Abstract:

Use of an effective concentration of polyalkenylsuccinimides comprising the reaction product of hydrocarbonyl dicarboxylic acid producing reaction intermediates and nucleophilic reactants, as additives in unleaded gasoline compositions suitable in spark ignition engines, for reducing injector nozzle fouling in direct injection spark ignition engines. Furthermore, a fuel additive composition essentially comprising nitrogen-containing dispersants selected from polyisobutene monoamines and polyisobutene polyamines, carrier oils which are substantially free of nitrogen and selected from synthetic carrier oils and mineral carrier oils, and the above polyalkenylsuccinimides.
Polyalkenylsuccinimides for Reducing Injector Nozzle Fouling in Direct Injection Spark Ignition Engines

Description

The present invention relates to the use of a polyalkenylsuccinimide as an additive in an unleaded gasoline composition suitable in spark ignition engines, for reducing injector nozzle fouling in direct injection spark ignition engines. Furthermore, the present invention relates to a novel fuel additive composition comprising selected nitrogen-containing dispersants, carrier oils and the above-mentioned polyalkenylsuccinimides. Furthermore, the present invention relates to a gasoline fuel composition comprising a minor amount of the said fuel additive composition.

Technical Background

Modern gasolines are unleaded in order to be compatible with catalytic convertors, and fuel injection has to be used in modern spark ignition engines, in order to achieve the required stoichiometric fuel/air mixtures. A typical fuel-injected spark ignition engine has multipoint fuel injection, in which fuel from the injectors impinges directly onto inlet valves. An unleaded base gasoline in such an engine tends to give rise to inlet valve deposits. A relatively new class of spark ignition engines is the class described as direct injection spark ignition engines, also known as gasoline direct injection engines; problems in such direct injection engines can arise with unleaded gasoline by fouling of injector nozzles.

For trouble-free running, modern direct injection spark ignition engines require automotive fuels having a complex set of properties which can only be guaranteed when use is made of appropriate gasoline additives. Such fuels usually consist of a complex mixture of chemical compounds and are characterized by physical parameters. Fuel additives are used among other things in order to avoid formation of deposits in the intake system and the intake valves of engines (keep-clean effect); on the other hand, fuel additives may be used in order to remove deposits already formed at the valves and in the intake system (clean-up effect). Special additives have been developed to reduce or minimise inlet valve deposits and also injector nozzle fouling.

Aliphatic primary, secondary and tertiary monoamines with C1 to C20-alkyl residues, C3 to C20-cycloalkyl residues or cycloalkyl residues are known as dispersant additives in gasoline fuels, preferably in combination with Mannich-type dispersant additives, from WO 04/050806. The said monoamines can be used in gasoline fuels together with other dispersants additives, such as polyisobutene monoamines or polyisobutene polymamines based on polyisobutene with a number average molecular weight of from 600 to 5,000 g/mol, and with polyether carrier oils, such as tridecanol butoxylate or isotride-
canol butoxylate. The use of the said monoamines results in a reduction of injector nozzle fouling in direct injection spark ignition engines.

WO 03/076554 relates to the use of primary hydrocarbyl amines wherein the hydrocarbyl moiety has a number average molecular weight in the range of from 140 to 255 for reducing injector nozzle fouling in direct injection spark ignition engines, either for "keep clean" or for "clean-up" purposes of such engines. In Fuel D of the examples of WO 03/076554, a gasoline fuel was prepared by "dosing into the base fuel 645 ppmw of a commercial additive package ex BASF A.G., containing polyisobutylene monoamine (PIBA), in which the polyisobutylene (PIB) chain has a number average molecular weight (Mn) of approximately 1000, a polyether carrier fluid and an antioxidant, with further inclusion of 50 ppmw dodecylamine". Fuel D was subjected to a clean-up test determining the average injector diameter reduction after running a direct injection spark ignition engine with this Fuel.

WO 90/10051 relates to a gasoline fuel composition containing an intake valve deposit control additive formulation comprising long-chain primary amines exhibiting typically C6-C40 aliphatic radicals as substituents, e.g. dodecyl amine (lauryl amine), in combination with fuel dispersants selected from polyalkenylamines (such as polyisobutyl amine) and Mannich bases, and with fluidizer oils such as refined napthenic lubricating oil or a polyolefin like polypropylene or polybutylene.

WO 2009/074608 relates to a fuel additive composition and to a fuel composition comprising nitrogen-containing dispersants selected from polyisobutyl monoamines and polyisobutenyl polyamines, synthetic or mineral carrier oils and primary, secondary or tertiary amines. Suitable tertiary amines may exhibit three C1- to C30- hydrocarbyl residues, the majority of the examples listed for such tertiary amines exhibit three identical C1- to C30- hydrocarbyl residues, furthermore, N-methylidicyclohexylamine and N-ethylidicyclohexylamine are mentioned. The said amines are recommended as an intake valve clean-up booster in gasoline-operated port fuel injection internal combustion engines.

EP 1 518 918 A1 discloses that succinimide dispersants such as polyisobutenylsuccinic polyimides in combination with Mannich detergents or polyetheramine detergents reduce or eliminate injector deposits and soot formation in spark-ignition internal combustion engines such as direct injection gasoline engines ("DIG" engines).

The performance of the additives of the art to reduce or minimise inlet valve deposits and/or especially injector nozzle fouling in direct injection spark ignition engines and their interrelationship with gasoline fuels and further fuel additives in fuel compositions may still be unsatisfactory. It is, therefore, an object of the present invention to provide an improved additive for reducing inlet valve deposits and/or injector nozzle fouling and to provide an improved fuel additive formulation which allow an efficient control of de-
posits formed in the engine, especially an improved injector nozzle fouling clean-up and keep-clean performance.

**Brief Description of the Invention**

It has now been observed that the use of an effective concentration of a polyalkenylsuccinimide comprising the reaction product of (1) a hydrocarbyl dicarboxylic acid producing reaction intermediate and (2) a nucleophilic reactant, as an additive in an unleaded gasoline composition suitable in spark ignition engines, reduces injector nozzle fouling in direct injection spark ignition engines.

Moreover, it has now been observed that a fuel additive composition essentially comprising:

(A) at least one nitrogen-containing dispersant selected from (A1) polyisobutenyl monoamines and (A2) polyisobutenyl polyamines;

(B) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils; and

(C) at least one polyalkenylsuccinimide comprising the reaction product of (1) a hydrocarbyl dicarboxylic acid producing reaction intermediate and (2) a nucleophilic reactant,

still further reduces injector nozzle fouling in direct injection spark ignition engines. Therefore, the said fuel additive composition is also a subject matter of the instant invention.

A further subject matter of the instant invention is a fuel composition comprising a major amount of a liquid fuel in gasoline boiling range and a minor amount of the above fuel additive composition.

**Details Description of the Invention and Preferred Embodiments**

The nitrogen-containing dispersant (Component A)

The polyisobutenes which are suitable for preparing the polyisobutenyl monoamines (A1) and polyisobutenyl polyamines (A2) used in the present invention include polyisobutenes which comprise at least about 20%, preferably at least 50% and more preferably at least 70% of the more reactive methylvinylidene isomer. Suitable polyisobutenes include those prepared using BF3 catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high percentage of the total composition is for example described in US-A 4,152,499 and US-A 4,605,808.
Examples of suitable polyisobutenes having a high alkylvinylidene content include Ul-
travis® 30, a polyisobutene having a number average molecular weight (M_n) of about
1300 g/mol and a methylvinylidene content of about 74%, and Ultravis® 10, a 950
g/mol molecular weight polyisobutene having a methylvinylidene content of about 76%,
both available from British Petroleum. Another example of a suitable polyisobutene
having a number average molecular weight (M_n) of about 1000 and a high methylvinylid-
en content is Glissopal® 1000, available from BASF SE.

In most instances, the polyisobutene precursors are not a pure single product, but ra-
ther a mixture of compounds having an average molecular weight in the above range.
Usually, the range of molecular weights will be relatively narrow having a maximum
near the indicated molecular weight.

The amine component of the polyisobutenyl monoamines or polyisobutenyl polyam-
ines, respectively, may be derived from ammonia, a monoamine or a polyamine.

The monoamine or polyamine component comprises amines having from 1 to about 12
amine nitrogen atoms and from 1 to 40 carbon atoms. The carbon to nitrogen ratio may
be between about 1:1 and about 10:1. Generally, the monoamine will contain from 1 to
about 40 carbon atoms and the polyamine will contain from 2 to about 12 amine nitro-
gen atoms and from 2 to about 40 carbon atoms.

The amine component may be a pure single product or a mixture of compounds having
a major quantity of the designated amine.

When the amine component is a polyanine, it will preferably be a polyalkylene polyan-
ine, including alkylene diamine. Preferably, the alkylene group will contain from 2 to 6
carbon atoms, more preferably from 2, 3 or 4 carbon atoms. Examples of such polyan-
ines include ethylene diamine, diethylene triamine, triethylene tetramine and tetraethyl-
ene pentamine. Preferred polyamines are ethylene diamine and diethylene triamine.

Particularly preferred polyisobutenyl polyamines include polyisobutenyl ethylene dia-
mine and polyisobutenyl amine. The polyisobutenyl group is substantially saturated.

The polyisobutenyl monoamines or polyisobutenyl polyamines employed in the fuel
additive composition of the instant invention are prepared by conventional procedures
known in the art, especially by reductive amination. Such polyisobutenyl monoamines
or polyisobutenyl polyamines and their preparations are described in detail e.g. in EP-A
0 244 616.

The amine portion of the molecule may carry one or more substituents. Thus, the car-
bon and/or, in particular, the nitrogen atoms of the amine may carry substituents se-
lected from hydrocarbyl groups of from 1 to about 10 carbon atoms, acyl groups of from
2 to about 10 carbon atoms, and monoketo, monohydroxy, mononitro, monocyano, lower alkyl and lower alkoxy derivatives thereof. "Lower" as used herein means a group containing from 1 to about 6 carbon atoms. At least one of hydrogen atoms on one of the basic nitrogen atoms of the polyamine may not be substituted so that at least one of the basic nitrogen atoms of the polyamine is a primary or secondary amino nitrogen.

A polyamine finding use within the scope of the present invention as amine component for the polyisobutenyl polyamines may be a polyalkylene polyamine, including substituted polyamines, e.g., alkyl and hydroxyalkyl-substituted polyalkylene polyamine. Among the polyalkylene polyamines, those containing 2 to 12 amino nitrogen atoms and 2 to 24 carbon atoms should be mentioned, in particular C₂ to C₃-alkylene polyamines. Preferably, the alkylene group contains from 2 to 6 carbon atoms, there being preferably from 2 to 3 carbon atoms between the nitrogen atoms. Such groups are exemplified by ethylene, 1,2-propylene, 2,2-dimethylpropylene, trimethylene, and 2-hydroxy-1,3-propylene.

Examples of such polyamines comprise 1,2-ethylene diamine, diethylene triamine, di(trimethylene) triamine, 1,2-propylene diamine, 1,3-propylene diamine, dipropylene triamine, triethylene tetramine, tripropylene tetramine, tetraethylene pentamine, pentethylen hexamine, 1,4-tetramethylene diamine, 1,5-pentamethylene diamine, 1,6-hexamethylene diamine and N,N-dimethylaminopropylene diamine. Such amines encompass isomers such as branched-chain polyamines and previously-mentioned substituted polyamines, including hydroxy- and hydrocarbyl-substituted polyamines.

The amine component for the polyisobutenyl monoamines or polyisobutenyl polyamines also may be derived from heterocyclic polyamines, heterocyclic substituted amines and substituted heterocyclic compounds, wherein the heterocycle comprises one or more 5- to 6-membered rings containing oxygen and/or nitrogen. Such heterocyclic rings may be saturated or unsaturated and substituted with groups as defined above.

As examples of heterocyclic compounds there may be mentioned 2-methylpiperazine, N-(2-hydroxyethyl)piperazine, 1,2-bis(N-piperazinyl)ethane, N,N'-bis(N-piperazinyl)-piperazine, 2-methylimidazoline, 3-aminopiperidine, 3-aminopyridine, N-(3-aminopropyl)-morpholine, N-(beta-amoenoethyl)piperazine, N-(betaamineoethyl)piperidine, 3-amino-N-ethylpiperidine, N-(betaamineoethyl) morpholine, N,N'-di(beta-amineoethyl)-piperazine, N,N'-di(beta-amineoethyl)imidazolidone-2, 1,3-dimethyl-5(beta-amineoethyl)hexahydrotiazine, N-(betaamineoethyl)-hexahydrotiazine, 5-(beta-amineoethyl)-1,3,5-dioxazine.

Alternatively, the amine component for the polyisobutenyl monoamines may be derived from a monoamine having the formula HNR₄R₅ wherein R⁴ and R⁵ are independently selected from the group consisting of hydrogen and hydrocarbyl of 1 to about 20 car-
bon atoms and, when taken together, R\textsuperscript{4} and R\textsuperscript{5} may form one or more 5- or 6-
membered rings containing up to about 20 carbon atoms. Preferably, R\textsuperscript{4} is hydrogen and R\textsuperscript{5} is a hydrocarbyl group having 1 to about 10 carbon atoms. More preferably, R\textsuperscript{4}
and R\textsuperscript{5} are hydrogen. The hydrocarbyl groups may be straight-chain or branched and may be aliphatic, alicyclic, aromatic or combinations thereof. The hydrocarbyl groups may also contain one or more oxygen atoms.

Typical primary amines are exemplified by N-methylamine, N-ethylamine, N-n-propyl-
amine, N-isopropylamine, N-n-butylamine, N-isobutylamine, N-sec.-butylamine, N-tert-
butylamine, N-n-pentylamine, N-cyclopentylamine, N-n-hexylamine, N-cyclohexyl-
amine, N-octylamine, N-decylamine, N-dodecylamine, N-octadecylamine, N-benzyl-
amine, N-(2-phenylethyl)amine, 2-aminoethanol, 3-amino-1-propanol, 2-(2-amino-
ethoxy)ethanol, N-(2-methoxyethyl)amine, N-(2-ethoxyethyl)amine, and the like. Preferred primary amines are N-methylamine, N-ethylamine and N-n-propylamine.

Typical secondary amines include N,N-dimethylamine, N,N-diethylamine, N,N-di-n-
propylamine, N,N-diisopropylamine, N,N-di-n-butylamine, N,N-di-sec-butylamine, N,N-
di-n-pentylamine, N,N-di-n-hexylamine, N,N-dicyclohexylamine, N,N-diocetylamine, N-
ethyl-N-methylamine, N-methyl-N-n-propylamine, N-n-butyl-N-methylamine, N-methyl-
N-octylamine, N-ethyl-N-isopropylamine, N-ethyl-N-octylamine, N,N-di-(2-hydroxy-
ethyl)amine, N,N-di(3-hydroxypropyl)amine, N,N-di(ethoxyethyl)amine, N,N-di-(pro-
proxyethyl)amine, and the like. Preferred secondary amines are N,N-dimethylamine, N,N-diethylamine and N,N-di-n-propylamine.

Cyclic secondary amines may also be employed to form the polyisobutyl monoam-
ines or polyisobutylpolyamines used in the instant invention. In such cyclic com-
ounds, R\textsuperscript{4} and R\textsuperscript{5} of the formula hereinabove, when taken together, form one or more 5- or 6-membered rings containing up to about 20 carbon atoms. The ring containing the amine nitrogen atom is generally saturated, but may be fused to one or more satu-
rated or unsaturated rings. The rings may be substituted with hydrocarbyl groups of from 1 to about 10 carbon atoms and may contain one or more oxygen atoms.

Suitable cyclic secondary amines include piperidine, 4-methylpiperidine, pyrrolidine, 
morpholine, 2,6-dimethylmorpholine, and the like.

The number average molecular weight (M\textsubscript{n}) of the polyisobutyl monoamines or poly-
isobutylpolyamines used in the instant invention is usually in the range of from 500 to 2,500 g/mol, typically about 550, about 750, about 1000 or about 1,300 g/mol. A pre-
ferred range for the number average molecular weight of the polyisobutyl monoam-
ines or polyisobutylpolyamines is from 550 to 1000 g/mol. As already stated for the 
polyisobutene precursors, the polyisobutylene monoamines or polyisobutylene polyam-
ines are mostly not pure single products, but rather mixtures of compounds having 
number average molecular weights as indicated above. Usually, the range of molecular
weights will be relatively narrow having a maximum near the indicated molecular weight.

In an especially preferred embodiment, dispersant component (A) is a polyisobutenyl monoamine (A1) with a number average molecular weight of from 550 to 1000 g/mol. The said polyisobutenyl monoamine is preferably based on ammonia and preferably prepared via hydroformylation of polyisobutene and subsequent reductive amination with ammonia, as described in EP-A 0 244 616.

The carrier oil (Component B)

The fuel-soluble, nonvolatile carrier oil of component (B) is to be used as a necessary part of the fuel additive composition of the instant invention in combination with components (A1) and/or (A2), in order to achieve the desired improvements. The carrier oil is a chemically inert hydrocarbon-soluble liquid vehicle. The carrier oil of component (B) may be a synthetic oil or a mineral oil; for the instant invention, a refined petroleum oil is also understood to be a mineral oil.

Such carrier oils (also called carrier fluids) are believed to act as a carrier for the fuel additives and to assist in removing and retarding deposits. The carrier oil (B) may also exhibit synergistic deposit control and deposit removing properties when used in combination with components (A) and (C) of the instant fuel additive composition.

The carrier oil of component (B) is typically employed in amounts ranging from about 50 to about 2,000 ppm by weight of the gasoline fuel, preferably from 100 to 800 ppm of the gasoline fuel. Preferably, the ratio of carrier oil (B) to nitrogen-containing dispersant (A1) or (A2) in the fuel additive composition as well as in the gasoline fuel will range from 0.5 : 1 to 10 : 1, typically from 1 : 1 to 4 : 1.

Examples for suitable mineral carrier oils are in particular those of viscosity class Solvent Neutral (SN) 500 to 2000, as well as aromatic and paraffinic hydrocarbons and alkoxyalkanols. Another useful mineral carrier oil is a fraction known as "hydrocrack oil" which is obtained from refined mineral oil (boiling point of approximately 360 to 500°C; obtainable from natural mineral oil which is isomerized, freed of paraffin components and catalytically hydrogenated under high pressure).

Examples for synthetic carrier oils which can be used for the instant invention are olefin polymers with a number average molecular weight of from 400 to 1,800 g/mol, based on poly-alpha-olefins or poly-internal-olefins, especially those based on polybutene or on polyisobutene (hydrogenated or nonhydrogenated). Further examples for suitable synthetic carrier oils are polyesters, polyalkoxyates, polyethers, alkylphenol-initiated polyethers, and carboxylic acids of long-chain alkanols.
Examples for suitable polyethers which can be used for the instant invention are compounds containing polyoxy-C2-C4-alkylene groups, especially polyoxy-C3-C4-alkylene groups, which can be obtained by reacting Cl-C30-alkanols, C2-C60-alkandiols, Cl-C30-alkylcyclohexanols or Cl-C30-alkylenphenols with 1 to 30 mol ethylene oxide and/or propylene oxide and/or butylene oxides per hydroxyl group, especially with 1 to 30 mol propylene oxide and/or butylene oxides per hydroxyl group. This type of compounds is described, for example, in EP-A 310 875, EP-A 356 725, EP-A 700 985 and US-A 4,877,416.

Typical examples for suitable polyethers are tridecanol propoxylates, tridecanol butyloxylates, isotridecanol butyloxylates, 2-propyleheptanol propoxylates, 2-propyleheptanol butyloxylates, isononylphenol butyloxylates, polyisobutenol butyloxylates and polyisobutenol propoxylates.

Hydrocarbyl-terminated poly(oxyalkylene) polymers which may be employed in the present invention as component (B), are monohydroxy compounds, i.e., alcohols, and are often termed monohydroxy polyethers, or polyalkylene glycol monohydrocarbyl-ethers, or "capped" poly(oxyalkylene).

The hydrocarbyl-terminated poly(oxyalkylene) alcohols may be produced by the addition of lower alkylene oxides, such as ethylene oxide, propylene oxide, the butylene oxides, or the pentylene oxides to the hydroxy compound under polymerization conditions. Methods of production and properties of these polymers are disclosed in U.S. Patents Nos. 2,841,479 and 2,782,240 and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd Ed. Volume 19, p. 507. In the polymerization reaction, a single type of alkylene oxide may be employed, e.g., propylene oxide, in which case the product is a homopolymer, e.g., a poly(oxyalkylene) propanol. However, copolymers are equally satisfactory and random copolymers are readily prepared by contacting the hydroxyl-containing compound with a mixture of alkylene oxides, such as a mixture of propylene and butylene oxides. Block copolymers of oxyalkylene units also provide satisfactory poly(oxyalkylene) polymers for the practice of the present invention. Random polymers are more easily prepared when the reactivities of the oxides are relatively equal. In certain cases, when ethylene oxide is copolymerized with other oxides, the higher reaction rate of ethylene oxide makes the preparation of random copolymers difficult. In either case, block copolymers can be prepared. Block copolymers are prepared by contacting the hydroxyl-containing compound with first one alkylene oxide, then the others in any order, or repetitively, under polymerization conditions. A particular block copolymer is represented by a polymer prepared by polymerizing propylene oxide on a suitable monohydroxy compound to form a poly(oxypropylene) alcohol and then polymerizing butylene oxide on the poly(oxyalkylene) alcohol.
In general, the poly(oxyalkylene) polymers are mixtures of compounds that differ in polymer chain length. However, their properties closely approximate those of the polymer represented by the average composition and molecular weight.

Examples of carboxylic esters of long-chain alkanols are esters of mono-, di- and tri-carboxylic acids with long-chain alkanols or polyhydric alcohols such as described e.g. in DE-A 38 38 918. Suitable mono-, di- and tricarboxylic acids are aliphatic or aromatic carboxylic acids. Suitable alkanols and polyhydric alcohols contain 6 to 24 carbon atoms. Typical examples of such esters are the adipates, phthalates, iso-phthalates, terephthalates and trimellitates of isooctanol, isononanol, isodecanol and isotridecanol, e.g. di-n-tridecyl phthalate or di-iso-tridecyl phthalate.

Examples for particularly useful synthetic carrier oils are alcohol-initiated polyethers containing about 5 to 35, e.g. 5 to 30 C3- to C6-alkylenoxide units, such as propylene oxide, n-butylene oxide and iso-butylene oxide units or mixtures thereof. Non-limiting examples for alcoholic starters are long-chain alkanols or phenols substituted by long-chain alkyl groups, where the alkyl group preferably is linear or branched C6- to C12-alkyl. Preferred examples for the alcoholic starters are tridecanol and nonylphenol.

Further suitable synthetic carrier oils are alkoxylated alkenophenols, such as described e.g. in DE-A 10 102 913.

Preferably, synthetic carrier oils are used. Preferred synthetic carrier oils are alkanol alkoxylates, in particular alkanol propoxylates and alkanol butoxylates.

In an especially preferred embodiment, carrier oil component (B) comprises at least one polyether obtained from C1- to C30-alkanols, especially C6- to C12-alkanols, or C2- to C60-alkandiols, especially C8- to C24-alkandiols, and from 1 to 30 mol, especially 5 to 30 mol, in sum, of propylene oxide and/or butylene oxides. Other synthetic carrier oils and/or mineral carrier oils may be present in component (B) in minor amounts.

The polyalkenylsuccinimide (Component C)

The hydrocarbonyl dicarboxylic acid producing reaction intermediate (1)

The reaction intermediate (1) typically comprises the reaction product of (a) a polyolefin comprising C2- to C18-olefin units and having a number average molecular weight (Mn) of about 500 to 5,000 g/mol, and (b) a C4- to C10-monounsaturated acid reactant. The polyolefin (a) and the monounsaturated acid reactant (b) can be reacted by way of various reaction mechanisms under various conditions to form the reaction intermediate (1).
For example, the reaction intermediate (1) can be formed via an "ene" reaction by heating a mixture of the polyolefin (a) and the monounsaturated acid reactant (b). In such an "ene" reaction, the polyolefin (a) undergoes an addition of the monounsaturated acid reactant (b) at a double bond. As another example, the polyolefin (a) can be first halogenated, for example, chlorinated or brominated with from 1 to 8, alternatively from 3 to 7 weight % chlorine or bromine, based on the weight of polyolefin (a). By passing the chlorine or bromine through the polyolefin (a) at a temperature of from 60 to 160°C, alternatively from 110 to 130°C, for from 0.5 to 10 hours, alternatively from 1 to 7 hours, a halogenated polyolefin is formed. The halogenated polyolefin is then reacted with the $c_1$ to $c_{10}$-monounsaturated acid reactant (b) at a temperature of from 100 to 250°C, alternatively from 180 to 235°C, for a time of from 0.5 to 10 hours, alternatively from 3 to 8 hours, to form the reaction intermediate (1).

The hydrocarbyl dicarboxylic acid producing reaction intermediate (1) typically comprises a polyolefin substituted with dicarboxylic acid producing moieties. Specifically, the reaction intermediate (1) is typically an acid, an anhydride, or ester which includes a long chain hydrocarbon derived from polyolefin (a), substituted typically with an average of from 0.5 to 10.0, alternatively from 0.5 to 5, alternatively from 1.2 to 2.0, alternatively from 1.3 to 1.8, alternatively from 1.4 to 1.7 mol, of the $c_1$ to $c_{10}$-monounsaturated acid reactant (b), i.e., dicarboxylic acid producing moieties, per mol of polyolefin (a). In one embodiment, the reaction intermediate (1) is a polyalkenylsuccinic anhydride, e.g. a polyisobutenylsuccinic anhydride. These functionality ratios of dicarboxylic acid producing moieties to polyolefin, e.g. 1.2 to 2.0, etc., are based upon the total amount of polyolefin (a) that is present in the resulting product formed in the aforementioned reactions.

The polyolefin (a)

The polyolefin (a) of the subject disclosure comprises $c_2$ to $c_{18}$, alternatively $c_2$ to $c_{10}$, alternatively $c_2$ to $c_5$, alternatively $c_2$ to $c_6$-olefin units. Non-limiting examples of olefin units include ethylene, propylene, butylene, isobutylene, pentene, octene-1, and styrene. Typically, the polyolefin (a) is a polyalkene. The polyolefin (a) can be a homopolymer, such as a polyisobutylene, or a copolymer of two or more of different olefin units. Non-limiting examples of copolymers which can be used to form the polyolefin (a) include ethylene and propylene, butylene and isobutylene, propylene and isobutylene. Additional non-limiting examples of copolymers include copolymers that comprise a minor molar amount of olefin units, e.g. 1 to 10 mol %, are $c_4$ to $c_{10}$-non-conjugated diolefin units such as a copolymer of isobutylene and butadiene or a copolymer of ethylene, propylene, and 1,4-hexadiene.

The polyolefin (a) can be linear or branched. Typically, the polyolefin (a) has a number average molecular weight ($M_n$) of from 500 to 5,000, alternatively from 750 to 4,000, alternatively from 1,000 to 3,000, alternatively from 1,000 to 2,000 g/mol.
The polyolefin (a) can be saturated or unsaturated. One non-limiting example of the polyolefin (a) which is saturated is an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight. However, the polyolefin (a) is typically unsaturated. In a preferred embodiment, the polyolefin (a) includes a terminal double bond.

To this end, in one embodiment, the polyolefin (a) is a reactive polyisobutene. The reactive polyisobutene is typically a highly reactive polyisobutene which has a high content of terminal ethylenic double bonds. Terminal double bonds are alpha-olefinic double bonds, e.g. vinylidene double bonds. The reactive polyisobutene typically has a content of terminal double bonds of greater than 50, alternatively greater than 70, alternatively greater than 80, alternatively greater than 85 mol %. The reactive polyisobutene typically has a uniform polymer backbone which includes greater than 85, alternatively greater than 90, alternatively greater than 95 % by weight of isobutene units.

The reactive polyisobutene typically has a number average molecular weight \( (M_n) \) of from 500 to 5,000, alternatively from 800 to 4,000, alternatively from 800 to 3,000, alternatively from 800 to 2,000 g/mol. The dispersity \( D \) \( (M_w/M_n) \), i.e., the quotient of the weight average molecular weight \( M_w \) divided \( M_n \), of the reactive polyisobutene is less than 7, alternatively less than 3, alternatively from 1.05 to 7. In a preferred embodiment, the dispersity \( D \) \( (M_w/M_n) \) of the reactive polyisobutene is less than 3. A reactive polyisobutene having a dispersity of less than 2.0 for \( M_n \), less than or equal to 2,000 and less than 1.5 for \( M_w \), less than or equal to 1,000 is preferred. The reactive polyisobutene is typically free of organic and inorganic bases, water, alcohols, ethers, acids and peroxides.

Suitable non-limiting examples of the said reactive polyisobutene are commercially available from BASF SE under the GLISSOPAL® brand of polyisobutenes.

The \( \text{C}_4 \text{- to C}_{10} \) monounsaturated acid reactant (b)

The \( \text{C}_4 \text{- to C}_{10} \) monounsaturated acid reactant (b) reacts with the polyolefin (a) to form the reaction intermediate (1). The monounsaturated acid reactant (b) is typically an alpha- or beta-unsaturated \( \text{C}_4 \text{- to C}_{10} \) dicarboxylic acid, anhydride or ester thereof. Non-limiting examples of the \( \text{C}_4 \text{- to C}_{10} \) monounsaturated acid reactant (b) include fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, and combinations thereof.

In one embodiment, the \( \text{C}_4 \text{- to C}_{10} \) monounsaturated acid reactant (b) is selected from the group of maleic acid, maleic anhydride, functional derivatives thereof, and combinations thereof. The term functional derivative describes derivatives of maleic acid or maleic anhydride which react with the polyolefin (a) to form the same or a comparable
result or product, i.e., the reaction intermediate (1). In the case of maleic acid, functional derivatives include, for example, monoalkyl maleates, dialkyl maleates, maleyl dichloride, maleyl dibromide, maleic acid monoalkyl ester monochloride, or maleic acid monoalkyl ester monobromide. The alcohol components in the case of the maleates are, for example, lower alkyl radicals of, for example, 1 to 6, in particular 1 to 4 carbon atoms, for example methyl or ethyl or n-butyl. In a preferred embodiment, the monounsaturated acid reactant (b) is maleic anhydride. In one embodiment, maleic anhydride is reacted with the reactive polyisobutene to form the reaction intermediate (1) comprising polyisobutenylsuccinic anhydride.

The nucleophilic reactant (2)

As set forth above, the instant polyalkenylsuccinimide comprises the reaction product of the hydrocarbyl dicarboxylic acid producing reaction intermediate (1) and the nucleophilic reactant (2). Typically, the instant polyalkenylsuccinimide is formed via a neutralization reaction of the nucleophilic reactant (2) with the hydrocarbyl dicarboxylic acid producing reaction intermediate (1). The nucleophilic reactant (2) is typically selected from the group of amines, alcohols, amino alcohols, and combinations thereof.

The nucleophilic reactant (2) can be a monoamine, an oligoamine or a polyamine. Since tertiary amines are generally unreactive with anhydrides, it is desirable to have at least one primary or secondary amine group on the amine.

The nucleophilic reactant (2) can comprise an amine having formula 1a or 1b immediately below:

\[ R-N-R' \]  
(1a)

\[ R-N(CH_2)_X-[\text{NH}-(CH_2)_X]-N-R' \]  
(1b)

wherein R, R', and R'' are independently selected from the group consisting of hydrogen, C1- to C12-straight or branched chain alkyl radicals, C1- to C12-alkoxy, C2- to C6-alkylene radicals, C2- to C12-hydroxy amino alkylene radicals, and C2- to C12-alkylamino alkylene radicals; each X can be the same or a different number of from 2 to 6, alternatively from 2 to 4; and Y is a number from 0 to 10, alternatively from 2 to 7, alternatively from 3 to 7.
In a preferred embodiment, the nucleophilic reactant (2) comprises an amine having Formula II:

\[
\text{H}_x\text{N(CH}_2\text{x-NH-[(CH}_2\text{)_y-NH]}_z\text{-(CH}_2\text{)}_x\text{NH}_2 \quad \text{(II)}
\]

where \(x\) and \(y\) are each independently an integer from 1 to 5, alternatively from 2 to 4, and \(z\) is an integer from 0 to 8, or mixtures thereof.

The nucleophilic reactant (2) can comprise an alkylenepolyamine, such as a methylenepolyamine, ethylenepolyamine, butylenepolyamine, propylenepolyamine and pentylenepolyamine. In various embodiments, the alkylenepolyamine can comprise from 2 to 40, alternatively from 2 to 20, alternatively from 2 to 12, alternatively from 2 to 6 total carbon atoms and from 1 to 12, alternatively from 2 to 12, alternatively from 2 to 9, alternatively from 3 to 9 nitrogen atoms per molecule. To form the instant polyalkenylsuccinimide of such embodiments, from 0.1 to 3.0, alternatively from 0.1 to 2.0, alternatively from 0.2 to 1.0, alternatively from 0.2 to 0.6 mol of succinic moieties are typically reacted per equivalent of the nucleophilic reactant (2), e.g. amine, to form the instant polyalkenylsuccinimide.

The nucleophilic reactant (2) can also comprise a polyoxyalkylene polyamine, e.g. polyoxyalkylene amines, polyoxyalkylene diamines, and polyoxyalkylene trimamines which have a number average molecular weight (\(M_n\)) of from 200 to about 4000, alternatively from 400 to 2000 g/mol. Non-limiting examples of polyoxyalkylene polyamines include the polyoxyethylene, polyoxypropylene diamines, and the polyoxypropylene trimamines having a number average molecular weight (\(M_n\)) of from 200 to 2000 g/mol.

Furthermore the amine groups may be substituted, preferably by alkyl groups, very preferably by C1-C4-alkyl groups. Hence, further examples comprise N-substituted polyoxyalkylene amines, \(N_N_N',N'-teta\) alkyl substituted polyoxyalkylene diamines, and \(N_N,N',N',N',N'-hexa\) alkyl substituted polyoxyalkylene trimamines which have a number average molecular weight (\(M_n\)) of from 200 to about 4000, alternatively from 400 to 2000 g/mol.

The nucleophilic reactant (2) can also comprise a hydrocarbyl amine or a hydrocarbyl amine which includes other functional groups, e.g. hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, etc. For example, in one embodiment, the nucleophilic reactant (2) comprises a hydrocarbyl amine with from 1 to 6, alternatively from 1 to 3 hydroxy groups. Such amines are capable of reacting with the acid or anhydride groups of the reaction intermediate (1) via their amine functional groups or the other functional groups (described immediately above). Specific, non-limiting examples of the nucleophilic reactant (2) include hydroxyamines such as 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, \(p\)-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol,
The nucleophilic reactant (2) can also comprise an unsaturated alcohol such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding the instant polyalkenylsuccinimide of this disclosure include ether-alcohols and amino-alcohols, e.g. the oxyalkylene, oxyarylene-, aminoalkylene-, and aminoarylene-substituted alcohols having one or more oxyalkylene, aminoalkylene or aminoarylene oxyarylene radicals exemplified by N,N,N',N'-tetrahydroxy-trimethylene diamine, and ether-alcohols having up to about 150 oxyalkylene radicals in which the alkyene radical includes from 1 to about 8 carbon atoms.

Additional non-limiting examples of the nucleophilic reactant (2) include alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines. Specific, non-limiting examples of such amines include 2-pentadecyl imidazoline, N-(2-aminoethyl) piperazine, and combinations thereof.

In one embodiment, the nucleophilic reactant (2) comprises a polyamine selected from the group of ethylenediamine, triethylenetetramine, propylenediamine, trimethyleneamine, tripropylenetetramine, tetraethylenepentamine, hexaethylenepentamine, pentaethylenepentamine, and combinations thereof. In this embodiment, the nucleophilic reactant (2) can be the reaction product of ethylene dichloride and ammonia or the reaction product of an ethyleneimine with a ring-opening agent, for example water or ammonia.

In another embodiment, the nucleophilic reactant (2) comprises an ethylene polyamine, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine. In this embodiment, the ethylene polyamine can be the reaction product of an alkylene chloride with ammonia or an ethylene imine with ammonia. These reactions result in a mixture of alkylene polyamines, including cyclic products such as piperazines.

Obviously, combinations of the various types and specific embodiments and examples of the nucleophilic reactant (2) referenced above can be reacted with the reaction intermediate (1) to form the instant polyalkenylsuccinimide.

The instant polyalkenylsuccinimide of the subject disclosure is broadly defined herein to include polyalkenylsuccinimides (e.g. polyisobutenylsuccinimides), diesters of sue-
cinic acids or acidic esters (e.g. partially esterified succinic acids), and also partially esterified polyhydric alcohols or phenols, e.g. esters having free alcohols or phenolic hydroxyl radicals.

The instant polyalkenylsuccinimide can be, or include, a polyisobutenylsuccinimide which includes monosuccinimides and bissuccinimides. A ratio of monosuccinimides to bissuccinimides in the polyisobutenylsuccinimide can be influenced, for example, by the varying the molar ratio of the reaction intermediate (1), e.g. polyisobutenylsuccinic anhydride, to the nucleophilic reactant (2), e.g. amine, reacted to form the polyalkenylsuccinimide, e.g. polyisobutenylsuccinimide. The larger the molar amount of the reaction intermediate (1), e.g. polyisobutenylsuccinic anhydride in relation to the the nucleophilic reactant (2), e.g. amine, the larger the resulting amounts of monosuccinimide, and vice versa. In order to obtain a higher proportion of monosuccinimide, a molar ratio of the reaction intermediate (1), e.g. polyisobutenylsuccinic anhydride, to the nucleophilic reactant (2), e.g. amine, of from 0.7 to 1.3, alternatively from 0.9 to 1.1, is typically employed. In order to obtain a higher proportion of bissuccinimide, a molar ratio of the reaction intermediate (1), e.g. polyisobutenylsuccinic anhydride, to the nucleophilic reactant (2), e.g. amine, of from 3 to 18, alternatively from 2.3 to 1.9, is typically employed. A polyalkenylsuccinimide, e.g. polyisobutenylsuccinimide, having a higher monosuccinimide content is particularly suitable as an additive for fuels (diesel fuel, heating oil, gasoline fuel), while a polyalkenylsuccinimide, e.g. polyisobutenylsuccinimide, having a higher content of bissuccinimides is particularly suitable as an additive for lubricants.

To form the instant polyalkenylsuccinimide, the nucleophilic reactant (2), e.g. amines described above, can be reacted with the reaction intermediate (1), e.g. alkenylsuccinic anhydride, by heating an oil solution including 5 to 95 weight % of the reaction intermediate (1) to a temperature of from 100 to 200°C, alternatively from 125 to 175°C, for a time of from 0.5 to 10 hours, alternatively 1 to 6 hours, to remove any residual water and adding the nucleophilic reactant (2). The step of heating the reaction intermediate (1) can facilitate formation of imides or mixtures of imides and amides, rather than amides and salts. The reaction ratios of the reaction intermediate (1) to equivalents of amine as well as the other nucleophilic reactants (2) described herein can vary considerably, depending upon the reactants and type of bonds formed. Typically, from 0.1 to 2.0, alternatively from 0.1 to 2.0, alternatively from 0.2 to 0.6 mol of dicarboxylic acid moiety content (e.g. grafted maleic anhydride content) is used, per equivalent of nucleophilic reactant (2), e.g. amine. For example, about 0.8 mol of a pentamine (having two primary amino groups and 5 equivalents of nitrogen per molecule) can be used to form a mixture of amides and imides, the product formed by reacting one mol of olefin with sufficient maleic anhydride to add 1.6 mol of succinic anhydride groups per mol of olefin, i.e., preferably the pentamine is used in an amount sufficient to provide about 0.4 mol (that is 1.6/(0.8 × 5) mol) of succinic anhydride moiety per nitrogen equivalent of the amine.
In one specific embodiment, the instant polyalkenylsuccinimide is formed from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g. tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxy-propylene amines, e.g. polyoxypropylene diamine, tris(methylolaminomethane and pentaerythritol, and combinations thereof. As one example, the instant polyalkenylsuccinimide can be formed by reacting a polyisobutene substituted with succinic anhydride groups with a hydroxy compound, e.g. pentaerythritol, a polyoxyalkylene polyamine, e.g. polyoxypropylene diamine, and a polyalkylene polyamine, e.g. polyethylene diamine and tetraethylene pentamine.

In another embodiment, the instant polyalkenylsuccinimide comprises the reaction product of a polyisobutenylsuccinic anhydride, a first amine, and an alcohol. The polyisobutenylsuccinic anhydride, the first amine, and the alcohol are typically reacted at a temperature of from 50 to 200°C, alternatively 80 to 180°C, alternatively 80 to 160°C, alternatively 100 to 160 °C, to form the polyisobutenylsuccinimide.

The first amine typically has the following formula:

$$H_2N(CH_2)x-NH-[(CH_2)y-NH]_z(CH_2)xNH_2$$

where x and y are each independently an integer from 1 to 5, alternatively from 2 to 4, and z is an integer from 0 to 8, or mixtures thereof.

The alcohol is selected from the group consisting of monohydric alcohols of the formula R^4OH, where R^4 is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16 carbon atoms, and combinations thereof. The alcohol is typically a monohydric alcohol, but polyhydric alcohol is also suitable. The alcohol is typically a monohydric alcohol of the formula R^4OH, where R^4 is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16, alternatively 6 to 16 carbon atoms.

Specific, non-limiting examples of the alcohol include methanol, ethanol, n-propanol, isopropanol, cyclopropylcarbinol, n-butanol, sec-butanol, isobutanol, tert-butanol, 2-hydroxymethylfuran, amyl alcohol, isoamyl alcohol, vinylcarbinol, cyclohexanol, n-hexanol, 4-methyl-2-pentanol, 2-ethylbutyl alcohol, sec-capryl alcohol, 2-ethylhexanol, n-decanol, lauryl alcohol, isocetyl alcohol and mixtures thereof. In one embodiment, the alcohol is 2-ethylhexanol. Additional specific, non-limiting examples of the alcohol include phenol, naphthol, (o,p)-alkylphenols, e.g. di-tert-butylphenol, and salicylic acid.

The molar ratio of the polyisobutenylsuccinic anhydride to the alcohol can vary. It is not necessary to use stoichiometric amounts of the alcohol, and even comparatively small molar amounts of the alcohol can be sufficient to form the polyisobutenylsuccinimide. A
typical molar ratio of the polyisobutenylsuccinic anhydride to alcohol is from 10 to 0.5, alternatively from 4 to 0.8.

In this embodiment, the polyisobutenylsuccinic anhydride can be first reacted with the alcohol, then reacted with the first amine to form the polyisobutenylsuccinimide. More specifically, the polyisobutenylsuccinic anhydride can be first reacted with the alcohol to form a second reaction intermediate comprising a monoester of polyisobutenylsuccinic acid, which is then reacted with the first amine. In this embodiment, the polyisobutenylsuccinic anhydride and the alcohol are combined in a reaction vessel. After the polyisobutenylsuccinic anhydride and the alcohol react, the first amine can be introduced into the reaction vessel. After the reaction, any alcohol, which is either unreacted or cleaved, can be removed in a conventional manner.

In a specific embodiment, the second reaction intermediate comprises the reaction product of the reactive polyisobutene having a molecular weight $M_n$ of from 500 to 5,000 g/mol and a content of terminal double bonds of greater than 50, alternatively greater than 70 mol %, maleic anhydride, and the alcohol (3) selected from the group consisting of monohydrad alcohols of the formula $R^4OH$, where $R^4$ is straight-chain or branched, cyclic or branched cyclic alkyl of 1 to 16 carbon atoms.

The second reaction intermediate which is formed during the formation of the polyisobutenylsuccinimide can, if desired, also be isolated. The reaction intermediate is not only useful in the formation of the instant polyalkenylsuccinimid, but, alone or in combination with other additives, can also be used as additives for fuels or lubricants.

Alternatively in this embodiment, isolation of the second reaction intermediate is not necessary. That is, the polyisobutenylsuccinic anhydride, the first amine and the alcohol are reacted simultaneously, i.e., in a single step to from the polyisobutenylsuccinimide. After the reaction, any alcohol, which is either unreacted or cleaved, can be removed in a conventional manner.

In another embodiment, the instant polyalkenylsuccinimide can be the reaction product of the reactive polyisobutene having a molecular weight ($M_n$) of from 500 to 5,000 g/mol and a content of terminal double bonds of greater than 50, alternatively greater than 75 mol %, maleic anhydride, and the first amine (2) having the formula:

$$H_2N(CH2)_{x-y}-NH-[(CH2)_y-NH]_z-(CH2)_xNH_2$$

where $x$ and $y$ are each independently an integer from 1 to 5, alternatively from 2 to 4, and $z$ is an integer from 0 to 8, or mixtures thereof.

In another embodiment, the instant polyalkenylsuccinimide comprises the reaction product of the reactive polyisobutene having a number average molecular weight ($M_n$)
of from 500 to 5,000 g/mol and a content of terminal double bonds of greater than 50, alternatively greater than 70 mol %, maleic anhydride, and a linear, branched, cyclic or cyclic branched alkyleneopolyamine having 1 to 10, alternatively 2 to 4, carbon atoms in each alkylene group and 1 to 12, alternatively 2 to 12, alternatively 2 to 9, alternatively 3 to 9 nitrogen atoms, of which at least one nitrogen atom is present as a primary amino group, or mixtures thereof, including less than 30% by weight, based on the total weight of the product, of the corresponding polyisobutylsuccinamide.

In another embodiment, the instant polyalkenylsuccinimide comprises the reaction product of the reaction intermediate (1), e.g. polyisobutylsuccinic anhydride, and the nucleophilic reactant (2) comprising a C2- to C40-, alternatively C2- to C20-, alternatively C2- to C12-polyalkylene polyamine which includes from 2 to 12, alternatively 2 to 9, alternatively 3 to 9 nitrogen atoms per molecule an amine. To form the instant polyalkenylsuccinimide, e.g. polyisobutylsuccinimide, of this embodiment, 0.1 to 3.0, alternatively 0.2 to 1.0, alternatively 0.2 to 0.6 mol of succinic moieties are reacted per equivalent of the nucleophilic reactant (2), e.g. amine, to form the polyalkenylsuccinimide.

In a typical embodiment, the instant polyalkenylsuccinimide has the following structure:

![Structure Image]

wherein m is an integer of from 2 to 80, alternatively from 2 to 40, alternatively from 2 to 20, alternatively from 6 to 16. A typical example for such polyisobutylsuccinimide is a polyisobutylsuccinimide made from polyisobutylsuccinanhydride with a polyisobutyl radical of $M_n = 1000$ and tetraethylenepentamine.

The instant polyalkenylsuccinimide of the subject disclosure typically includes a minimal amount of corresponding amides (polyisobutylsuccinimide or polyisobutylsuccinic acid monoamide). More specifically, the instant polyalkenylsuccinimide typically includes less than 30, alternatively less than 25, alternatively less than 20, alternatively less than 15 % by weight corresponding amides, based on the total weight of the instant polyalkenylsuccinimide, of the corresponding amides. In addition, the instant polyalkenylsuccinimide typically includes no ester fractions, even when the polyalkenylsuccinimide comprises the reaction product of the reaction intermediate (1), the nucleophilic reactant (2), and the alcohol (3), as defined above, and the reaction with the alcohol (3) is carried out in an intermediate stage. Increased purity (minimal corresponding amides/amide bi-products and lack of ester fractions) of the instant poly-
alkenylsuccinimide be attributed to the process by which the polyalkenylsuccinimide is formed.

The instant polyalkenylsuccinimide typically has a number average molecular weight (Mn) of greater than 500, alternatively greater than 800, alternatively greater than 1,000, alternatively from 500 to 5,000, alternatively from 750 to 5,000, alternatively from 1,000 to 4,000, alternatively from 1,000 to 3,000, g/mol. A hydrophobic moiety of such molecules known in the art may be derived from synthetic or natural mono or oligo fatty acids with a chain length of typically C12 to C20. Preferably the instant polyalkenylsuccinimide, as is described above, is formed form the reactive polyisobutene typically having a chain length of C40 to C400, alternatively from C40 to C200, and a number average molecular weight (Mn) of from 500 to 5,000 g/mol.

The fuel additive composition

The present fuel additive composition of component (A), (B), (C) and optionally (D) normally comprises from 5 to 75% by weight, preferably from 25 to 50% by weight of (A), from 5 to 75% by weight, preferably from 25 to 50% by weight of (B), from 1 to 90% by weight, preferably from 2 to 25% by weight of (C) and from 0 to 40% by weight, preferably from 0.5 to 40% by weight of (D). In each case, the sum of the amounts of all four components (A), (B), (C) and (D) results in 100% by weight.

The present fuel additive composition may be formulated as a concentrate, using an inert stable oleophilic (i.e., dissolves in fuel) organic solvent boiling in the range of about 65°C to 300°C. Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol, 2-ethylhexanol, and the like, in combination with hydrocarbon solvents, are also suitable for use in such concentrate.

The present fuel additive composition may or may not contain suitable friction modifier components (D), which are sometimes also called lubricity additives. Such friction modifier components, if any, are usually selected from fatty acids, alkenylsuccinic esters, bis-(hydroxyalkyl)fatty amines, hydroxylacetamides or castor oil. Such products are commercially available. Special suitable friction modifiers are also the reaction products from carboxylic acids and alkanolamines, as described in WO 2009/050256, and nitrogen-containing heterocycles such as tolutriazoles, as described in WO 2006/015800. The instant polyalkenylsuccinimide components (C) themselves may also function as friction modifiers. For the avoidance of doubt, friction modifier components (D), if any, are in each case different from polyalkenylsuccimide components (C).
In the concentrate, the amount of the present fuel additive composition of components (A), (B), (C) and optionally (D) will be ordinarily at least 10% by weight to about 90% by weight, as for example 40 to 85 weight percent or 50 to 80 weight percent.

In gasoline fuels, other fuel additives may be employed with the additives of the present invention, including, for example, oxygenates, such as tert.-butyl methyl ether, antiknock agents, such as methycyclopentadienyl manganese tricarbonyl, and other dispersants/detergents, such as various hydrocarbyl amines, polyether amines or Mannich reaction products. A list of suitable other detergent additives is for example given in WO 00/47698 or in EP-A 1 155 102.

Also included may be lead scavengers, such as aryl halides, e.g., dichlorobenzene, or alkyl halides, e.g., ethylene dibromide. In addition, antioxidants, metal deactivators, pour point depressants, corrosion inhibitors and demulsifiers may be present.

Preferably, the weight ratio of dispersant component (A) to amine component (C) is in the range of from 0.3 : 1 to 25 : 1, especially of from 1 : 1 to 15 : 1, thus providing the best improvement of deposit control performance of gasoline fuels.

An interaction between components (A), (B), (C) and optionally (D) is necessary to achieve the desired improvement in deposit control performance. In the instant fuel additive composition, the tertiary amine (C) may exhibit a synergistic effect in this respect when used in combination with components (A), (B) and optionally (D) of the present fuel additive composition.

The fuel composition

The fuel additive composition of the present invention will generally be employed in a liquid hydrocarbon distillate fuel boiling in the gasoline range. It is in principle suitable for use in all types of gasoline, including "light" and "severe" gasoline species. The gasoline fuels may also contain amounts of other fuels such as, for example, ethanol.

The proper concentration of the instant fuel additive composition necessary in order to achieve the desired intake valve clean-up performance varies depending upon the type of fuel employed, and may also be influenced by the presence of other detergents, dispersants and other additives, etc. Generally, however, from 200 to 10,000 weight ppm by weight, especially from 400 to 2800 weight ppm by weight, of the instant fuel additive composition of components (A), (B), (C) and optionally (D) per part of base fuel is needed to achieve the best results.

In a preferred embodiment of the present invention, dispersant component (A) is present in the present fuel composition at a level of from more than 50 to 3000 ppm, preferably from 75 to 1000 ppm, more preferably from 100 to 750 ppm, most preferably
from 125 to 500 ppm, carrier oil component (B) at a level of from 50 to 2000 ppm, preferably from 75 to 800 ppm, more preferably from 100 to 600 ppm, most preferably from 125 to 400 ppm, hydrocarbyl amine component (C) at a level of from 10 to 3000 ppm, preferably from 20 to 1000 ppm, more preferably from 30 to 500 ppm, most preferably from 45 to 300 ppm, and friction modifier component (D), if present, at a level of from 5 to 2000 ppm, preferably from 10 to 800 ppm, more preferably from 25 to 500 ppm, most preferably from 40 to 300 ppm. All ppm values above refer to the weight.

Typically, gasoline fuels, which may be used according to the present invention exhibit, in addition, one or more of the following features:

The aromatics content of the gasoline is preferably not more than 50 volume % and more preferably not more than 45 volume %. Preferred ranges for the aromatics content are from 1 to 45 volume % and particularly from 5 to 40 volume %.

The sulfur content of the gasoline is preferably not more than 100 ppm by weight and more preferably not more than 50 ppm by weight. Preferred ranges for the sulfur content are from 0.5 to 150 ppm by weight and particularly from 1 to 100 ppm by weight.

The gasoline has an olefin content of not more than 21 volume %, preferably not more than 18 volume %, and more preferably not more than 10 volume %. Preferred ranges for the olefin content are from 0.1 to 21 volume % and particularly from 2 to 18 volume %.

The gasoline has a benzene content of not more than 1.0 volume % and preferably not more than 0.9 volume %. Preferred ranges for the benzene content are from 0 to 1.0 volume % and preferably from 0.05 to 0.9 volume %.

The gasoline has an oxygen content of not more than 45 weight %, preferably from 0 to 45 weight %, and most preferably from 0.1 to 2.7 weight % (first type) or most preferably from 2.7 to 45 weight % (second type). The gasoline of the second type mentioned above is a mixture of lower alcohols such as methanol or especially ethanol, which derive preferably from natural source like plants, with mineral oil based gasoline, i.e. usual gasoline produced from crude oil. An example for such gasoline is "E 85", a mixture of 85 volume % of ethanol with 15 volume % of mineral oil based gasoline. Also a fuel containing 100 % of a lower alcohol, especially ethanol, is suitable.

The content of alcohols, especially lower alcohols, and ethers in a gasoline of the first type mentioned in the above paragraph is normally relatively low. Typical maximum contents are for methanol 3 volume %, for ethanol 5 volume %, for isopropanol 10 volume %, for tert-butanol 7 volume %, for iso-butanol 10 volume %, and for ethers containing 5 or more carbon atoms in the molecule 15 volume %.
For example, a gasoline which has an aromatics content of not more than 38 volume % and at the same time an olefin content of not more than 21 volume %, a sulfur content of not more than 50 ppm by weight, a benzene content of not more than 1.0 volume % and an oxygen content of from 0.1 to 2.7 weight % may be applied.

The summer vapor pressure of the gasoline is usually not more than 70 kPa and preferably not more than 60 kPa (at 37°C).

The research octane number ("RON") of the gasoline is usually from 90 to 100. A usual range for the corresponding motor octane number ("MON") is from 80 to 90.

The above characteristics are determined by conventional methods (DIN EN 228).

Experimental Part

The following examples are presented to illustrate specific embodiments of this invention and are not to be construed in any way as limiting the scope of the invention.

Determination of injector cleanliness with a direct injection spark ignition engine:

According to an internal BASF test procedure, a loaded commercially available four-cylinder direct injection spark ignition engine (1.6 liters cylinder capacity) was run with a commercially available gasoline fuel containing 7 volume % of oxygen-containing components, during 50 hours. In Run 1, the fuel contained 75 ppm by weight of a polyisobutenylsuccinimide made from polyisobutenylsuccinanhydride with a polyisobutenyl radical of $M_n = 1000$ and tetraethylenepentamine. In Run 2 (for comparison), the same fuel did not contain any polyalkenylsuccinimide. Furthermore, the fuel used contained 150 ppy by weight of a usual nitrogen-containing dispersant (A) and 185 ppm by weight of a usual carrier oil.

In both Runs, the "FR" value was determined. FR is a parameter generated by engine steering, corresponding to the time of the process of injection of the fuel into the combustion chamber. If FR increases during a run, the injection nozzles suffer deposits, the more increase the more deposits. If FR is kept constant or decreases during a run, the injection nozzles stays free of deposits.

As a result, in Run 1 the FR value decreased by 2 % from the beginning to the end of the run, and in Run 2 the FR value increased by 2 % from the beginning to the end of the run.
Claims

1. Use of an effective concentration of a polyalkenylsuccinimide comprising the reaction product of (1) a hydrocarbyl dicarboxylic acid producing reaction intermediate and (2) a nucleophilic reactant, as an additive in an unleaded gasoline composition suitable in spark ignition engines, for reducing injector nozzle fouling in direct injection spark ignition engines.

2. The use according to Claim 1, wherein said hydrocarbyl dicarboxylic acid producing reaction intermediate (1) comprises the reaction product of (a) a polyolefin comprising C2- to C8-olefin units and having a number average molecular weight (Mn) of about 500 to 5,000 g/mol, and (b) a C4- to C10-monounsaturated acid reactant, wherein said hydrocarbyl dicarboxylic acid producing reaction intermediate includes from 0.5 to 10 dicarboxylic acid producing moieties per molecule of said polyolefin.

3. The use according to Claim 2, wherein said C4- to C10-monounsaturated acid reactant (b) is selected from the group of maleic acid, maleic anhydride, functional derivatives thereof and combinations thereof.

4. The use according to any of the preceding Claims, wherein said polyolefin (a) is a reactive polyisobutene having a content of terminal double bonds of greater than 50 mol-%.

5. The use according to any of the preceding Claims, wherein said hydrocarbyl dicarboxylic acid producing reaction intermediate (1) is a polyisobutenylsuccinic anhydride.

6. The use according to any of the preceding Claims, wherein said nucleophilic reactant (2) is selected from the group of amines, alcohols, amino alcohols and combinations thereof.

7. The use according to Claim 6, wherein said nucleophilic reactant (2) comprises tetraethylenepentamine.

8. A fuel additive composition essentially comprising:
24

(A) at least one nitrogen-containing dispersant selected from (A1) polyisobutenyl monoamines and (A2) polyisobutenyl polyamines;

(B) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils; and

(C) at least one polyalkenylsuccinimide according to Claims 1 to 7, comprising the reaction product of (1) a hydrocarbyl dicarboxylic acid producing reaction intermediate and (2) a nucleophilic reactant.

9. The fuel additive composition according to Claim 8, wherein said dispersant component (A) is a polyisobutenyl monoamine (A1) with a number average molecular weight (M_n) of from 550 to 1000 g/mol.

10. The fuel additive composition according to Claims 8 or 9, wherein the weight ratio of dispersant component (A) to polyalkenylsuccinimide component (C) is in the range of from 0.3 : 1 to 25 : 1.

11. A fuel composition comprising a major amount of a liquid fuel in gasoline boiling range and a minor amount of a fuel additive composition according to Claims 8 to 10.

12. The fuel composition according to Claim 11, wherein dispersant component (A) is present at a level of from more than 50 to 3000 ppm, carrier oil component (B) at a level of from 50 to 2000 ppm and polyisobutenylsuccinimide component (C) at a level of from 10 to 3000 ppm.
A. CLASSIFICATION OF SUBJECT MATTER

INV. ClOIL/18
ADD.

According to International Patent Classification (IPC) into both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOL

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>CN 1 594 513 A (XIAMEN WEIHUAN CLEAN OIL TECHN [CN]) 16 March 2005 (2005-03-16) claim 1; examples 3, 7, 8</td>
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<td>Wo 2009/074608 Al (BASF SE [DE]; VÖELKEL LUDWIG [DE]; SCHREYER PETER [DE]; LOCKEMANN CHRIST) 18 June 2009 (2009-06-18) cited in the application on page 2, line 30 - line 34 page 13, line 21; claim 1</td>
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[ ] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search

30 September 2014

Date of mailing of the international search report

09/10/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, 340-2049, Fax (+31-70) 340-3016

Klaes, Daphne

Form PCT/ISA/210 (second sheet) (April 2005)
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