

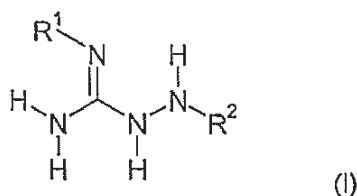
Use of the reaction product of a hydrocarbyl-substituted dicarboxylic acid and a nitrogen compound for reducing fuel consumption

Description

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The present invention relates to the use of the reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid whose hydrocarbyl radical has 8 to 250 carbon atoms, or the anhydride thereof, and (b) a nitrogen compound of the general formula I

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or a salt of the nitrogen compound I, where R¹ and R² are each independently hydrogen or a C₁- to C₂₀-hydrocarbyl radical,

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as an additive in a fuel for reducing fuel consumption in the operation of a spark-ignited internal combustion engine with this fuel or as an additive in a gasoline fuel for reduction of fuel consumption in the operation of a self-ignition internal combustion engine with this fuel.

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The present invention further relates to a fuel composition which comprises a gasoline fuel, the reaction product mentioned and at least one fuel additive with detergent action.

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The present invention further relates to an additive concentrate which comprises the reaction product mentioned and at least one fuel additive with detergent action.

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It is known that particular substances in the fuel reduce internal friction in the internal combustion engines, especially in gasoline engines, and thus help to save fuel. Such substances are also referred to as lubricity improvers, friction reducers or friction modifiers. Lubricity improvers customary on the market for gasoline fuels are usually condensation products of naturally occurring carboxylic acids such as fatty acids with polyols such as glycerol or with alkanolamines, for example glyceryl monooleate.

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A disadvantage of the prior art lubricity improvers mentioned is poor miscibility with other typically used fuel additives, especially with detergent additives such as polyisobuteneamines and/or carrier oils such as polyalkylene oxides. An important requirement in practice is that the component mixtures or additive concentrates provided are readily pumpable even at relatively low temperatures, especially at

outside winter temperatures of, for example, down to -20°C, and remain homogeneously stable over a prolonged period, i.e. no phase separation and/or precipitates may occur.

- 5 Typically, the miscibility problems outlined are avoided by adding relatively large amounts of mixtures of paraffinic or aromatic hydrocarbons with alcohols such as tert-butanol or 2-ethylhexanol as solubilizers to the component mixtures or additive concentrates. In some cases, however, considerable amounts of these expensive solubilizers are necessary in order to achieve the desired homogeneity, and so this
10 solution to the problem becomes uneconomic.

- The low molecular weight carboxylic acids and carboxylic acid derivatives, glycol ethers and alkylated phenols recommended in WO 2007/053787 as solubilizers for such component mixtures or additive concentrates are also uneconomic owing to their high
15 feedstock costs and, apart from their function as solubilizers, do not have any further positive effects. On the contrary, they harbor the risk of causing adverse effects, for example undesired oil dilution and increased formation of combustion chamber deposits.

- 20 In addition, the prior art lubricity improvers mentioned often have the tendency to form emulsions with water in the component mixtures or additive concentrates or in the fuel itself, such that water which has penetrated can be removed again via a phase separation only with difficulty or at least only very slowly.

- 25 For instance, the lubricity improvers described in EP-A 1 424 322 and WO 03/070860, which are based on polyisobutenylsuccinimides with mono- or polyamines or alkanolamines such as butylamine, diethylenetriamine, tetraethylenepentamine or aminoethyleneethanolamine, exhibit good miscibility with further additive components in corresponding mixtures or concentrates, but have a marked tendency to form stable
30 emulsions with water, which can lead to the effect that water and soil particles are entrained into the fuel supply chain and ultimately can also get into the engine. Water can cause corrosion; soil particles can lead to damage in fuel pumps, fuel filters and injectors.

- 35 It was an object of the present invention to provide fuel additives which firstly bring about effective fuel saving in the operation of a spark-ignited internal combustion engine, and secondly no longer have the outlined shortcomings of the prior art, i.e. more particularly poor miscibility with other fuel additives and the tendency to form emulsions with water. In addition, they should not worsen the high level of intake valve
40 cleanliness achieved by the modern fuel additives.

Accordingly, the use, defined at the outset, of the reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) a nitrogen

compound of the general formula I has been found. It can be assumed that the cause of the fuel saving by virtue of the reaction product mentioned is based substantially on the effect thereof as an additive which reduces internal friction in the internal combustion engines, especially in gasoline engines. The reaction product mentioned
 5 thus functions in the context of the present invention essentially as a lubricity improver.

Reaction products formed from a hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and an aminoguanidine or a salt thereof are described in US published specifications US 2009/0282731 A1 and US 2010/0037514 A1 as additives for
 10 improving the performance of diesel engines and for cleaning injectors in the diesel engines.

British patents GB 998 869 and GB 1 020 059 disclose that the reaction product formed from polyisobutenylsuccinic anhydride and aminoguanidine bicarbonate is also
 15 suitable as a detergent additive in gasoline fuels.

European published specification EP 0 310 367 A1 states that the reaction product formed from polyisobutenylsuccinic anhydride and aminoguanidinebicarbonate protects copper and copper alloys in diesel engines when it is present in the motor oil.

20 Spark-ignition internal combustion engines are preferably understood to mean gasoline engines, which are typically ignited with spark plugs. In addition to the customary four- and two-stroke gasoline engines, spark-ignition internal combustion engines also include other engine types, for example the Wankel engine. These are generally
 25 engines which are operated with conventional gasoline types, especially gasoline types according to EN 228, gasoline-alcohol mixtures such as Flex fuel with 75 to 85% by volume of ethanol, liquid pressure gas ("LPG") or compressed natural gas ("CNG") as fuel.

30 However, the inventive use of the reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) a nitrogen compound of the general formula I also relates to newly developed internal combustion engines such as the "HCCI" engine, which is self-igniting and is operated with gasoline fuel.

35 The nitrogen compounds of the general formula I for reaction component (a) are guanidine, substituted guanidines or salts thereof. Possible hydrocarbyl radicals in these compounds comprise 1 to 20, especially 1 to 12 and in particular 1 to 8 carbon atoms. A hydrocarbyl radical shall be understood here to mean a hydrocarbyl radical of any structure which, however, in minor amounts, may also comprise heteroatoms such
 40 as oxygen and/or nitrogen atoms and/or halogen atoms, and/or bear functional groups such as hydroxyl groups, carboxyl groups, carboxylic ester groups, cyano groups, nitro groups and/or sulfo groups, provided that the dominant hydrocarbon character of the radical is not distorted thereby. Said hydrocarbyl radical may be saturated or

unsaturated in nature; it may have a linear or branched structure; it may comprise aromatic and/or heterocyclic substructures.

- 5 The nitrogen compound I may have two such hydrocarbyl radicals for R¹ and R², or only one such hydrocarbyl radical for R¹ or R², in which latter case the other substituent is hydrogen. Preferably, however, both substituents R¹ and R² are hydrogen, i.e. the compound is unsubstituted aminoguanidine.

- 10 Possible hydrocarbyl radicals for R¹ and/or R² are preferably linear or branched alkyl or alkenyl radicals, especially those having 1 to 8 and preferably 1 to 4 carbon atoms, such as methyl, ethyl, vinyl, n-propyl, isopropyl, 1-propenyl, 2-propenyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl, neooctyl, nonyl, neononyl, isononyl, decyl, neodecyl, 2-propylheptyl, undecyl, neoundecyl, dodecyl, tridecyl, isotridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl
15 (stearyl), oleyl, linolyl, linolenyl, nonadecyl, eicosyl or constitutional isomers thereof.

- In addition, possible hydrocarbyl radicals for R¹ and/or R² may also refer to cycloalkyl radicals, for example cyclopentyl, cyclohexyl, 2-, 3- or 4-methylcyclohexyl or cycloheptyl.

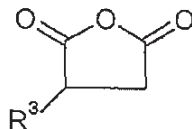
- 20 In addition, possible hydrocarbyl radicals for R¹ and/or R² may also be aryl, alkaryl or arylalkyl radicals, for example, phenyl, naphthyl, benzyl, 2-phenylethyl, 3-phenylpropyl, 4-phenylbutyl, tolyl or o-, m- or p-xylyl.

- 25 When the nitrogen compound I is used in the form of one of its salts, this is especially a halide such as chloride or bromide, carbonate, hydrogencarbonate (bicarbonate), nitrate or orthophosphate. Preference is given to using a hydrogencarbonate (bicarbonate).

- 30 In a preferred embodiment, the nitrogen compound of component (b) is unsubstituted aminoguanidine hydrogencarbonate.

- The hydrocarbyl-substituted dicarboxylic acid or anhydride thereof of component (a) typically has a saturated C₂- to C₁₀-dicarboxylic acid or anhydride thereof as the base
35 skeleton. The dicarboxylic acid or anhydride thereof may bear a plurality of, for example two or three, hydrocarbyl substituents, but preferably only one hydrocarbyl substituent. The anhydride is typically in cyclic form when the anhydride is formed intramolecularly. However, open-chain anhydrides which have formed by intermolecular anhydride formation are also suitable. Examples of such dicarboxylic
40 acids are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid. Aromatic dicarboxylic acids such as phthalic acid or terephthalic acid are likewise suitable.

In a preferred embodiment, the hydrocarbyl-substituted dicarboxylic acid used as reaction component (a) is based on succinic acid or the anhydride thereof. More particularly, the corresponding succinic anhydride of the formula II



(II)

in which R³ denotes a hydrocarbyl radical having 8 to 250 carbon atoms is suitable here. A hydrocarbyl radical shall also be understood here to mean a hydrocarbyl radical of any structure which, however, in a minor amount, may also comprise heteroatoms such as oxygen and/or nitrogen atoms and/or halogen atoms, and/or bear functional groups such as hydroxyl groups, carboxyl groups, carboxylic ester groups, cyano groups, nitro groups and/or sulfo groups, provided that the dominant hydrocarbon character of the radical is not distorted thereby. This hydrocarbyl radical is typically an alkyl, alkenyl, cycloalkyl, aryl, heteroaryl, aralkyl or alkylaryl radical. In the case of longer-chain hydrocarbyl radicals, it may be based on an olefin polymer, for example on a polyethylene, polypropylene or polyisobutylene.

The hydrocarbyl radical in component (a), i.e. the R³ radical, in a preferred embodiment is a linear or branched C₈- to C₄₀-alkyl or -alkenyl radical or a polyisobutenyl radical having 24 to 250 carbon atoms.

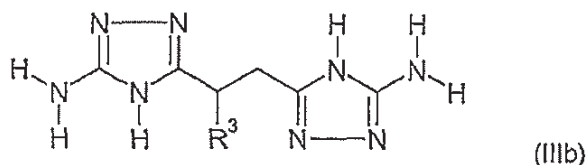
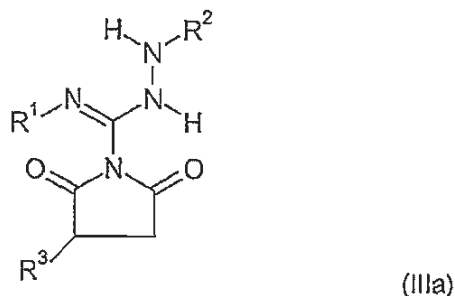
Linear or branched C₈- to C₄₀-alkenyl radicals and polyisobutenyl radicals are typically obtained by a thermal ene reaction between the unsubstituted dicarboxylic acid or anhydride thereof and a long-chain α -olefin to obtain an olefinic double bond in the α,β position of the hydrocarbyl side chain. For this purpose, the reactants are heated typically to temperatures of 150 to 250°C. Alkenyl radicals can subsequently be hydrogenated to the corresponding saturated alkyl radicals.

Useful C₈- to C₄₀-alkenyl radicals, especially C₁₀- to C₂₄-alkenyl radicals, are, for example, 1-nonenyl, 1-decenyl, 1-undecenyl, 1-dodecenyl, 1-tridecenyl, 1-tetradecenyl, 1-pentadecenyl, 1-hexadecenyl, 1-octadecenyl, 1-eicosenyl, and the corresponding alkenyl radicals formed from oligoisobutenes such as di-, tri-, tetra- or penta-isobutene, or formed from technical α -olefin mixtures such as C₂₀-C₂₄- α -olefin.

In the case of presence of a polyisobutenyl radical, it comprises preferably 24 to 250, especially 28 to 180 and in particular 36 to 80 carbon atoms, or thus has a number-average molecular weight M_n of preferably 330 to 3500, especially 390 to 2500, in particular 500 to 1100. Such polyisobutenyl radicals have normally been prepared from high-reactivity polyisobutenes, i.e. from polyisobutenes having a high proportion, typically at least 60%, especially at least 70%, in particular at least 80%, of terminal vinylidene double bonds.

Polyisobutenylsuccinimides ("PIBSAs") thus obtained generally have a degree of succinylation, i.e. a molar ratio of succinic anhydride unit to polyisobutene units, of 0.8 to 2.0, especially of 1.0 to 1.3. It is thus also possible for two succinic anhydride units to be bonded to one polyisobutene chain.

The reaction product obtained from (a) the hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) the nitrogen compound I is often a mixture of several compounds of different structure. Constituents of this mixture may especially be imides formed from a primary amino group of I, for example the compound IIIa, and/or compounds which comprise one or two aminotriazole moieties, for example the compound IIIb in the case that $R^1 = R^2 = H$:



The inventive reaction product formed from (a) the hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) the nitrogen compound I are outstandingly suitable as a fuel additive which brings about an effective fuel saving in the operation of a spark-ignition internal combustion engine, especially of a gasoline engine, and has good miscibility with other fuel additives and does not have any significant tendency to form emulsions with water. The advantageous properties mentioned are manifested to a particular degree in the case of use in gasoline fuels with additional use of fuel additives with detergent action.

Accordingly, the present invention also provides a fuel composition which comprises, in a major amount, a gasoline fuel and, in a minor amount, at least one inventive reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid and (b) a nitrogen compound of the general formula I, and at least one fuel additive which is different than the reaction product mentioned and has detergent action.

Typically, the amount of this at least one inventive reaction product in the gasoline fuel is 10 to 5000 ppm by weight, more preferably 20 to 2000 ppm by weight, even more preferably 30 to 1000 ppm by weight and especially 40 to 500 ppm by weight, for example 50 to 300 ppm by weight.

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Useful gasoline fuels include all conventional gasoline fuel compositions. A 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 present invention. In addition, in the context of the present invention, gasoline fuels shall also be understood to mean alcohol-containing gasoline fuels, especially ethanol-containing gasoline fuels, as described, for example, in WO 2004/090079, for example Flex fuel with an ethanol content of 75 to 85% by volume, or gasoline fuel comprising 85% by volume of ethanol ("E85"), but also the "E100" fuel type, which is typically azeotropically distilled ethanol and thus consists of approx. 96% by volume of C₂H₅OH and approx. 4% by volume of H₂O.

The inventive reaction product formed from (a) the hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) the nitrogen compound I may be added to the particular base fuel either alone or in the form of fuel additive packages. Such packages are fuel additive concentrates and generally also comprise, as well as solvents, and as well as the at least one fuel additive which is different than the inventive reaction product and has detergent action, a series of further components as coadditives, which are especially carrier oils, corrosion inhibitors, demulsifiers, dehazers, antifoams, combustion improvers, antioxidants or stabilizers, antistats, metallocenes, metal deactivators, solubilizers, markers and/or dyes.

Detergents or detergent additives, referred to hereinafter as component (D), typically refer to deposition inhibitors for fuels. The detergent additives are preferably amphiphilic substances which possess at least one hydrophobic hydrocarbyl radical having a number-average molecular weight (M_n) of 85 to 20 000, especially of 300 to 5000, in particular of 500 to 2500, and at least one polar moiety.

In a preferred embodiment, the inventive fuel composition comprises, as the at least one fuel additive which is different than the inventive reaction product and has detergent action (D), at least one representative which is selected from:

- (Da) mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties;
- (Db) nitro groups, optionally in combination with hydroxyl groups;

- (Dc) hydroxyl groups in combination with mono- or polyamino groups, at least one nitrogen atom having basic properties;
- (Dd) carboxyl groups or their alkali metal or alkaline earth metal salts;
- 5 (De) sulfo groups or their alkali metal or alkaline earth metal salts;
- (Df) polyoxy-C₂-C₄-alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups;
- 10 (Dg) carboxylic ester groups;
- (Dh) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or
- 15 (Di) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.
- 20 The hydrophobic hydrocarbon radical in the above detergent additives, which ensures the adequate solubility in the fuel composition, has a number-average molecular weight (M_n) of 85 to 20 000, especially of 300 to 5000, in particular of 500 to 2500. Useful typical hydrophobic hydrocarbyl radicals, especially in conjunction with the polar moieties (Da), (Dc), (Dh) and (Di), are relatively long-chain alkyl or alkenyl groups, especially the
- 25 polypropenyl, polybutenyl and polyisobutenyl radicals each having $M_n = 300$ to 5000, especially 500 to 2500, in particular 700 to 2300.

Examples of the above groups of detergent additives include the following:

- 30 Additives comprising mono- or polyamino groups (Da) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or conventional (i.e. having predominantly internal double bonds) polybutene or polyisobutene having $M_n = 300$ to 5000. When the preparation of the additives proceeds from polybutene or polyisobutene having predominantly internal double bonds (usually in the β and γ positions), one possible
- 35 preparative route is by chlorination and subsequent amination or by oxidation of the double bond with air or ozone to give the carbonyl or carboxyl compound and subsequent amination under reductive (hydrogenating) conditions. The amines used here for the amination may be, for example, ammonia, monoamines or polyamines such as dimethylaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine
- 40 or tetraethylenepentamine. Corresponding additives based on polypropene are described in particular in WO-A-94/24231.

Further preferred additives comprising monoamino groups (Da) are the hydrogenation products of the reaction products of polyisobutenes having an average degree of polymerization $P = 5$ to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO-A-97/03946.

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Further preferred additives comprising monoamino groups (Da) are the compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols, as described in particular in DE-A-196 20 262.

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Additives comprising nitro groups (Db), optionally in combination with hydroxyl groups, are preferably reaction products of polyisobutenes having an average degree of polymerization $P = 5$ to 100 or 10 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO-A-96/03367 and in WO-A 96/03479.

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These reaction products are generally mixtures of pure nitropolyisobutenes (e.g. α,β -dinitropolyisobutene) and mixed hydroxynitropolyisobutenes (e.g. α -nitro- β -hydroxypolyisobutene).

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Additives comprising hydroxyl groups in combination with mono- or polyamino groups (Dc) are in particular reaction products of polyisobutene epoxides obtainable from polyisobutene having preferably predominantly terminal double bonds and $M_n = 300$ to 5000, with ammonia or mono- or polyamines, as described in particular in EP-A-476 485.

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Additives comprising carboxyl groups or their alkali metal or alkaline earth metal salts (Dd) are preferably copolymers of C_2 - C_{40} -olefins with maleic anhydride which have a total molar mass of 500 to 20 000 and some or all of whose carboxyl groups have been converted to the alkali metal or alkaline earth metal salts and any remainder of the carboxyl groups has been reacted with alcohols or amines. Such additives are disclosed in particular by EP-A-307 815. Such additives serve mainly to prevent valve seat wear and can, as described in WO-A-87/01126, advantageously be used in combination with customary fuel detergents such as poly(iso)buteneamines or polyetheramines.

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Additives comprising sulfo groups or their alkali metal or alkaline earth metal salts (De) are preferably alkali metal or alkaline earth metal salts of an alkyl sulfosuccinate, as described in particular in EP-A-639 632. Such additives serve mainly to prevent valve seat wear and can be used advantageously in combination with customary fuel detergents such as poly(iso)buteneamines or polyetheramines.

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Additives comprising polyoxy- C_2 - C_4 -alkylene moieties (Df) are preferably polyethers or polyetheramines which are obtainable by reaction of C_2 - C_{60} -alkanols, C_6 - C_{30} -alkanediols, mono- or di- C_2 - C_{30} -alkylamines, C_1 - C_{30} -alkylcyclohexanols or C_1 - C_{30} -alkylphenols with 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene

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oxide per hydroxyl group or amino group and, in the case of the polyetheramines, by subsequent reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP-A-310 875, EP-A-356 725, EP-A-700 985 and US-A-4 877 416. In the case of polyethers, such products also have carrier oil
 5 properties. Typical examples of these are tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and also the corresponding reaction products with ammonia.

Additives comprising carboxylic ester groups (Dg) are preferably esters of mono-, di- or
 10 tricarboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mm²/s at 100°C, as described in particular in DE-A-38 38 918. The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids, and particularly suitable ester alcohols or ester polyols are long-chain representatives having, for example, 6 to 24 carbon atoms. Typical representatives of the esters are adipates,
 15 phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol. Such products also have carrier oil properties.

Additives comprising moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups (Dh) are preferably corresponding de-
 20 rivatives of alkyl- or alkenyl-substituted succinic anhydride and especially the corresponding derivatives of polyisobutenylsuccinic anhydride which are obtainable by reacting conventional or high-reactivity polyisobutene having $M_n = 300$ to 5000 with maleic anhydride by a thermal route or via the chlorinated polyisobutene. Of particular interest in this context are derivatives with aliphatic polyamines such as ethylenedia-
 25 mine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. The moieties having hydroxyl and/or amino and/or amido and/or imido groups are, for example, carboxylic acid groups, acid amides of monoamines, acid amides of di- or polyamines which, in addition to the amide function, also have free amine groups, succinic acid derivatives having an acid and an amide function, carboximides with monoamines, car-
 30 boximides with di- or polyamines which, in addition to the imide function, also have free amine groups, or diimides which are formed by the reaction of di- or polyamines with two succinic acid derivatives. Such fuel additives are described especially in US-A-4 849 572.

35 The detergent additives from group (Dh) are preferably the reaction products of alkyl- or alkenyl-substituted succinic anhydrides, especially of polyisobutenylsuccinic anhydrides ("PIBSAs"), with amines and/or alcohols. These are thus derivatives which are derived from alkyl-, alkenyl- or polyisobutenylsuccinic anhydride and have amino and/or amido and/or imido and/or hydroxyl groups. It is self-evident that these reaction
 40 products are obtainable not only when substituted succinic anhydride is used, but also when substituted succinic acid or suitable acid derivatives, such as succinyl halides or succinic esters, are used.

The additized fuel preferably comprises at least one detergent based on a polyisobutenyl-substituted succinimide. Especially of interest are the imides with aliphatic polyamines. Particularly preferred polyamines are ethylenediamine, diethylenetriamine, triethylenetetramine, pentaethylenhexamine and in particular
 5 tetraethylenepentamine. The polyisobutenyl radical has a number-average molecular weight M_n of preferably from 500 to 5000, more preferably from 500 to 2000 and in particular of about 1000.

Additives comprising moieties (Di) obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and mono- or polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. The polyisobutenyl-substituted phenols may originate from conventional or high-reactivity polyisobutene having $M_n = 300$ to 5000. Such "polyisobutene Mannich bases" are described especially in EP-A-831 141.
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The inventive fuel composition comprises the at least one fuel additive which is different than the inventive reaction product and has detergent action, and is normally selected from the above groups (Da) to (Di), in an amount of typically 10 to 5000 ppm by weight, more preferably of 20 to 2000 ppm by weight, even more preferably of 30 to 1000 ppm by weight and especially of 40 to 500 ppm by weight, for example of 50 to 250 ppm by weight.
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The detergent additives (D) mentioned are preferably used in combination with at least one carrier oil. In a preferred embodiment, the inventive fuel composition comprises, in addition to the at least one inventive reaction product and the at least one fuel additive which is different than the inventive reaction product and has detergent action, as a further fuel additive in a minor amount, at least one carrier oil.
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Suitable mineral carrier oils are the fractions obtained in crude oil processing, such as brightstock or base oils having viscosities, for example, from the SN 500 - 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 abovementioned mineral carrier oils.
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Examples of suitable synthetic carrier oils are selected from: polyolefins (poly- α -olefins or poly(internal olefin)s), (poly)esters, (poly)alkoxylates, polyethers, aliphatic polyetheramines, alkylphenol-started polyethers, alkylphenol-started polyetheramines and carboxylic esters of long-chain alkanols.
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Examples of suitable polyolefins are olefin polymers having M_n = from 400 to 1800, in particular based on polybutene or polyisobutene (hydrogenated or unhydrogenated).

5 Examples of suitable polyethers or polyetheramines are preferably compounds comprising polyoxy- C_2 - C_4 -alkylene moieties which are obtainable by reacting C_2 - C_{60} -
 10 alkanols, C_6 - C_{30} -alkanediols, mono- or di- C_2 - C_{30} -alkylamines, C_1 - C_{30} -alkylcyclohexanols or C_1 - C_{30} -alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group, and, in the case of the polyetheramines, by subsequent reductive amination with ammonia,
 15 monoamines or polyamines. Such products are described in particular in EP-A-310 875, EP-A-356 725, EP-A-700 985 and US-A-4,877,416. For example, the polyetheramines used may be poly- C_2 - C_6 -alkylene oxide amines or functional derivatives thereof. Typical examples thereof are tridecanol butoxylates or isotridecanol butoxylates, isononylphenol butoxylates and also polyisobutenol butoxylates and
 20 propoxylates, and also the corresponding reaction products with ammonia.

Examples of carboxylic esters of long-chain alkanols are in particular esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, as described in particular in
 25 DE-A-38 38 918. The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids; suitable ester alcohols or polyols are in particular long-chain representatives having, for example, from 6 to 24 carbon atoms. Typical representatives of the esters are adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, isononanol, isodecanol and isotridecanol, for example di(n- or isotridecyl) phthalate.

Further suitable carrier oil systems are described, for example, in DE-A-38 26 608, DE-A-41 42 241, DE-A-43 09 074, EP-A-0 452 328 and EP-A-0 548 617.

30 Examples of particularly suitable synthetic carrier oils are alcohol-started polyethers having from about 5 to 35, for example from about 5 to 30, C_3 - C_6 -alkylene oxide units, for example selected from propylene oxide, n-butylene oxide and isobutylene oxide units, or mixtures thereof. Nonlimiting examples of suitable starter alcohols are long-chain alkanols or phenols substituted by long-chain alkyl in which the long-chain alkyl radical is in particular a straight-chain or branched C_6 - C_{18} -alkyl radical. Preferred
 35 examples include tridecanol and nonylphenol.

Further suitable synthetic carrier oils are alkoxyated alkylphenols, as described in DE-A-101 02 913.

40 Preferred carrier oils are synthetic carrier oils, particular preference being given to polyethers.

When a carrier oil is used in addition, it is added to the inventive additized fuel in an amount of preferably from 1 to 1000 ppm by weight, more preferably from 10 to 500 ppm by weight and in particular from 20 to 100 ppm by weight.

- 5 In a preferred embodiment, the inventive fuel composition comprises, in addition to the at least one inventive reaction product, the at least one fuel additive which is different than the inventive reaction product and has detergent action, and optionally the at least one carrier oil, as a further fuel additive in a minor amount, at least one corrosion inhibitor.
- 10 Corrosion inhibitors suitable as such coadditives are, for example, succinic esters, in particular with polyols, fatty acid derivatives, for example oleic esters, oligomerized fatty acids and substituted ethanolamines.
- 15 Demulsifiers suitable as further coadditives are, for example, the alkali metal and alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal and alkaline earth metal salts of fatty acid, and also alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylates or tert-pentylphenol ethoxylates, fatty acid, alkylphenols, condensation products of ethylene
- 20 oxide and propylene oxide, e.g. ethylene oxide-propylene oxide block copolymers, polyethyleneimines and polysiloxanes.
- Dehazers suitable as further coadditives are, for example, alkoxyated phenol-formaldehyde condensates.
- 25 Antifoams suitable as further coadditives are, for example, polyether-modified polysiloxanes.
- Antioxidants suitable as further coadditives are, for example, substituted phenols, e.g.
- 30 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-3-methylphenol, and also phenylenediamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine.
- Metal deactivators suitable as further coadditives are, for example, salicylic acid derivatives, e.g. N,N'-disalicylidene-1,2-propanediamine.
- 35 Suitable solvents, especially also for fuel additive packages, are, for example, nonpolar organic solvents, especially aromatic and aliphatic hydrocarbons, for example toluene, xylenes, "white spirit" and the technical solvent mixtures of the designations Shellsol® (manufacturer: Royal Dutch / Shell Group), Exxol® (manufacturer: ExxonMobil) and
- 40 Solvent Naphtha. Also useful here, especially in a blend with the nonpolar organic solvents mentioned, are polar organic solvents, in particular alcohols such as tert-butanol, isoamyl alcohol, 2-ethylhexanol and 2-propylheptanol.

When the coadditives and/or solvents mentioned are used in addition in gasoline fuel, they are used in the amounts customary therefor.

5 The present invention also provides an additive concentrate which comprises at least one inventive reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) a nitrogen compound of the general formula I, and at least one fuel additive which is different than the reaction product mentioned and has detergent action. Otherwise, the inventive additive concentrate may comprise the further coadditives mentioned above.

10 The inventive reaction product is present in the inventive additive concentrate preferably in an amount of 1 to 99% by weight, more preferably of 15 to 95% by weight and especially of 30 to 90% by weight, based in each case on the total weight of the concentrate. The at least one fuel additive which is different than the reaction product
15 mentioned and has detergent action is present in the inventive additive concentrate preferably in an amount of 1 to 99% by weight, more preferably of 5 to 85% by weight and especially of 10 to 70% by weight, based in each case on the total weight of the concentrate.

20 The examples which follow are intended to further illustrate the present invention without restricting it.

Example 1: Mixing performance

25 The reaction product ("RP1") formed from a polyisobutenylsuccinic anhydride, obtained by thermal ene reaction (200°C) from maleic anhydride with a polyisobutene of number-average molecular weight M_n 1000 with a content of terminal vinylidene double bonds of 85%, and aminoguanidine hydrogencarbonate, was prepared in analogy to Example 1 of US 2009/0282731 A1, using Solvesso™ 150 (manufacturer: ExxonMobil)
30 as a diluent.

The reaction product thus prepared ("RP1") was used to prepare an additive concentrate ("AC1") by simply mixing in the components listed below:

- 35
- 400 parts by weight of the inventive reaction product RP1 (50% by weight in Solvesso 150)
 - 390 parts by weight (polymer content) of a conventional detergent additive component (polyisobutene monoamine based on a polyisobutene with $M_n = 1000$)
 - 40 • 310 parts by weight of a commercial carrier oil based on an alcohol-started polyether

- 270 parts by weight of Solvent Naphtha as a diluent
- 470 parts by weight of 2-propylheptanol as a further diluent
- 5 • 4 parts by weight of a customary dehazer component (based on an alkoxyated phenol-formaldehyde condensate)

10 It was possible to mix the components mentioned with one another without any problem to give a clear liquid, the consistency of which remains stable over several days.

For comparison, the additive concentrate "AC2" was prepared, which differed from AC1 merely in that the inventive reaction product RP1 was replaced by the same amount of active ingredient of a commercial prior art lubricity improver ("RP2"), namely the imide
15 formed from polyisobutenylsuccinic anhydride (based on a polyisobutene with $M_n = 1000$) and tetraethylenepentamine. After mixing together, RP2 was present as a turbid liquid, from which a precipitate separated out after a few days.

20 Example 2: Emulsion performance

A typical Eurosuper base fuel to EN 228, which is customary on the market, was additized as a gasoline fuel in each case with additive concentrate AC1 (inventive) and AC2 (for comparison) in such an amount that the dosage of lubricity improver RP1 (inventive) and RP2 (for comparison) was in each case 390 ppm by weight. According
25 to the ASTM D 1094 phase separation test, water was added to the systems and the phase separation behavior was assessed. After 5 minutes, AC1 gave two clear and sharply separated phases (phase separation rating according to ASTM D 1094: 1), whereas, after 5 minutes, AC2 resulted in an emulsion in the water phase and a turbid fuel phase (phase separation rating to ASTM D 1094: 4).

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Example 3: Fuel economy

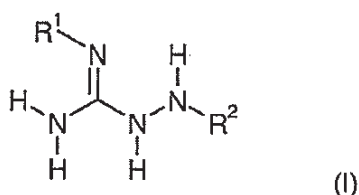
A gasoline fuel produced on the basis of a base fuel customary on the U.S. market by additization with AC1 in the dosage rate specified in Example 2, was used to determine
35 fuel economy in a fleet test with three different automobiles according to U.S. Environmental Protection Agency Test Protocol, C.F.R. Title 40, Part 600, Subpart B. For each automobile, the fuel consumption was determined first with unadditized fuel and then with the same fuel which now, however, comprised the additive concentrate AC1 in the dosage specified in Example 2. On average, over all automobiles used, the
40 result was an average fuel saving of 1.3%.

Example 4: Intake valve cleanliness

The intake valve deposits ("IVD") were determined to CEC F-20-98 in a Mercedes Benz M111 engine with the two gasoline fuels additized with AC1 (inventive) or AC2 (for comparison). Given a base value of 94 mg per valve for the unadditized gasoline fuel, the gasoline fuel additized with AC1 (inventive) gave a value of 2 mg per valve, and the gasoline fuel additized with AC2 (for comparison) a value of 6 mg per valve.

Claims

1. The use of the reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid whose hydrocarbyl radical is a linear or branched C₈- to C₄₀-alkyl or -alkenyl radical or a polyisobutenyl radical having 24 to 250 carbon atoms, or the anhydride thereof, and (b) a nitrogen compound of the general formula I



- or a salt of the nitrogen compound I, where R¹ and R² are each independently hydrogen or a C₁- to C₂₀-hydrocarbyl radical,
- together with a detergent additive being an amphiphilic substance which possesses 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.
- as an additive in a fuel for reducing fuel consumption in the operation of a spark-ignited internal combustion engine with this fuel or as an additive in a gasoline fuel for reduction of fuel consumption in the operation of a self-ignition internal combustion engine with this fuel.
2. The use according to claim 1, wherein the hydrocarbyl-substituted dicarboxylic acid of component (a) is based on succinic acid or the anhydride thereof.
3. The use according to claim 1 or 2, wherein the nitrogen compound of component (b) is unsubstituted aminoguanidine hydrogencarbonate.
4. A fuel composition when used for reducing fuel consumption, the fuel composition comprising, in a major amount, a gasoline fuel and, in a minor amount, at least one reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid and (b) a nitrogen compound of the general formula I as defined in any one of claims 1 to 3, and at least one fuel additive which is different than the reaction product mentioned and has detergent action, wherein the at least one fuel additive is an amphiphilic substance which possesses at least one hydrophobic hydrocarbyl radical being a polypropenyl, polybutenyl or polyisobutenyl radical having a number-average molecular weight (M_n) of 700 to 2300 and at least one polar moiety.

5. The fuel composition according to claim 4, comprising as the fuel additive which is different than the reaction product mentioned and has detergent action at least one representative selected from:
 - 5 (Da) mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties;
 - (Db) nitro groups, optionally in combination with hydroxyl groups;
 - 10 (Dc) hydroxyl groups in combination with mono- or polyamino groups, at least one nitrogen atom having basic properties;
 - (Dd) carboxyl groups or their alkali metal or alkaline earth metal salts;
 - 15 (De) sulfonic acid groups or their alkali metal or alkaline earth metal salts;
 - (Df) polyoxy-C₂-C₄-alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups;
 - 20 (Dg) carboxylic ester groups;
 - (Dh) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or
 - 25 (Di) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.
6. The fuel composition according to claim 4 or 5, additionally comprising, as a further fuel additive in a minor amount, at least one carrier oil.
 - 30
7. The fuel composition according to any one of claims 4 to 6, additionally comprising, as a further fuel additive in a minor amount, at least one corrosion inhibitor.
8. A fuel additive concentrate comprising at least one reaction product formed from (a) a hydrocarbyl-substituted dicarboxylic acid or anhydride thereof and (b) a nitrogen compound of the general formula I as defined in any one of claims 1 to 3, and at least one fuel additive which is different than the reaction product mentioned and has detergent action, wherein the at least one additive is selected from the group consisting of (Da), (Dc), (Dh) and (Di) as defined in Claim 5, bearing polypropenyl, polybutenyl or polyisobutenyl radicals having Mn = 700 to 2300.
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 - 40