

Amine mixture

Description

5 The present invention relates to an amine mixture comprising, as predominant components,

(A) 0.1 to 99.9 parts by weight of a polyisobuteneamine of the general formula (I)



in which

15 the PIB moiety is a skeleton derived from 0% to 20% by weight of n-butene-comprising polybutene or polyisobutene or a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene,

20 the variables R^2 and R^3 , which may be the same or different, may be hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with the nitrogen atom to which they are bonded form a ring in which further heteroatoms may be present, and

25 the variable x may assume the value of 0 or 1, the variable m the value of 0 or 1 and the variable n the value of 1, 2 or 3,

where the polyisobuteneamine (I) has a number-average molecular weight of 300 to 2500,

30 and

(B) 0.1 to 99.9 parts by weight of an aliphatic amine of the general formula (II)



in which the variable R^4 denotes a mixture of

40 (i) 0% to 20% by weight of linear or branched C_{13} -alkyl radicals,

(ii) 50% to 99% by weight of linear or branched C_{17} -alkyl radicals,

(iii) 1% to 50% by weight of linear or branched C_{21} -alkyl radicals and

- (iv) 0% to 20% by weight of linear or branched alkyl radicals having 25 and/or 29 and/or 33 carbon atoms,

5 where the sum total of the percentages by weight of all the radicals (i) to (iv) for R^4 is 100% by weight,

and the variables R^2 and R^3 are each as defined above,

10 where the sum total of the parts by weight of components (A) and (B) is 100 parts by weight,

and preferably obtainable by hydroformylation and subsequent reductive amination of a mixture of appropriate parts by weight of the parent polybutene or polyisobutene and a
15 mixture of C_{12} to C_{32} olefins originally underlying the variable R^4 with ammonia or an amine of the formula HNR^2R^3 .

The present invention further relates to a fuel composition comprising this amine mixture, and to the use of this amine mixture for cleaning and keeping clean intake
20 valves in port injection gasoline engines and injection nozzles in direct injection gasoline engines.

Mixtures of polyisobuteneamines and aliphatic amines are known from the prior art. They are especially used as components in gasoline fuel additive formulations. For
25 instance, WO 03/076554 (1) teaches the use of hydrocarbylamines having a number-average molecular weight of 140 to 255 for the hydrocarbyl radical; for example linear alkylamines of the formula $CH_3(CH_2)_nNH_2$ with $n = 9$ to 17, together with nitrogen-containing fuel detergents such as polyisobutenemonoamines in unleaded gasoline fuels, in order to reduce deposits in the injection nozzles of direct injection internal
30 combustion engines. However, the hydrocarbylamines and the nitrogen-containing fuel detergents are prepared separately and only combined in the additive formulation.

WO 2009/074608 (2) describes fuel additive formulations comprising polyisobutenylmonoamines or polyisobutenylpolyamines as nitrogen-containing
35 dispersants, synthetic or mineral carrier oils and amines such as di-n-tridecylamine, hydrogenated tallowamine or cocoamine. Amines of this kind serve as boosters in valve cleaning and keeping valves clean in the internal combustion engines. However, the nitrogen-containing dispersants and the amines are prepared separately and only combined in the additive formulation.

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Longer-chain amines of this kind are typically prepared from the corresponding alcohols by a complex amination step with ammonia or low molecular weight amines before they can be incorporated into the fuel additive formulations. If amines of this

kind are to be used as part of fuel additive formulations, one object is to provide a simpler and less expensive synthesis for these amines.

International patent application PCT/EP2012/072498 (3) describes an amine mixture of polyisobuteneamine and linear or branched C₆- to C₆₀₀-alkylamines, which is recommended for cleaning and keeping clean intake valves and injection nozzles in gasoline engines. Individual C₆- to C₆₀₀-alkylamine compounds for use here include heptadecylamine and heneicosylamine.

It has now been found that an amine mixture comprising not only polyisobuteneamine but also a mixture of alkylamines comprising a linear or branched C₁₇-alkyl radical, alkylamines comprising a linear or branched C₂₁-alkyl radical, and optionally alkylamines comprising a linear or branched C₁₃- and/or C₂₅- and/or C₂₉- and/or C₃₃-alkyl radical is suitable in a particularly advantageous manner for cleaning and keeping clean intake valves and injection nozzles in gasoline engines.

The present invention thus provides the amine mixture defined at the outset, referred to hereinafter as "amine mixture of the invention".

Preferably, the amine mixture of the invention is prepared by hydroformylation and subsequent reductive amination of a mixture of appropriate parts by weight of the parent polybutene or polyisobutene and a mixture of C₁₂ to C₃₂ olefins originally underlying the variable R⁴ with ammonia or an amine of the formula HNR²R³. The hydroformylation reaction proceeds from the olefins and forms, as intermediates, the corresponding oxo products which are generally aldehyde/alcohol mixtures.

The amine mixture of the invention preferably comprises 50 to 95 parts by weight, especially 70 to 90 parts by weight, of component (A) and 5 to 50 parts by weight, especially 10 to 30 parts by weight, of component (B), where the sum total of the parts by weight of components (A) and (B) is 100 parts by weight.

If the PIB moiety is a skeleton derived from 0% to 20% by weight, especially 0% to 5% by weight and particularly 0% to 1% by weight of n-butene-comprising polybutene or preferably polyisobutene, in the case that x = 0, the hydroxyl groups (-OH) and/or the amino groups (-NR²R³) according to the general formula (I) are generally on the carbon atoms of the last isobutene unit in the polymer chain, usually on the α-, β- and/or γ-carbon atom.

In the case that x = 1, PIB is a polybutyl or polyisobutyl radical (referred to hereinafter as R¹) which is derived from isobutene and 0% to 20% by weight, especially 0% to 5% by weight and particularly 0% to 1% by weight of n-butene and bears only one amino group (-NR²R³) on the additional methylene moiety (n = 1). This aminomethylene

moiety is typically predominantly on the α - and β -carbon atom or preferably predominantly on the α -carbon atom of the last isobutene unit in the polymer chain.

EP-A 244 616 (4) describes the preparation of polybutyl- and polyisobutylamines of the formula $R^1\text{-CH}_2\text{-NR}^2\text{R}^3$ by hydroformylation of polybutene or polyisobutene and subsequent reductive amination of the oxo product formed with ammonia or amines HNR^2R^3 . The meaning of the variables R^2 and R^3 for the formulae that determine the present invention are encompassed by the definitions of the variables R^2 and R^3 as defined by (4).

The variables R^2 and R^3 for the present invention are the same or different and are preferably each hydrogen or linear or branched C_1 - to C_{13} -alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, sec-pentyl, isopentyl, tert-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, 2-propylheptyl, n-undecyl, n-dodecyl, n-tridecyl or isotridecyl, or unsubstituted or alkyl-substituted amino groups and/or hydroxyl group-comprising radicals such as $-\text{CH}_2\text{-CH}_2\text{-NH}_2$, $-\text{CH}_2\text{-CH}_2\text{-N}(\text{CH}_3)_2$, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-N}(\text{CH}_3)_2$, $[-\text{CH}_2\text{-CH}_2\text{-NH-}]_p\text{-CH}_2\text{-CH}_2\text{-NH}_2$ in which p is an integer from 1 to 7, especially from 1 to 3, $-\text{CH}_2\text{-CH}_2\text{-OH}$, $-\text{CH}(\text{CH}_3)\text{-CH}_2\text{-OH}$ or $[-\text{CH}_2\text{-CH}_2\text{-O-}]_q\text{-CH}_2\text{-CH}_2\text{-OH}$ in which q is an integer from 1 to 30.

Examples of suitable amines HNR^2R^3 are methylamine, dimethylamine, ethylamine, diethylamine, ethylmethylamine, n-propylamine, di-n-propylamine, isopropylamine, diisopropylamine, n-butylamine, di-n-butylamine, n-butylmethylamine, isobutylamine, diisobutylamine, tert-butylamine, di-tert-butylamine, 2-ethylhexylamine, 2-propylheptylamine, 1,2-ethylenediamine, dimethylaminopropylamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. More preferably, both variables R^2 and R^3 are hydrogen, which means that the amine HNR^2R^3 denotes ammonia.

The variable R^1 is preferably a polybutyl or polyisobutyl radical which is derived from isobutene and 0% to 20% by weight, especially 0% to 5% by weight and particularly 0% to 1% by weight, of n-butene and comprises 20 to 176, especially 36 to 104 and particularly 60 to 88 carbon atoms.

The polyisobuteneamine of the general formula (I) preferably has a number-average molecular weight of 500 to 1500, especially 900 to 1300.

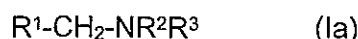
The hydroformylation of the mixture of polybutene or polyisobutene and C_{12} - to C_{32} -olefins is generally conducted – according to the teaching of document (4) – with carbon monoxide/hydrogen in the presence of a suitable rhodium or cobalt catalyst at temperatures between 80 and 200°C and pressures of up to 600 bar.

The reductive amination of the mixture of the oxo product formed in the hydroformylation of polybutene or polyisobutene and the C₁₂- to C₃₂-olefins, which is generally an aldehyde/alcohol mixture, is typically conducted as described in document (4). This reaction with ammonia or amines of the formula NHR²R³ in a hydrogen atmosphere is generally undertaken at temperatures of 80 to 200°C and pressures of up to 600 bar, preferably 80 to 300 bar. It is appropriate to work in the presence of a standard hydrogenation catalyst, for example Raney nickel or Raney cobalt. The additional use of organic solvents that are inert under the reaction conditions, such as hydrocarbons, may be advantageous, as will be explained further down.

The oxo product component formed from polybutene or polyisobutene which is produced in the mixture in the prior stage is typically – according to the teaching of (4) – prepared by hydroformylation of polybutene or polyisobutene preferably having a high content of terminal double bonds (vinylidene double bonds), especially at least 70% and particularly at least 80% of vinylidene double bonds. In the case of preparation of the oxo product, rather than the high-reactivity polybutene or polyisobutene described, it is also possible to proceed from medium-reactivity or conventional polybutene or polyisobutene having a content of less than 70% of terminal double bonds (vinylidene double bonds), for example 10% to less than 70% or 50% to less than 70%.

A preferred embodiment of the present invention is an amine mixture comprising, as predominant components,

- (A) 0.1 to 99.9, especially 50 to 95 and particularly 70 to 90 parts by weight of a polyisobuteneamine of the general formula (Ia)



in which the variable R¹ is a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene and the variables R² and R³ are each as defined above,

and

- (B) 0.1 to 99.9, especially 5 to 50 and particularly 10 to 30 parts by weight of an aliphatic amine of the general formula (II).

Component (B) is a mixture of aliphatic amines comprising mid- to longer-chain linear or branched alkyl radicals in the range from 13 to 33 carbon atoms each differing by 4 carbon atoms. The main constituent is an aliphatic amine having a linear or branched C₁₇-alkyl radical. In general, an aliphatic amine having a linear or branched C₂₁-alkyl

radical is the second most common in the mixture. Preference is given here to branched alkyl radicals.

The variable R^4 in the aliphatic amine (II) for component (B) is a mixture of

- 5 (i) 0% to 20% by weight, especially 1% to 15% by weight and particularly 2% to 10% by weight of linear or preferably branched, especially lightly branched, C_{13} -alkyl radicals,
- 10 (ii) 50% to 99% by weight, especially 55% to 85% by weight and particularly 60% to 75% by weight of linear or preferably branched, especially lightly branched, C_{17} -alkyl radicals,
- 15 (iii) 1% to 50% by weight, especially 5% to 35% by weight and particularly 10% to 25% by weight of linear or preferably branched, especially lightly branched, C_{21} -alkyl radicals and
- 20 (iv) 0% to 20% by weight, especially 1% to 12% by weight and particularly 2% to 8% by weight of linear or preferably branched, especially lightly branched, alkyl radicals having 25 and/or 29 and/or 33 carbon atoms,

where the sum total of the percentages by weight of all the radicals (i) to (iv) for R^4 is 100% by weight.

- 25 For every member of groups (i) to (iv), at least one species in each case should be present in the amine mixture (B); however, it is also possible in each case for there to be a plurality of preferably isomeric species having a C_{17} -alkyl radical and/or a C_{21} -alkyl radical and also, if present, having a C_{13} -, C_{25} -, C_{29} - and/or C_{33} -alkyl radical.
- 30 In a preferred embodiment, the amine mixture of the invention comprises, as component (B), an aliphatic amine of the formula R^4-NH_2 in which the variable R^4 denotes a mixture of lightly branched alkyl radicals (i) to (iv) based on a hydroformylated C_{12} to C_{32} olefin mixture obtained in the oligomerization of C_4 hydrocarbon streams. In that case, the radicals of groups (i) to (iv) are trimeric to
- 35 heptameric butene structures each extended by one methylene group by hydroformylation.

- 40 "Lightly branched" shall be understood here to mean a mean degree of branching according to the iso index of 1.2 to 3.0, especially of 1.7 to 2.5. In general, the degree of branching in the C_{12} to C_{32} olefin mixture originally used is the same as after the hydroformylation of this mixture and after the reductive amination of the hydroformylated mixture.

Oligomerization of C₄ hydrocarbon streams shall especially be understood here to mean the homogeneously or heterogeneously catalyzed oligomerization of technical C₄ streams composed of 10% to 90% by weight of butane, 10% to 90% by weight of linear butenes (butene-1, cis- and trans-butene-2) and 1% to 5% by weight of isobutene, for example of raffinate II, to essentially unbranched octenes and dodecenes. A heterogeneous catalyst which is typical for this purpose comprises nickel. The oligomerization is usually conducted at temperatures of 30 to 280°C and pressures of 10 to 300 bar. Oligomerization reactions of this kind are described, for example, in WO 99/25668 (5).

Typically, the C₁₂ to C₃₂ olefin mixtures used have densities in the range from 0.75 to 0.85 g/cm³ and boiling ranges in the range from 220 to 350°C.

In the reductive amination, it is possible to additionally use organic solvents that are inert under the reaction conditions. The additional use of such inert organic solvents is appropriate especially when the proportion of component (B) is relatively low compared to the proportion of component (A). Suitable inert organic solvents of this kind are particularly aliphatic, cycloaliphatic and aromatic hydrocarbons such as alkanes, e.g. n-pentane, n-hexane or n-heptane, or technical alkane mixtures, cyclohexane, cycloheptane, cyclooctane, toluene, xylenes, naphthalenes or tetrahydronaphthalene ("tetralin"); in addition, it is also possible to use, for example, ethers such as diethyl ether, tert-butyl methyl ether or tetrahydrofuran. It is advantageous to use technical hydrocarbon mixtures commercially available, for example, under the Solvent Naphtha or Solvesso® names. The solvents mentioned can usually be used in the preliminary stage of hydroformylation.

Particular preference is given to using, as organic solvents that are inert under the reaction conditions, either

- L1) at least one n- or iso-C₁₀ to C₁₄ paraffin or a mixture of such paraffins or
- L2) at least one C₁₀ to C₁₄ naphthene or a mixture of such naphthenes or
- a mixture of L1) and L2) in a volume mixing ratio of 10:90 to 90:10.

The use of inert organic solvents of this kind has been described for the preparation of polyisobutene in WO 2004/087808 (6).

Suitable paraffinic solvents L1) are, for example, the products sold under the Mihagol® name by BP Deutschland, e.g. Mihagol M having a proportion of n-paraffins having a chain length of 11 to 13 carbon atoms of at least 99% by weight.

Suitable naphthenic solvents L2) are, for example, the products sold under the LIAV® name by Fortum Oil and Gas, e.g. Nessoil LIAV 230 having predominant proportions of saturated cyclic aliphatics having a carbon number of 10 to 14.

In the case of additional use of organic solvents that are inert under the reaction conditions, especially also in the case of additional use of L1), L2) or mixtures of L1) and L2) in a volume mixing ratio of 10:90 to 90:10, these are generally used in a weight ratio of amine mixture of (A) and (B) to solvent of 50 to 99:1 to 50, especially 55 to 90:5 to 10 and particularly 60 to 75:25 to 40.

The present invention also provides a process for preparing an amine mixture comprising, as predominant components,

(A) 0.1 to 99.9 parts by weight of a polyisobuteneamine of the general formula (I)



in which

the PIB moiety is a skeleton derived from 0% to 20% by weight of n-butene-comprising polybutene or polyisobutene or a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene,

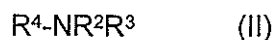
the variables R^2 and R^3 , which may be the same or different, may be hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with the nitrogen atom to which they are bonded form a ring in which further heteroatoms may be present, and

the variable x may assume the value of 0 or 1, the variable m the value of 0 or 1 and the variable n the value of 1, 2 or 3,

where the polyisobuteneamine (I) has a number-average molecular weight of 300 to 2500,

and

(B) 0.1 to 99.9 parts by weight of an aliphatic amine of the general formula (II)



in which the variable R^4 denotes a mixture of

(i) 0% to 20% by weight of linear or branched C_{13} -alkyl radicals,

(ii) 50% to 99% by weight of linear or branched C₁₇-alkyl radicals,

(iii) 1% to 50% by weight of linear or branched C₂₁-alkyl radicals and

5 (iv) 0% to 20% by weight of linear or branched alkyl radicals having 25 and/or 29 and/or 33 carbon atoms,

where the sum total of the percentages by weight of all the radicals (i) to (iv) for R⁴ is 100% by weight,

10

and the variables R² and R³ are each as defined above,

where the sum total of the parts by weight of components (A) and (B) is 100 parts by weight,

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which comprises hydroformylating a mixture of appropriate parts by weight of the parent polybutene or polyisobutene and a mixture of C₁₂ to C₃₂ olefins originally underlying the variable R⁴ and then reductively aminating the product with ammonia or an amine of the formula HNR²R³.

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The amine mixture of the invention, composed of the predominant components (A) and (B), is outstandingly suitable as a fuel additive, especially for cleaning and keeping clean intake valves in port injection gasoline engines and injection nozzles in direct injection gasoline engines. Therefore, a fuel composition, especially a gasoline fuel
25 composition, comprising the amine mixture of the invention also forms part of the subject matter of the present invention. Preferably, such a fuel composition has an alcohol content, especially a content of C₁- to C₄-alkanols such as methanol or especially ethanol, of 0% to 100% by volume, more preferably of more than 0% to 90% by volume, especially of 5% to 90% by volume and particularly of 50% to 85% by
30 volume, and is suitable for operation of gasoline engines.

The present invention further provides for the use of the amine mixture of the invention, composed of the predominant components (A) and (B), for cleaning and keeping clean intake valves in port injection gasoline engines and injection nozzles in direct injection
35 gasoline engines.

The amine mixture of the invention displays very good detergency in the operation of an internal combustion engine with a fuel composition comprising it. In addition to this effect in the cleaning and keeping-clean of the intake valves, the injection nozzles and
40 the whole intake system of the engine, it additionally exerts a series of further advantageous effects as fuel additives: They reduce valve sticking and/or they improve the compatibility of the detergents with carrier oils, particularly polyether and polyetheramine carrier oils, especially at low temperatures, and/or they improve

compatibility in fuel compositions comprising a mineral fuel component and C₁-C₄-alkanols. In addition, fuel additive concentrates comprising the amine mixture of the invention are sufficiently mobile (meaning that they have a sufficiently low viscosity), and so bottlenecks in the production of such fuel additive concentrates owing to time-limited flow volumes through the apparatuses and lines – even in the case of additional use of inert solvents or diluents – are avoided; the comparatively low viscosity also has an unforeseeable favorable effect on efficacy as fuel additives.

In connection with the present invention, a fuel composition is preferably understood to mean a gasoline fuel composition. Useful gasoline fuels include all commercial gasoline fuel compositions. One typical representative which shall be mentioned here is the Eurosuper base fuel to EN 228, which is customary on the market. In addition, gasoline fuel compositions of the specification according to WO 00/47698 are also possible fields of use for the amine mixture of the invention.

One example is a gasoline fuel composition having an aromatics content of not more than 60% by volume, for example not more than 42% by volume, and a sulfur content of not more than 2000, for example a maximum of 150, ppm by weight.

The aromatics content of the gasoline fuel composition is preferably not more than 50% by volume, especially 1% to 45% by volume and particularly 5% to 40% by volume. The sulfur content of the gasoline fuel is preferably not more than 500 ppm by weight, especially 0.5 to 150 ppm by weight and particularly 1 to 100 ppm by weight.

In addition, the gasoline fuel compositions may have, for example, an olefin content of up to 50% by volume, preferably of 0.1% to 21% by volume and especially of 2% to 18% by volume, a benzene content of up to 5% by volume, preferably 0% to 1.0% by volume and especially 0.05% to 0.9% by volume, and/or an oxygen content of up to 47.5% by weight, for example 0.1% to 2.7% by weight or, for example, 2.7% by weight to 47.5% by weight (for gasoline fuel compositions comprising predominantly lower alcohols).

Particular mention may also be made by way of example of those gasoline fuel compositions simultaneously having an aromatics content of not more than 38% by volume, an olefin content of not more than 21% by volume, a sulfur content of not more than 50 ppm by weight, a benzene content of not more than 1.0% by volume and an oxygen content of 0.1% to 47.5% by weight.

The summer vapor pressure of the gasoline fuel composition is typically not more than 70 kPa, especially 60 kPa (in each case at 37°C).

The RON of the gasoline fuel composition is generally 75 to 105. A typical range for the corresponding MON is 65 to 95.

The specifications mentioned are determined by customary methods (DIN EN 228).

5 In addition to use in gasoline fuels, however, use of the amine mixture of the invention in other fuel types, for example diesel fuels, kerosene or turbine fuels, is also possible in principle. Use in lubricant compositions is also conceivable.

10 Useful C₁- to C₄-alkanols include methanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol and especially ethanol; other possible lower alcohol fuel components are mixtures of the C₁- to C₄-alkanols mentioned. As well as the lower alcohol fuel components mentioned, the fuel composition of the invention may also comprise ethers having 5 or more carbon atoms, for example methyl tert-butyl ether, in the molecule in an amount of up to 30% by volume.

15 The amine mixture of the invention may be added to the fuel composition to be additized alone or in a mixture with further active additive components (coadditives).

20 Examples of such coadditives may be additives having detergent action and/or having valve seat wear-inhibiting action other than component (A) of the amine mixture of the invention (referred to collectively hereinafter as detergent additives). Such a detergent additive generally has at least one hydrophobic hydrocarbon radical having a number-average molecular weight (M_n) of 85 to 20 000 and at least one polar moiety selected from:

- 25 (a) mono- or polyamino groups having up to 6 nitrogen atoms, where at least one nitrogen atom has basic properties;
- (b) nitro groups, optionally in combination with hydroxyl groups;
- 30 (c) hydroxyl groups in combination with mono- or polyamino groups, where at least one nitrogen atom has basic properties;
- (d) carboxyl groups or the alkali metal or alkaline earth metal salts thereof;
- 35 (e) sulfonic acid groups or the alkali metal or alkaline earth metal salts thereof;
- (f) polyoxy-C₂- to C₄-alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups;
- 40 (g) carboxylic ester groups;

- (h) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or
- (i) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

The hydrophobic hydrocarbon radical in the above detergent additives which ensures sufficient solubility in the fuel has a number-average molecular weight (M_n) of 85 to 20 000, especially of 113 to 10 000 and particularly of 300 to 5000. Useful typical hydrophobic hydrocarbon radicals, especially in conjunction with the polar moieties (a), (c), (h) and (i), include the polypropenyl, polybutenyl and polyisobutenyl radicals each having $M_n = 300$ to 5000, especially 500 to 2500 and particularly 700 to 2300.

The amine mixture of the invention can additionally be combined with further customary components and additives. Mention should be made here, for example, of mineral-based or synthetic-based carrier oils without any marked detergency.

Suitable mineral carrier oils are the fractions obtained in crude oil processing, such as kerosene or naphtha, brightstock or base oils having viscosities, for example, from the SN 500 to 2000 class; but also aromatic hydrocarbons, paraffinic hydrocarbons and alkoxyalkanols. Likewise useful is a fraction which is obtained in the refining of mineral oil and is known as "hydrocrack oil" (vacuum distillate cut having a boiling range of from about 360 to 500°C, obtainable from natural mineral oil which has been catalytically hydrogenated under high pressure and isomerized and also deparaffinized). Likewise suitable are mixtures of the abovementioned mineral carrier oils.

Examples of usable synthetic carrier oils may be selected from polyolefins (polyalphaolefins or polyinternalolefins), (poly)esters, (poly)alkoxylates, polyethers, aliphatic polyetheramines, alkylphenol-started polyethers, alkylphenol-started polyetheramines and carboxylic esters of long-chain alkanols. Examples of particularly suitable synthetic carrier oils are alcohol-started polyethers having about 5 to 35 C₃- to C₆-alkylene oxide units, usually selected from propylene oxide, n-butylene oxide and isobutylene oxide units or mixtures thereof. Nonlimiting examples of starter alcohols suitable for the purpose are long-chain alkanols or phenols substituted by long-chain alkyl where the long-chain alkyl radical is especially a straight-chain or branched C₆- to C₁₈-alkyl radical. Preferred examples of these include tridecanol and nonylphenol.

Further customary fuel additives are corrosion inhibitors, for example based on ammonium salts of organic carboxylic acids, said salts having a tendency to form films, or on cyclic heteroaromatics in the case of nonferrous metal corrosion protection; antioxidants or stabilizers, for example based on amines such as p-phenylenediamine, dicyclohexylamine or derivatives thereof, or on phenols such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid; demulsifiers; antistats; metallocenes

such as ferrocene; methylcyclopentadienylmanganese tricarbonyl; lubricity improvers (lubricity additives) such as particular fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl) fatty amines, hydroxyacetamides or castor oil; and dyes (markers). It is optionally also possible to add amines to lower the pH of the fuel.

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The components or additives mentioned can be added to the fuel composition individually or as a preprepared concentrate (additive package) together with the amine mixture of the invention.

- 10 The amine mixture of the invention is added to the fuel composition – either separately or in the form of a concentrate with other components or additives and optionally customary solvents and diluents – generally in an amount of 5 to 5000, preferably 10 to 2000, especially 25 to 1000 and particularly 50 to 500 ppm by weight, in each case reported as the pure substance content (i.e. without solvents and diluents and other
- 15 components or additives) and based on the total amount of the fuel composition. The other components or additives mentioned are, if desired, added in amounts customary for the purpose.

- The present invention is to be elucidated by the example which follows, which should
- 20 not be interpreted in a restrictive manner.

Example

- 500 g of polyisobutene having a number-average molecular weight of 1000 and a
- 25 proportion of vinylidene double bonds of more than 70%, 70 g of a mixture of oligomeric butenes composed of 6.8% by weight of trimer, 69.8% by weight of tetramer, 17.2% by weight of pentamer, 5.2% by weight of hexamer and 1.0% by weight of heptamer (mean degree of branching according to iso index: 2.1; density: 0.81 g/cm³), obtained by distilling a fraction of boiling range from 241 to 328°C
- 30 (standard pressure) out of the reaction mixture of a heterogeneously nickel-catalyzed oligomerization of a technical C₄ carbon stream, 200 g of a solvent mixture of 80% by weight of Mihagol® M and 20% by weight of Nessel LIAV® 230, and 2.8 g of cobalt carbonyl catalyst were heated at 185°C in a 2.5 liter autoclave stirred by reciprocating stirrer at 280 bar carbon monoxide/hydrogen for 5 hours. Thereafter, the mixture was
- 35 cooled to room temperature, the catalyst was removed with 400 ml of 10% by weight acetic acid and the mixture was washed to neutrality. The resulting oxo product was treated at 180°C under a hydrogen pressure of 200 bar together with 1.0 liter of ammonia and 100 g of Raney cobalt in a 5 liter roll autoclave. After the mixture had been cooled down, the Raney cobalt catalyst was filtered off, excess ammonia was
- 40 evaporated off and the solvent was distilled off.

Claims

1. An amine mixture comprising, as predominant components,

5 (A) 0.1 to 99.9 parts by weight of a polyisobuteneamine of the general formula (I)



in which

10

the PIB moiety is a skeleton derived from 0% to 20% by weight of n-butene-comprising polybutene or polyisobutene or a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene,

15

the variables R^2 and R^3 , which may be the same or different, may be hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with the nitrogen atom to which they are bonded form a ring in which further heteroatoms may be present,

20

and

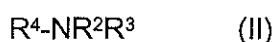
the variable x may assume the value of 0 or 1, the variable m the value of 0 or 1 and the variable n the value of 1, 2 or 3,

25

where the polyisobuteneamine (I) has a number-average molecular weight of 300 to 2500,

and

30 (B) 0.1 to 99.9 parts by weight of an aliphatic amine of the general formula (II)



in which the variable R^4 denotes a mixture of

35

(i) 0% to 20% by weight of linear or branched C_{13} -alkyl radicals,

(ii) 50% to 99% by weight of linear or branched C_{17} -alkyl radicals,

40

(iii) 1% to 50% by weight of linear or branched C_{21} -alkyl radicals and

(iv) 0% to 20% by weight of linear or branched alkyl radicals having 25

and/or 29 and/or 33 carbon atoms,

where the sum total of the percentages by weight of all the radicals (i) to (iv) for R⁴ is 100% by weight,

5

and the variables R² and R³ are each as defined above,

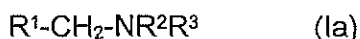
where the sum total of the parts by weight of components (A) and (B) is 100 parts by weight.

10

2. The amine mixture according to claim 1, comprising, as predominant components,

(A) 0.1 to 99.9 parts by weight of a polyisobuteneamine of the general formula (Ia)

15



in which the variable R¹ is a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene and the variables R² and R³ are each as defined above,

20

and

(B) 0.1 to 99.9 parts by weight of an aliphatic amine of the general formula (II).

25 3. The amine mixture according to claim 1 or 2, comprising, as component (A), a polyisobuteneamine of the formula (I) having a mean molecular weight of 500 to 1500.

30 4. The amine mixture according to claims 1 to 3, comprising, as component (B), an aliphatic amine of the formula R⁴-NH₂ in which the variable R⁴ denotes a mixture of lightly branched alkyl radicals (i) to (iv) based on a hydroformylated C₁₂ to C₃₂ olefin mixture obtained in the oligomerization of C₄ hydrocarbon streams.

35 5. The amine mixture according to claims 1 to 4, comprising 50 to 95 parts by weight, especially 70 to 90 parts by weight, of component (A) and 5 to 50 parts by weight, especially 10 to 30 parts by weight, of component (B), where the sum total of the parts by weight of components (A) and (B) is 100 parts by weight.

40 6. An amine mixture comprising, as predominant components,

(A) 0.1 to 99.9 parts by weight of a polyisobuteneamine of the general formula (I)



in which

the PIB moiety is a skeleton derived from 0% to 20% by weight of n-butene-comprising polybutene or polyisobutene or a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene,

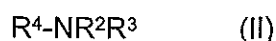
the variables R^2 and R^3 , which may be the same or different, may be hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with the nitrogen atom to which they are bonded form a ring in which further heteroatoms may be present, and

the variable x may assume the value of 0 or 1, the variable m the value of 0 or 1 and the variable n the value of 1, 2 or 3,

where the polyisobuteneamine (I) has a number-average molecular weight of 300 to 2500,

and

(B) 0.1 to 99.9 parts by weight of an aliphatic amine of the general formula (II)



in which the variable R^4 denotes a mixture of

- (i) 0% to 20% by weight of linear or branched C_{13} -alkyl radicals,
- (ii) 50% to 99% by weight of linear or branched C_{17} -alkyl radicals,
- (iii) 1% to 50% by weight of linear or branched C_{21} -alkyl radicals and
- (iv) 0% to 20% by weight of linear or branched alkyl radicals having 25 and/or 29 and/or 33 carbon atoms,

where the sum total of the percentages by weight of all the radicals (i) to (iv) for R^4 is 100% by weight,

and the variables R^2 and R^3 are each as defined above,

where the sum total of the parts by weight of components (A) and (B) is 100 parts by weight,

obtainable by hydroformylation and subsequent reductive amination of a mixture of appropriate parts by weight of the parent polybutene or polyisobutene and a mixture of C_{12} to C_{32} olefins originally underlying the variable R^4 with ammonia or an amine of the formula HNR^2R^3 .

7. A process for preparing an amine mixture comprising, as predominant components,

(A) 0.1 to 99.9 parts by weight of a polyisobuteneamine of the general formula (I)



in which

the PIB moiety is a skeleton derived from 0% to 20% by weight of n-butene-comprising polybutene or polyisobutene or a polybutyl or polyisobutyl radical derived from isobutene and 0% to 20% by weight of n-butene,

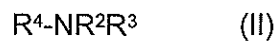
the variables R^2 and R^3 , which may be the same or different, may be hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with the nitrogen atom to which they are bonded form a ring in which further heteroatoms may be present, and

the variable x may assume the value of 0 or 1, the variable m the value of 0 or 1 and the variable n the value of 1, 2 or 3,

where the polyisobuteneamine (I) has a number-average molecular weight of 300 to 2500,

and

(B) 0.1 to 99.9 parts by weight of an aliphatic amine of the general formula (II)



in which the variable R^4 denotes a mixture of

- 5 (i) 0% to 20% by weight of linear or branched C_{13} -alkyl radicals,
- (ii) 50% to 99% by weight of linear or branched C_{17} -alkyl radicals,
- 10 (iii) 1% to 50% by weight of linear or branched C_{21} -alkyl radicals and
- (iv) 0% to 20% by weight of linear or branched alkyl radicals having 25
and/or 29 and/or 33 carbon atoms,

15 where the sum total of the percentages by weight of all the radicals (i) to
(iv) for R^4 is 100% by weight,

and the variables R^2 and R^3 are each as defined above,

20 where the sum total of the parts by weight of components (A) and (B) is 100 parts
by weight,

25 which comprises hydroformylating a mixture of appropriate parts by weight of the
parent polybutene or polyisobutene and a mixture of C_{12} to C_{32} olefins originally
underlying the variable R^4 and then reductively aminating the product with ammonia
or an amine of the formula HNR^2R^3 .

8. A fuel composition comprising an amine mixture according to claims 1 to 7.
9. The fuel composition according to claim 8, having an alcohol content of 0% to
30 100% by volume and being suitable for operation of gasoline engines.
10. The use of an amine mixture according to claims 1 to 7 for cleaning and keeping
clean intake valves in port injection gasoline engines and injection nozzles in direct
injection gasoline engines.