerocom LA 99 from BASF AG

Lubricity III: Fatty acid ester mixture using glycerol monooleate as the main component.

45

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An antifoam used is a polysiloxane derivative which is customary on the market and referred to by the term *antifoam*.

Example 1: Synthesis of a lubricity improver (*Lubricity I*)

5

58.4 g (0.2 mol) of

N,N,N',N'-tetrakis(2'-hydroxypropyl)-1,2-ethylenediamine

(obtained from 1,2-ethylenediamine and 4 mol of propylene oxide in the presence of 3% by weight of water based on the amount of

10 amine used) was heated to 60-80°C and admixed with 110.4 g (0.4 mol) of oleic acid within 2 hours with stirring. The pH did not fall below 7. Finally, the stirring was continued for another 2 hours. The product obtained had an N-titer of 2.39 mmol/g.

15 Example 2: Tests for determining the antifoam performance

The determination of the antifoam performance was carried out in accordance with the BNPe test according to Standard NF M 07-075.

20 The additized fuels or blends were obtained by adding the abovementioned combinations of 5 mg/kg of *antifoam* and 120 mg/kg of lubricity improver *Lubricity I* to III in each case. In the table which follows, the values determined in each case for the foam volume and the foam degradation time in dry fuels are

25 listed.

	Fuel	Antifoam	Lubricity improver	Foam volume [ml]	Foam degradation time [s]
30	Diesel I	0	0	120	63
	Diesel II	0	0	115	46
	Diesel III	0	0	110	35
	Blend I	0	0	110	42
35	Blend II	0	0	100	40
	GTL	0	0	115	57
	Blend III	0	0	115	60
	Diesel I	Antifoam	0	60	14
	Diesel II	Antifoam	0	55	15
40	Diesel III	Antifoam	0	50	13
	Blend I	Antifoam	0	60	16
	Blend II	Antifoam	0	50	12
	GTL	Antifoam	0	60	14
	Blend III	Antifoam	0	60	14
45	Diesel I	Antifoam	Lubricity I	40	5
	Diesel II	Antifoam	Lubricity I	35	6
	Diesel III	Antifoam	Lubricity I	30	4

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Fuel	Antifoam	Lubricity improver	Foam volume [ml]	Foam degradation time [s]
5 Blend I	Antifoam	Lubricity I	35	6
Blend II	Antifoam	Lubricity I	30	4
GTL	Antifoam	Lubricity I	35	5
Blend III	Antifoam	Lubricity I	35	5
10 Diesel I	Antifoam	Lubricity II	55	11
Diesel II	Antifoam	Lubricity II	55	12
Diesel III	Antifoam	Lubricity II	60	10
Diesel I	Antifoam	Lubricity III	60	13
Diesel II	Antifoam	Lubricity III	55	16
Diesel III	Antifoam	Lubricity III	50	13

15 The lubricity improvers alone had no positive influence on the foaming action.

The combinations of *antifoam* and *Lubricity I, II and III* according to the invention compared to the action of *antifoam* alone showed a distinctly improved antifoam performance at the same lubricity-improving action. Particularly outstanding results are achieved when lubricity improvers of the lubricity I type are used.

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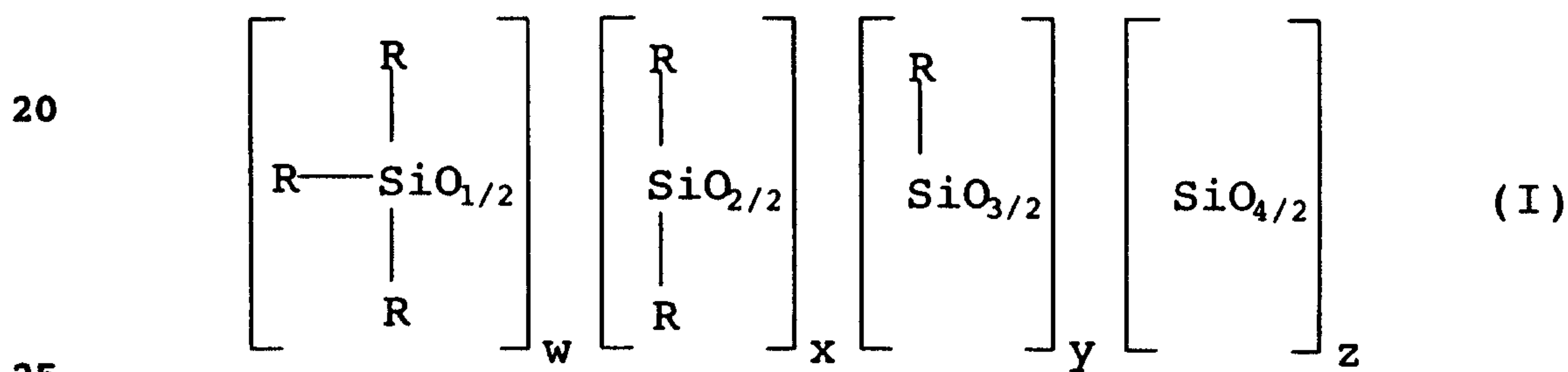
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We claim:

- 5 1. An additive mixture consisting of a component A and a component B, where
- i) component A is at least one polysiloxane antifoam and
- 10 ii) component B is at least one partially or completely neutralized fatty acid, a long-chain carboxylic acid, an ester of such a carboxylic acid or a mixture comprising at least one of these compounds.
- 15 2. An additive mixture as claimed in claim 1, which comprises, as component A, at least one polysiloxane of the general formula I



where

the R radicals are each independently an R¹, R², R³, R⁴ or R⁵ radical where

- 30
- R¹ is an aromatic or saturated aliphatic hydrocarbon radical,
- R² is an organic polyol,
- 35 R³ is a polyether radical,
- R⁴ is a phenol radical,
- R⁵ is an R² radical, except that some or all of the hydroxyl groups have been converted to diesters, diethers, acetals and/or ketals,

40 $w = 2 + y + 2z$,

y and z are each independently a number from 0 to 2 where the sum of y and z corresponds to a number from 0 to 2 and $w + x + y + z = \text{from } 20 \text{ to } 60$.

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3. An additive mixture as claimed in claim 2, wherein, in component A,
 R^1 is C_1 - C_{24} -alkyl, C_3 - C_{24} -cycloalkyl, C_4 - C_{24} -alkylcycloalkyl, C_6 - C_{10} -aryl or C_7 - C_{18} -arylalkyl,

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R^2 is a saturated or unsaturated, branched or unbranched, aliphatic hydrocarbon radical which is substituted by at least two hydroxyl groups and is optionally interrupted by one or more oxygen atoms,

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R^3 is a polyether radical which contains at least 50% by weight of copolymerized ethylene oxide units and has a molecular weight of up to 1500,

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the quotient of the number of R^1 groups to the number of R^2 groups (R^1/R^2) is from 3 to 19 and

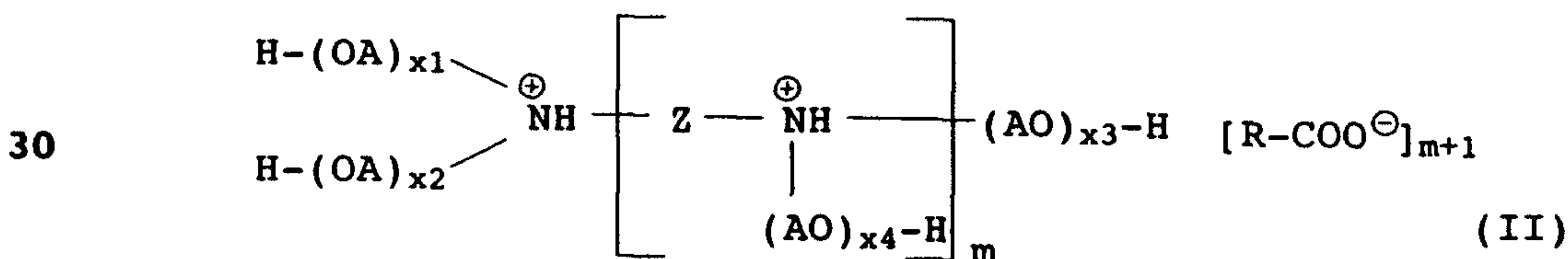
the quotient of the sum of the number of R^3 , R^4 and R^5 groups to the number of R^2 groups $[(R^3+R^4+R^5)/R^2]$ is from 0 to 2.

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4. An additive mixture as claimed in any of the preceding claims, wherein component B comprises at least one fatty acid neutralized by at least one amine.

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5. An additive mixture as claimed in claim 4, wherein component B comprises at least one fatty acid salt of the formula II



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where

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R is C_7 - C_{23} -alkyl or mono- or polyunsaturated C_7 - C_{23} -alkenyl, each of which are optionally substituted by one or more hydroxyl groups;

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A is C_2 - C_8 -alkylene;

Z is C_1 - C_8 -alkylene, C_3 - C_8 -cycloalkylene, C_6 - C_{12} -arylene or C_7 - C_{20} -arylalkylene;

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m is a number from 0 to 5; and

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x^1 , x^2 , x^3 and x^4 are each independently a number from 0 to 24,

5 and optionally at least one further fatty acid RCOOH where R is as defined above.

6. An additive mixture as claimed in any of claims 1 to 3, wherein component B comprises at least one saturated or unsaturated mono- or polycarboxylic acid having from 4 to 50
10 carbon atoms or at least one ester of such a carboxylic acid with a mono- or polyhydric alcohol having from 1 to 20 carbon atoms and from 1 to 8 hydroxyl groups.
7. An additive mixture as claimed in any of the preceding
15 claims, wherein component A and component B are present in a weight ratio of from 1:200 to 1:10.
8. The use of an additive mixture as defined in any of the preceding claims for additizing fuel compositions.
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9. The use as claimed in claim 8 for improving the antifoam performance of a fuel composition.
10. The use of at least one partially or completely neutralized
25 fatty acid, a long-chain carboxylic acid, an ester of such a carboxylic acid or a mixture comprising at least one of these compounds for improving the antifoam action of a polysiloxane antifoam in fuel compositions.
- 30 11. A fuel composition comprising a majority of a hydrocarbon fuel and an effective amount of an additive mixture as defined in any of claims 1 to 7.
12. A fuel composition comprising a majority of a hydrocarbon
35 fuel and an effective amount of an additive mixture, which comprises
- i) as component A, at least one polysiloxane antifoam and
 - 40 ii) as component B, at least one fatty acid partially or completely neutralized by at least one amine,
- and optionally at least one further additive.

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13. A fuel composition as claimed in claim 11 or 12 or the use as claimed in any of claims 8 to 10, wherein the fuel is diesel fuel, heating oil or kerosene.
- 5 14. A fuel composition or the use as claimed in claim 13, wherein the diesel fuel is one obtainable by refining, coal gasification or gas liquefaction, or a mixture thereof with renewable fuels.
- 10 15. An additive concentrate comprising an additive mixture as defined in any of claims 1 to 7 and at least one diluent.

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