

Amine mixture

Description

5 The present invention relates to an amine mixture which comprises, 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 structure derived from polybutene or polyisobutene comprising 0 to 20% by weight of n-butene 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, are each 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,

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

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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 linear or branched $\text{C}_6\text{-}$ to $\text{C}_{600}\text{-}$ alkyl radical

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

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where the sum of the parts by weight of components (A) and (B) adds up to 100 parts by weight,

and which is obtainable by reductive amination of a mixture of corresponding parts by

weight

- 5 (i) of the oxo process product formed in the hydroformylation of polybutene or polyisobutene, and of an alkanol of the formula $R^4\text{-OH}$ or
- (ii) of the epoxide formed in the epoxidation of polybutene or polyisobutene, and of an alkanol of the formula $R^4\text{-OH}$ or
- 10 (iii) of the nitro compound which is formed in the reaction of polybutene or polyisobutene with nitrogen oxides or mixtures of nitrogen oxides and oxygen, and of an alkanol of the formula $R^4\text{-OH}$

with ammonia or an amine of the formula HNR^2R^3 .

- 15 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 valves in gasoline engines with intake pipe injection, and of injection nozzles in direct injection gasoline engines.
- 20 Mixtures of polyisobuteneamines and aliphatic amines are known from the prior art. They are used particularly as components in gasoline fuel additive formulations. For instance, WO 03/076554 (1) teaches using hydrocarbylamines having a number-average molecular weight of 140 to 255 for the hydrocarbyl radical, for example linear alkylamines of the formula $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$ where $n = 9$ to 17, together with nitrogen-
- 25 containing fuel detergents such as polyisobutenemonoamines in unleaded gasoline fuels, in order to reduce the level of deposits in the injection nozzles of direct injection internal combustion engines. The hydrocarbylamines and the nitrogen-containing fuel detergents are, however, prepared separately and not combined until in the additive formulation.
- 30 WO 2009/074608 (2) describes fuel additive formulations which comprise polyisobutenylmonoamines or polyisobutenylpolyamines as nitrogen-containing dispersants, synthetic or mineral carrier oils and amines such as di-n-tridecylamine, hydrogenated tallow fat amine or coconut amine. Such amines serve as boosters in
- 35 valve cleaning and keeping valves clean in the internal combustion engines. The nitrogen-containing dispersants and the amines are, however, prepared separately and are not combined until in the additive formulation.
- 40 Such comparatively long-chain amines are typically prepared from the corresponding alcohols by a complex amination step with ammonia or low molecular weight amines before they can be processed into the fuel additive formulations. If such amines are to be used as part of fuel additive formulations, the problem arises of providing a simpler and less expensive synthesis for these amines.

Accordingly, it has been found that the synthesis of such comparatively long-chain amines can be combined with the preparation of polyisobuteneamines in a single reaction step, and as a result of which the separate step for amination of the alcohols to the comparatively long-chain amines can be dispensed with.

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The present invention thus provides the amine mixture defined at the outset by the mode of preparation thereof, referred to hereinafter as "inventive amine mixture".

10 Since some of the amine mixtures described as substance mixtures - irrespective of their mode of preparation - constitute novel substances, such amine mixtures also form part of the subject matter of the present invention likewise referred to hereinafter as "inventive amine mixture".

15 The inventive amine mixture comprises preferably 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 of parts by weight of components (A) and (B) adds up to 100 parts by weight.

20 If the PIB moiety is a structure derived from polybutene or preferably polyisobutene comprising 0 to 20% by weight, especially 0 to 5% by weight and in particular 0 to 1% by weight of n-butene, 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. Such PIB moieties occur principally in the case of embodiments (ii) and
25 (iii).

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 in particular 0 to 1% by weight of n-butene, and which bears only one
30 amino group (-NR²R³) on the additional methylene moiety ($n = 1$). This aminomethylene moiety is typically present predominantly on the α and β carbon atoms, or preferably predominantly on the α carbon atom of the last isobutene unit in the polymer chain. Such polybutyl or polyisobutyl radicals R¹ occur principally in the case of embodiment (i).

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EP-A 244 616 (3) describes the preparation of polybutyl- and polyisobutylamines of the formula R¹-CH₂-NR²R³ by hydroformylation of polybutene or polyisobutene and subsequent reductive amination of the resulting oxo process product with ammonia or amines, in analogy to embodiment (i). The definitions of the variables R² and R³ for the
40 formulae which determine the present invention are encompassed by the definitions of variables R² and R³ as defined by (3).

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 radicals comprising unsubstituted or alkyl-substituted amino groups and/or hydroxyl groups, such as $-CH_2-CH_2-NH_2$, $-CH_2-CH_2-N(CH_3)_2$, $-CH_2-CH_2-CH_2-NH_2$, $-CH_2-CH_2-CH_2-N(CH_3)_2$, $[-CH_2-CH_2-NH-]_p-CH_2-CH_2-NH_2$ in which p is an integer from 1 to 7, especially from 1 to 3, $-CH_2-CH_2-OH$, $-CH(CH_3)-CH_2-OH$ or $[-CH_2-CH_2-O-]_q-CH_2-CH_2-OH$, 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, di-isopropylamine, n-butylamine, di-n-butylamine, n-butylmethylamine, isobutylamine, di-isobutylamine, 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, and thus the amine HNR^2R^3 is preferably 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 in particular 0 to 1% by weight of n-butene, and which comprises 20 to 176, especially 36 to 104 and in particular 60 to 88 carbon atoms.

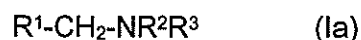
The polyisobuteneamine of the general formula (I) preferably has a number-average molecular weight of 500 to 1500, especially of 900 to 1300.

According to embodiment (i), the reductive amination of the mixture of the oxo process product which is formed in the hydroformylation of polybutene or polyisobutene and is generally an aldehyde/alcohol mixture, and the alcohol of the formula R^4-OH , is typically performed as described in document (3). This reaction with ammonia or amines of the formula NHR^2R^3 in a hydrogen atmosphere is undertaken generally at temperatures of 80 to 200°C and pressures up to 600 bar, preferably 80 to 300 bar. It is appropriate to work in the presence of a customary hydrogenation catalyst, for example Raney nickel or Raney cobalt. The additional use of organic solvents which are inert under the reaction conditions, such as hydrocarbons, may be advantageous. The oxo process product obtained in a preliminary stage is typically – according to the teaching of (3) – prepared by hydroformylating the polybutene or polyisobutene, which preferably has a high content of terminal double bonds (vinylidene double bonds), especially at least 70% and in particular at least 80% vinylidene double bonds, 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. Instead of

proceeding from the high-reactivity polybutene or polyisobutene described, the preparation of the oxo process product can, however, also proceed from moderate-reactivity or conventional polybutene or polyisobutene having a content of less than 70% terminal double bonds (vinylidene double bonds), for example 10 to less than 70% or 50 to less than 70%.

A preferred embodiment for the present invention is an amine mixture which comprises, as predominant components,

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



- 15 in which the variable R^1 is a polybutyl or polyisobutyl radical derived from isobutene and 0 to 20% by weight of n-butene and the variables R^2 and R^3 are each as defined above,

and

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

and is obtainable by reductive amination of a mixture of corresponding parts by weight of the oxo process product formed in the hydroformylation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH with ammonia or an amine of the formula HNR^2R^3 .

According to embodiment (ii), the reductive amination of the mixture of the epoxide formed in the epoxidation of polybutene or polyisobutene and the alcohol of the formula R^4-OH is typically performed as described in EP-A 476 485 (4). This reaction with ammonia or amines of the formula NHR^2R^3 is generally performed in bulk or in a solvent which is inert under the reaction conditions, for example dissolved in aliphatic or aromatic hydrocarbons or in ethers, at elevated temperature, for example at reflux of the particular solvent, or in a pressure vessel. For a rapid and complete conversion, the presence of usually stoichiometric amounts of water as a catalyst has been found to be advantageous. Catalysts to be used in addition may be acidic or Lewis-acidic compounds such as p-toluenesulfonic acid, carboxylic acids, boron trifluoride etherates, titanates or stannates. The epoxide obtained in a preliminary stage is typically - according to the teaching of (4) - obtained by means of customary epoxidizing agents such as m-chloroperbenzoic acid, tert-butyl hydroperoxide or peracetic acid, optionally in the presence of transition metal catalysts such as salts or complexes of molybdenum or tungsten, from polybutene or polyisobutene preferably

having a high content of terminal double bonds (vinylidene double bonds), especially at least 70% and in particular at least 80% vinylidene double bonds. Instead of proceeding from the high-reactivity polybutene or polyisobutene described, the preparation of the epoxide can also proceed from moderate-reactivity or conventional polybutene or polyisobutene having a content of less than 70% terminal double bonds (vinylidene double bonds), for example 10 to less than 70% or 50 to less than 70%.

Typically, in embodiment (ii), polyisobuteneamines (I) are obtained with one hydroxyl group (-OH) ($m = 1$) and with one amino group (-NR²R³) ($n = 1$) and without a methylene moiety ($x = 0$).

According to embodiment (iii), the reductive amination of the mixture of the nitro compound and the alcohol of the formula R⁴-OH formed in the reaction of polybutene or polyisobutene with nitrogen oxides or mixtures of nitrogen oxides and oxygen is typically performed as described in WO 96/03367 (5), WO 96/03479 (6) and WO 97/03946 (7). This reaction with ammonia or amines of the formula NHR²R³ is generally performed as a catalytic hydrogenation with hydrogen in the presence of hydrogenation catalysts, for example noble metal catalysts such as platinum, palladium, ruthenium, rhodium, osmium or iridium, Raney catalysts such as nickel, cobalt, iron or copper, mixed catalysts comprising, for example, nickel, zirconium, copper and molybdenum, or copper, chromium, zinc and barium, or oxidic or sulfidic hydrogenation catalysts, at elevated temperatures, especially at 150 to 220°C, and hydrogen pressures of 1 to 300 bar, and typically in solvents such as hydrocarbons or ethers. The nitro compound obtained in a preliminary stage is typically – according to the teachings of documents (5) to (7) – obtained by reaction of nitrogen oxides, especially nitrogen monoxide, nitrogen dioxide, dinitrogen trioxide and/or dinitrogen tetroxide, or mixtures of these nitrogen oxides and oxygen, with polybutene or polyisobutene preferably having a high content of terminal double bonds (vinylidene double bonds), especially at least 70% and in particular at least 80% vinylidene double bonds, at ambient pressure or under pressure, batchwise or continuously, and advantageously in inert organic solvents such as hydrocarbons, halohydrocarbons, ethers, amides and/or esters. Instead of proceeding from the high-reactivity polybutene or polyisobutene described, the preparation of the nitro compound can, however, also proceed from moderate-reactivity or conventional polybutene or polyisobutene having a content of less than 70% terminal double bonds (vinylidene double bonds), for example 10 to less than 70% or 50 to less than 70%.

Typically, in the embodiment (iii), polyisobuteneamines (I) are obtained with no or one hydroxyl group (-OH) ($m = 0$ or 1) and with one to three amino groups (-NR²R³) ($n = 1$ to 3) and without a methylene moiety ($x = 0$).

In a preferred embodiment, the variable R⁴ in the alkanols of the formula R⁴-OH and in the resulting aliphatic amines of component (B) denotes a linear or branched C₇- to

C₂₃-alkyl radical or a polybutyl or polyisobutyl radical having 24 to 600 carbon atoms. Particular preference is given to a branched C₇- to C₁₃-alkyl radical or a polybutyl or polyisobutyl radical having 24 to 600, especially 28 to 176 and in particular 32 to 88 carbon atoms. Examples of linear or branched C₆- to C₆₀₀-alkyl radicals, especially

5 linear or branched C₇- to C₂₃-alkyl radicals, and polybutyl or polyisobutyl radicals having 24 to 600 carbon atoms are n-hexyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2-ethylbutyl, n-heptyl, 1-methylhexyl, 2-methylhexyl, 3-methylhexyl, 4-methylhexyl, 5-methylhexyl, 1,1-dimethylpentyl, 1,2-dimethylpentyl, 2,2-dimethylpentyl, 2,3-dimethylpentyl, 2,4-

10 dimethylpentyl, 2,5-dimethylpentyl, 2-diethylpentyl, 3-diethylpentyl, n-octyl, 1-methylheptyl, 2-methylheptyl, 3-methylheptyl, 4-methylheptyl, 5-methylheptyl, 6-methylheptyl, 1,1-dimethylhexyl, 1,2-dimethylhexyl, 2,2-dimethylhexyl, 2,3-

15 dimethylhexyl, 2,4-dimethylhexyl, 2,5-dimethylhexyl, 2,6-dimethylhexyl, 2-ethylhexyl, 3-ethylhexyl, 4-ethylhexyl, n-nonyl, isononyl, n-decyl, 1-propylheptyl, 2-propylheptyl, 3-propylheptyl, n-undecyl, n-dodecyl, n-tridecyl, isotridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, cyclohexyl, 2-methylcyclohexyl, 3-methylcyclohexyl, 4-methylcyclohexyl, 2,3-

20 dimethylcyclohexyl, 2,4-dimethylcyclohexyl, 2,5-dimethylcyclohexyl, 2,6-dimethylcyclohexyl, 3,4-dimethylcyclohexyl, 3,5-dimethylcyclohexyl, 2-ethylcyclohexyl, 3-ethylcyclohexyl, 4-ethylcyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl and a polyisobutyl radical having 24, 28, 32, 36, 40, 44, 48, 52, 56, 60, 64, 68, 72, 76, 80, 84 or 88 carbon atoms.

It will be appreciated that it is also possible to use mixtures of different alkanols of the

25 formula R⁴-OH, the result of which is naturally a corresponding mixture of different aliphatic amines (II) in component (B).

In the reductive amination according to embodiment (i), (ii) and/or (iii), it is possible also to use organic solvents which are inert under the reaction conditions. The additional

30 use of such inert organic solvents is appropriate especially when the proportion of component (B) is relatively low with respect to the proportion of component (A). Suitable inert organic solvents of this kind are in particular aliphatic, cycloaliphatic and aromatic hydrocarbons, such as alkanes, e.g. n-pentane, n-hexane or n-heptane, or technical grade alkane mixtures, cyclohexane, cycloheptane, cyclooctane, toluene,

35 xylenes, naphthalenes or tetrahydronaphthalene ("tetralin"); in addition, however, it is also possible, for example, to use ethers such as diethyl ether, tert-butyl methyl ether or tetrahydrofuran. Advantageously, technical grade hydrocarbon mixtures commercially available, for example, under the Solvent Naphtha or Solvesso®

40 tradenames, are used. The solvents mentioned can usually already be added in the preliminary stages – i.e. in the hydroformylation in embodiment (i), in the epoxidation in embodiment (ii) and in the reaction with nitrogen oxides or nitrogen oxide/oxygen mixtures in embodiment (iii).

The organic solvent which is inert under the reaction conditions and is used with particular preference for embodiment (ii), (iii) and in particular for (i) is either

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

The use of such inert organic solvents is described for the preparation of polyisobutene in WO 2004/087808 (8).

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

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

20 In the case of additional use of organic solvents inert under the reaction conditions, especially also in the case of additional use of L1), L2) or mixtures of L1) and L2) in a mixture volume ratio of 10:90 to 90:10, they 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, in particular 60 to 75 : 25 to 40.

- 25 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

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

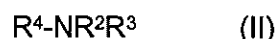
40 the variables R² and R³, which may be the same or different, are each hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with 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,

the polyisobuteneamine (I) having 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 linear or branched C_6 - to C_{800} -alkyl radical

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

where the sum of the parts by weight of components (A) and (B) adds up to 100 parts by weight, which comprises reductively aminating a mixture of corresponding parts by weight

- (i) of the oxo process product formed in the hydroformylation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH or
- (ii) of the epoxide formed in the epoxidation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH or
- (iii) of the nitro compound which is formed in the reaction of polybutene or polyisobutene with nitrogen oxides or mixtures of nitrogen oxides and oxygen, and of an alkanol of the formula R^4-OH

with ammonia or an amine of the formula HNR^2R^3 .

Since some of the amine mixtures described, as substance mixtures – irrespective of the mode of preparation thereof – are novel substances, the present invention also provides an amine mixture which comprises, 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 structure derived from polybutene or polyisobutene

comprising 0 to 20% by weight of n-butene or a polybutyl or polyisobutyl radical derived from isobutene and 0 to 20% by weight of n-butene,

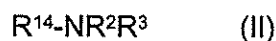
the variables R^2 and R^3 , which may be the same or different, are each hydrogen, aliphatic or aromatic hydrocarbyl radicals, primary or secondary, aromatic or aliphatic aminoalkylene radicals or polyaminoalkylene radicals, polyoxyalkylene radicals, heteroaryl or heterocyclyl radicals, or together with 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,

the polyisobuteneamine (I) having 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^{14} denotes a linear or branched C_6 - to C_9 -alkyl radical

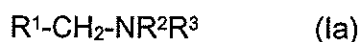
and the variables R^2 and R^3 are each as defined above,

where the sum of the parts by weight of components (A) and (B') adds up to 100 parts by weight.

Preferably, this amine mixture comprises, as component (B'), an aliphatic amine of the general formula (II) in which the variable R^{14} denotes a branched C_6 - to C_9 -alkyl radical and the variables R^2 and R^3 each denote hydrogen.

More preferably, this amine mixture comprises, as component (B'), an aliphatic amine of the general formula (II) in which the variable R^{14} denotes a 2-ethylhexyl radical and the variables R^2 and R^3 each denote hydrogen.

More particularly, this amine mixture comprises, as component (A), a polyisobuteneamine of the general formula (Ia)



in which the variable R^1 is a polybutyl or polyisobutyl radical which is derived from

isobutene and 0 to 20% by weight of n-butene and has a number-average molecular weight of 300 to 2500 and the variables R^2 and R^3 each denote hydrogen, and, as component (B'), an aliphatic amine of the general formula (II) in which the variable R^{14} denotes a 2-ethylhexyl radical and the variables R^2 and R^3 likewise each denote hydrogen.

The inventive amine mixture of predominant components (A) and (B), or (A) and (B'), is of excellent suitability as a fuel additive, especially for cleaning and keeping clean intake valves in gasoline engines with intake pipe injection, and of injection nozzles in direct injection gasoline engines. Therefore, the present invention also provides a fuel composition, especially a gasoline fuel composition, which comprises the inventive amine mixture. Preferably, such a fuel composition has an alcohol content, especially a content of C_1 - to C_4 -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 in particular of 50 to 85% by volume, and is suitable for operation of gasoline engines.

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

In the course of operation of an internal combustion engine with a fuel composition comprising the inventive amine mixture, it displays very good detergent action. In addition to this action in the cleaning and keeping clean of the intake valves, of the injection nozzles and of the entire intake system of the engine, it additionally exerts a series of further advantageous effects as a fuel additive: It reduces valve sticking and/or improves the compatibility of the detergents with carrier oils, in particular polyether and polyetheramine carrier oils, especially at low temperatures, and/or it improves compatibility in fuel compositions comprising a mineral fuel component and C_1 - C_4 -alkanols. In addition, fuel additive concentrates comprising the inventive amine mixture are sufficiently mobile (i.e. they have a sufficiently low viscosity) that capacity shortages in the course of production of such fuel additive concentrates due to limited flow rates 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 favourable effect on the mode of action as fuel additives.

In the context of the present invention, a fuel composition is preferably understood to mean a gasoline fuel composition. Useful gasoline fuels include all commercial gasoline fuel compositions. A typical representative specified here is the Eurosuper base fuel according 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 inventive amine mixture.

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 ppm by weight, for example not more than 150 ppm by weight.

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The aromatics content of the gasoline fuel composition is preferably not more than 50% by volume, especially 1 to 45% by volume and in particular 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 in particular 1 to 100 ppm by weight.

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In addition, the gasoline fuel composition may have, for example, an olefin content 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 to 47.5% by weight (for gasoline fuel compositions comprising predominantly lower alcohols).

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Another particular example is that of those gasoline fuel compositions which simultaneously have 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.

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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).

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

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

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

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Useful C₁- to C₄-alkanols include methanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol and especially ethanol; mixtures of the C₁-C₄-alkanols mentioned are also possible as lower alcohol fuel components. As well as the lower alcohol fuel components mentioned, the inventive fuel composition 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.

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The inventive amine mixture can be added to the fuel composition to be additized alone or in a mixture with further active additive components (coadditives).

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

- (a) mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties;
- (b) nitro groups, optionally in combination with hydroxyl groups;
- (c) hydroxyl groups in combination with mono- or polyamino groups, at least one nitrogen atom having basic properties;
- (d) carboxyl groups or the alkali metal or alkaline earth metal salts thereof;
- (e) sulfo 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;
- (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 hydrocarbyl 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, in particular of 300 to 5000. Useful typical hydrophobic hydrocarbyl radicals, especially in conjunction with the polar moieties (a), (c), (h) and (i), include the polypropenyl, polybutenyl and polyisobutenyl radical each having M_n = 300 to 5000, especially 500 to 2500, in particular 700 to 2300.

The inventive amine mixture can additionally be combined with further customary components and additives. Examples here include mineral-based or synthetic-based carrier oils without any marked detergent action.

Suitable mineral carrier oils are fractions obtained in mineral 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 usable is a fraction which is known as "hydrocrack oil" and is
5 obtained in the refining of mineral oil (vacuum distillate cut with a boiling range from about 360 to 500°C, obtainable from natural mineral oil which has been catalytically hydrogenated and isomerized under high pressure, and also deparaffinized). Likewise suitable are mixtures of the abovementioned mineral carrier oils.

10 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
15 C₆-alkylene oxide units, usually selected from propylene oxide, n-butylene oxide and isobutylene oxide units and mixtures thereof. Nonlimiting examples of starter alcohols suitable for this 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 thereof are tridecanol and nonylphenol.

20 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,
25 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
30 is optionally also possible to add amines to lower the pH of the fuel.

These components or additives can be added to the fuel composition individually or as a previously prepared concentrate (additive package) together with the inventive amine mixture.

35 The inventive amine mixture 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 in particular 50 to 500 ppm by weight, in each case specified
40 as the pure substance content (i.e. without solvents and diluents and other components or additives) and based on the total amount of the fuel composition. The other components and additives mentioned are, if desired, added in amounts customary therefor.

The present invention is to be illustrated by the example which follows, which should not be interpreted in a restrictive manner:

5 Example

500 g of polyisobutene having a number-average molecular weight of 1000 and a proportion of vinylidene double bonds of more than 70%, 200 g of a solvent mixture of 80% by weight of Mihagol® M and 20% by weight of Nessel LIAS® 230, and 2.8 g of
10 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 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
15 process product was treated at 180°C under a hydrogen pressure of 200 bar together with 75 g of 2-ethylhexanol, 1.0 liter of ammonia and 100 g of Raney cobalt in a 5 liter roller autoclave. After the mixture had been cooled, the Raney cobalt catalyst was filtered off, excess ammonia was evaporated off and the solvent was distilled off.

Claims

1. An amine mixture comprising, as predominant components,

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



10

in which

15

the PIB moiety is a structure derived from polybutene or polyisobutene comprising 0 to 20% by weight of n-butene 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, are each 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

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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,

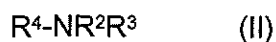
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the polyisobuteneamine (I) having a number-average molecular weight of 300 to 2500,

and

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

35



in which the variable R^4 denotes a linear or branched C_6 - to C_{600} -alkyl radical

40

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

where the sum of the parts by weight of components (A) and (B) adds up to 100 parts by weight,

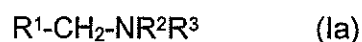
obtainable by reductive amination of a mixture of corresponding parts by weight

- 5 (i) of the oxo process product formed in the hydroformylation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH or
- (ii) of the epoxide formed in the epoxidation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH or
- 10 (iii) of the nitro compound which is formed in the reaction of polybutene or polyisobutene with nitrogen oxides or mixtures of nitrogen oxides and oxygen, and of an alkanol of the formula R^4-OH

with ammonia or an amine of the formula HNR^2R^3 .

- 15 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)



- 20 in which the variable R^1 is a polybutyl or polyisobutyl radical derived from isobutene and 0 to 20% by weight of n-butene and the variables R^2 and R^3 are each as defined above,

- 25 and

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

- 30 obtainable by reductive amination of a mixture of corresponding parts by weight of the oxo process product formed in the hydroformylation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH with ammonia or an amine of the formula HNR^2R^3 .

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

- 40 4. The amine mixture according to claims 1 to 3, comprising, as component (B), an aliphatic amine of the formula R^4-NH_2 in which the variable R^4 denotes a linear or branched C_7 - to C_{23} -alkyl radical or a polybutyl or polyisobutyl radical having 24 to 600 carbon atoms.

5. The amine mixture according to any of 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 of the parts by weight of components (A) and (B) adds up to 100 parts by weight.

5

6. 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)

10



in which

15

the PIB moiety is a structure derived from polybutene or polyisobutene comprising 0 to 20% by weight of n-butene 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, are each 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,

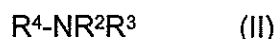
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the polyisobuteneamine (I) having a number-average molecular weight of 300 to 2500,

and

35

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



40

in which the variable R^4 denotes a linear or branched $\text{C}_6\text{-}$ to $\text{C}_{600}\text{-alkyl}$ radical

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

where the sum of the parts by weight of components (A) and (B) adds up to 100 parts by weight,

5 which comprises reductively aminating a mixture of corresponding parts by weight

- (i) of the oxo process product formed in the hydroformylation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH or
- 10 (ii) of the epoxide formed in the epoxidation of polybutene or polyisobutene, and of an alkanol of the formula R^4-OH or
- (iii) of the nitro compound which is formed in the reaction of polybutene or polyisobutene with nitrogen oxides or mixtures of nitrogen oxides and oxygen, and of an alkanol of the formula R^4-OH

15

with ammonia or an amine of the formula HNR^2R^3 .

7. An amine mixture comprising, as predominant components,

20

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



25

in which

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

30

the variables R^2 and R^3 , which may be the same or different, are each 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

35

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,

40

the polyisobuteneamine (I) having 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)

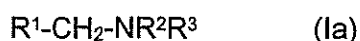


in which the variable R^{14} denotes a linear or branched C_6 - to C_9 -alkyl radical

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

where the sum of the parts by weight of components (A) and (B') adds up to 100 parts by weight.

8. The amine mixture according to claim 7, comprising, as component (B'), an aliphatic amine of the general formula (II) in which the variable R^{14} denotes a branched C_6 - to C_9 -alkyl radical and the variables R^2 and R^3 each denote hydrogen.
9. The amine mixture according to claim 8, comprising, as component (B'), an aliphatic amine of the general formula (II) in which the variable R^{14} denotes a 2-ethylhexyl radical and the variables R^2 and R^3 each denote hydrogen.
10. The amine mixture according to claim 9, comprising, as component (A), a polyisobuteneamine of the general formula (Ia)



in which the variable R^1 is a polybutyl or polyisobutyl radical which is derived from isobutene and 0 to 20% by weight of n-butene and has a number-average molecular weight of 300 to 2500 and the variables R^2 and R^3 each denote hydrogen, and, as component (B'), an aliphatic amine of the general formula (II) in which the variable R^{14} denotes a 2-ethylhexyl radical and the variables R^2 and R^3 likewise each denote hydrogen.

11. A fuel composition comprising an amine mixture according to claims 1 to 10.
12. The fuel composition according to claim 11, which has an alcohol content of 0 to 100% by volume and is suitable for operation of gasoline engines.
13. The use of an amine mixture according to claims 1 to 10 for cleaning and keeping clean intake valves in gasoline engines with intake pipe injection, and of injection nozzles in direct injection gasoline engines.