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Use of quaternised alkyl amines as additives in fuels and lubricants

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Abstract

The present invention relates to the use of quaternized alkylamine nitrogen compounds as a fuel additive and lubricant additive, such as, more particularly, as a detergent
5 additive; for reduction or prevention of deposits in the injection systems of direct injection diesel engines, especially in common rail injection systems, for reduction of the fuel consumption of direct injection diesel engines, especially of diesel engines with common rail injection systems, and for minimization of power loss in direct injection diesel engines, especially in diesel engines with common rail injection systems; and as
10 an additive for gasoline fuels, especially for operation of DISI engines.

Use of quaternized alkylamines as additives in fuels and lubricants

The present application is a divisional application from Australian Patent Application No. 2012351671, herein incorporated by reference in its entirety.

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The present invention relates to the use of quaternized alkylamine nitrogen compounds as a fuel additive and lubricant additive, such as, more particularly, as a detergent additive; for reduction or prevention of deposits in the injection systems of direct injection diesel engines, especially in common rail injection systems, for reduction of the fuel consumption of direct injection diesel engines, especially of diesel engines with common rail injection systems, and for minimization of power loss in direct injection diesel engines, especially in diesel engines with common rail injection systems; and as an additive for gasoline fuels, especially for operation of DISI engines.

15 State of the art:

In direct injection diesel engines, the fuel is injected and distributed ultrafinely (nebulized) by a multihole injection nozzle which reaches directly into the combustion chamber of the engine, instead of being introduced into a prechamber or swirl chamber as in the case of the conventional (chamber) diesel engine. The advantage of the direct injection diesel engines lies in their high performance for diesel engines and nevertheless low fuel consumption. Moreover, these engines achieve a very high torque even at low speeds.

25 At present, essentially three methods are being used for injection of the fuel directly into the combustion chamber of the diesel engine: the conventional distributor injection pump, the pump-nozzle system (unit-injector system or unit-pump system), and the common rail system.

30 In the common rail system, the diesel fuel is conveyed by a pump with pressures up to 2000 bar into a high-pressure line, the common rail. Proceeding from the common rail, branch lines run to the different injectors which inject the fuel directly into the combustion chamber. The full pressure is always applied to the common rail, which enables multiple injection or a specific injection form. In the other injection systems, in

contrast, only smaller variation in the injection is possible. The injection in the common rail is divided essentially into three groups: (1.) pre-injection, by which essentially softer combustion is achieved, such that harsh combustion noises ("nailing") are reduced and the engine seems to run quietly; (2.) main injection, which is responsible especially for a good torque profile; and (3.) post-injection, which especially ensures a low NO_x value. In this post-injection, the fuel is generally not combusted, but instead vaporized by residual heat in the cylinder. The exhaust gas/fuel mixture formed is transported to the exhaust gas system, where the fuel, in the presence of suitable catalysts, acts as a reducing agent for the nitrogen oxides NO_x .

The variable, cylinder-individual injection in the common rail injection system can positively influence the pollutant emission of the engine, for example the emission of nitrogen oxides (NO_x), carbon monoxide (CO) and especially of particulates (soot). This makes it possible, for example, for engines equipped with common rail injection systems to meet the Euro 4 standard theoretically even without additional particulate filters.

In modern common rail diesel engines, under particular conditions, for example when biodiesel-containing fuels or fuels with metal impurities such as zinc compounds, copper compounds, lead compounds and other metal compounds are used, deposits can form on the injector orifices, which adversely affect the injection performance of the fuel and hence impair the performance of the engine, i.e. especially reduce the power, but in some cases also worsen the combustion. The formation of deposits is enhanced further by further developments in the injector construction, especially by the change in the geometry of the nozzles (narrower, conical orifices with rounded outlet). For lasting optimal functioning of engine and injectors, such deposits in the nozzle orifices must be prevented or reduced by suitable fuel additives.

In the injection systems of modern diesel engines, deposits cause significant performance problems. It is common knowledge that such deposits in the spray channels can lead to a decrease in the fuel flow and hence to power loss. Deposits at the injector tip, in contrast, impair the optimal formation of fuel spray mist and, as a result, cause worsened combustion and associated higher emissions and increased fuel consumption. In contrast to these conventional "external" deposition phenomena, "internal" deposits (referred to collectively as internal diesel injector deposits (IDID)) in

particular parts of the injectors, such as at the nozzle needle, at the control piston, at the valve piston, at the valve seat, in the control unit and in the guides of these components, also increasingly cause performance problems. Conventional additives exhibit inadequate action against these IDIDs.

5

US 4,248,719 describes quaternized ammonium salts which are prepared by reacting an alkenylsuccinimide with a monocarboxylic ester and find use as dispersants in lubricant oils for prevention of sludge formation. More particularly, for example, the reaction of polyisobutylsuccinic anhydride (PIBSA) with N,N-dimethylaminopropylamine (DMAPA) and quaternization with methyl salicylate is described. However, use in fuels, more particularly diesel fuels, is not proposed therein. The use of PIBSA with low bismaleation levels of < 20% is not described therein.

10

US 4,171,959 describes quaternized ammonium salts of hydrocarbyl-substituted succinimides, which are suitable as detergent additives for gasoline fuel compositions. Quaternization is preferably accomplished using alkyl halides. Also mentioned are organic C₂-C₈-hydrocarbyl carboxylates and sulfonates. Consequently, the quaternized ammonium salts provided according to the teaching therein have, as a counterion, either a halide or a C₂-C₈-hydrocarbyl carboxylate or a C₂-C₈-hydrocarbyl sulfonate group. The use of PIBSA with low bismaleation levels of < 20% is likewise not described therein.

15

20

EP-A-2 033 945 discloses cold flow improvers which are prepared by quaternizing specific tertiary monoamines bearing at least one C₈-C₄₀-alkyl radical with a C₁-C₄-alkyl ester of specific carboxylic acids. Examples of such carboxylic esters are dimethyl oxalate, dimethyl maleate, dimethyl phthalate and dimethyl fumarate. Uses other than that for improvement of the CFPP value of middle distillates are not demonstrated in EP-A-2 033 945.

25

WO 2006/135881 describes quaternized ammonium salts prepared by condensation of a hydrocarbyl-substituted acylating agent and of an oxygen or nitrogen atom-containing compound with a tertiary amino group, and subsequent quaternization by means of hydrocarbyl epoxide in the presence of stoichiometric amounts of an acid such as, more particularly, acetic acid. Further quaternizing agents claimed in WO 2006/135881 are dialkyl sulfates, benzyl halides and hydrocarbyl-substituted carbonates, and

35

dimethyl sulfate, benzyl chloride and dimethyl carbonate have been studied experimentally.

5 The quaternizing agents used with preference in WO 2006/135881, however, have serious disadvantages such as: toxicity or carcinogenicity (for example in the case of dimethyl sulfate and benzyl halides), no residue-free combustion (for example in the case of dimethyl sulfate and alkyl halides), and inadequate reactivity which leads to incomplete quaternization or uneconomic reaction conditions (long reaction times, high reaction temperatures, excess of quaternizing agent; for example in the case of
10 dimethyl carbonate).

EP-A-2 033 945 describes the preparation of halogen- and sulfur-free quaternary ammonium salts of organic carboxylic acids (for example oxalic acid, phthalic acid, salicylic acid, malonic acid and maleic acid, and the alkyl esters thereof) and the use
15 thereof for improvement of the CFPP value of diesel fuels.

Quaternary ammonium salts of alpha-hydroxycarboxylic acids are proposed in EP-A-1 254 889 as cleaning agents for electronic components.

20 In addition, Japanese patent application, application number 61-012197, describes the use of quaternary ammonium salts of organic carboxylic acids as surfactants or raw materials for medicaments or cosmetics.

Advantageously, the present invention may provide further fuel additives which prevent
25 deposits in the injector tip and internal injector deposits in the course of operation of common rail diesel engines.

Brief description of the invention:

30

The present invention provides quaternized hydrocarbylamine compounds and fuel and lubricant compositions additized therewith.

Surprisingly, the inventive additives, as illustrated more particularly by the appended use examples, are surprisingly effective in common rail diesel engines and are notable for their particular suitability as an additive for reducing power loss resulting from external deposits and cold start problems resulting from internal deposits.

5

Description of figures:

Figure 1 shows a measurement of the time-dependent (h) change in the exhaust gas temperatures of the cylinders in the case of use of a fuel without additive; large deviations in the temperature are caused by internal injector deposits.

10

Figure 2 shows the time-dependent (h) change in the exhaust gas temperatures in the same cylinders as in figure 1, but now after treatment with the inventive additive from preparation example 3, dosage 394 mg/kg.

15

Figure 3 shows the profile of a one-hour engine test cycle to CEC F-098-08.

Detailed description of the invention:

A1) Specific embodiments

20

The present invention relates especially to the following specific embodiments:

1. A fuel composition or lubricant composition comprising, in a majority of a customary fuel or lubricant, a proportion, especially an effective amount, of at least one reaction product comprising a quaternized nitrogen compound, or a fraction thereof which comprises a quaternized nitrogen compound and is obtained from the reaction product by purification, said reaction product being obtainable by reacting a quaternizable alkylamine comprising at least one quaternizable tertiary amino group with a quaternizing agent which converts the at least one tertiary amino group to a quaternary ammonium group, the quaternizing agent being the alkyl ester of a cycloaromatic or cycloaliphatic mono- or polycarboxylic acid, especially of a mono- or dicarboxylic acid, or of an aliphatic polycarboxylic acid, especially dicarboxylic acid, a hydrocarbyl epoxide,

25

30

optionally in combination with a free acid, or a dialkyl carbonate such as di-C₁-C₄-carbonate, especially dimethyl carbonate.

2. The fuel composition or lubricant composition according to embodiment 1, wherein the alkylamine comprises at least one compound of the following general formula 3



in which

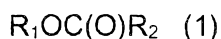
at least one of the R_a, R_b and R_c radicals, for example one or two, is a straight-chain or branched, saturated or unsaturated C₈-C₄₀-hydrocarbyl radical (especially straight-chain or branched C₈-C₄₀-alkyl) and the remaining radicals are identical or different, straight-chain or branched, saturated or unsaturated C₁-C₆-hydrocarbyl radicals (especially C₁-C₆-alkyl); or

- 2a. The fuel composition or lubricant composition according to embodiment 1, wherein the alkylamine comprises at least one compound of the following general formula 3



in which all R_a, R_b and R_c radicals are identical or different, straight-chain or branched, saturated or unsaturated C₈-C₄₀-hydrocarbyl radicals, especially straight-chain or branched C₈-C₄₀-alkyl radicals.

3. The fuel composition or lubricant composition according to any of the preceding embodiments, wherein the quaternizing agent is a compound of the general formula 1

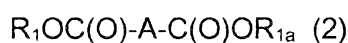


in which

R_1 is a low molecular weight hydrocarbyl radical such as alkyl or alkenyl radical, especially a lower alkyl radical such as, more particularly, methyl or ethyl, and

R_2 is an optionally substituted monocyclic hydrocarbyl radical, especially an aryl or cycloalkyl or cycloalkenyl radical, especially aryl such as phenyl, where the substituent is selected from OH, NH_2 , NO_2 , $\text{C}(\text{O})\text{OR}_3$, and $\text{R}_1\text{OC}(\text{O})-$, in which R_1 is as defined above and R_3 is H or R_1 , where the substituent is especially OH. More particularly, the quaternizing agent is a phthalate or a salicylate, such as dimethyl phthalate or methyl salicylate.

4. The fuel composition according to either of embodiments 1 and 2, wherein the quaternizing agent is a compound of the general formula 2

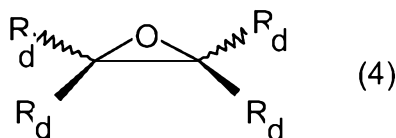


in which

R_1 and R_{1a} are each independently a low molecular weight hydrocarbyl radical such as an alkyl or alkenyl radical, especially a lower alkyl radical, and

A is an optionally mono- or polysubstituted hydrocarbylene (such as, more particularly, an optionally mono- or polysubstituted C_1 - C_7 -alkylene or C_2 - C_7 -alkenylene); where suitable substituents, for example, are selected from OH, NH_2 , NO_2 , or $\text{C}(\text{O})\text{OR}_3$, especially OH and $\text{C}(\text{O})\text{OR}_3$, where R_3 is as defined above.

5. The fuel composition or lubricant composition according to either of embodiments 1 and 2, wherein the quaternizing agent comprises an epoxide of the general formula 4



where

the R_d radicals present therein are the same or different and are each H or a hydrocarbyl radical, where the hydrocarbyl radical is an aliphatic or aromatic

radical having at least 1 to 10 carbon atoms and the free acid of the quaternizing agent is a free protic acid, especially a C₁₋₁₂-mono-, -di- or -oligocarboxylic acid.

- 5 6. The fuel composition or lubricant composition according to any of the preceding embodiments, wherein the quaternizable tertiary amine is a compound of the formula 3 in which at least two of the R_a, R_b and R_c radicals are the same or different and are each a straight-chain or branched C₁₀-C₂₀-alkyl radical and the other radical is C₁-C₄-alkyl.
- 10 7. The fuel composition or lubricant composition according to any of the preceding embodiments, wherein the quaternizing agent is selected from lower alkylene oxides in combination with a monocarboxylic acid, alkyl salicylates, dialkyl phthalates and dialkyl oxalates.
- 15 8. The fuel composition or lubricant composition according to any of the preceding embodiments, selected from diesel fuels, biodiesel fuels, gasoline fuels, and alkanol-containing gasoline fuels, such as bioethanol-containing fuels, especially diesel fuels.
- 20 9. A quaternized nitrogen compound as defined in any of embodiments 1 to 7.
10. A process for preparing a quaternized nitrogen compound according to embodiment 9,
comprising the reaction of a quaternizable alkylamine comprising at least one
25 quaternizable tertiary amino group with a quaternizing agent which converts the
at least one tertiary amino group to a quaternary ammonium group,
the quaternizing agent being the alkyl ester of a cycloaromatic or cycloaliphatic
mono- or polycarboxylic acid, especially of a mono- or dicarboxylic acid, or of an
aliphatic polycarboxylic acid, especially dicarboxylic acid, or a hydrocarbyl
30 epoxide in combination with an acid.
11. The use of a quaternized nitrogen compound according to embodiment 9 or prepared according to embodiment 10 as a fuel additive or lubricant additive.

12. The use according to embodiment 11 as an additive for reducing the fuel consumption of direct injection diesel engines, especially of diesel engines with common rail injection systems, and/or for minimizing power loss in direct injection diesel engines, especially in diesel engines with common rail injection systems (for example determined in a DW10 test based on CEC F-098-08, as described in detail in the experimental below).
13. The use according to embodiment 11 as a gasoline fuel additive for reducing the level of deposits in the intake system of a gasoline engine, such as, more particularly, DISI and PFI (port fuel injector) engines.
14. The use according to embodiment 10 as a diesel fuel additive for reducing and/or preventing deposits in the injection systems, for example determined in a XUD 9 test to CEC-F-23-1-01, such as, more particularly, the internal diesel injector deposits (IDIDs), and/or valve sticking in direct injection diesel engines, especially in common rail injection systems (for example determined by an IDID test procedure as described in detail in the experimental below).
15. An additive concentrate comprising, in combination with further diesel fuel additives or gasoline fuel additives or lubricant additives, at least one quaternized nitrogen compound as defined in embodiment 9 or prepared according to embodiment 10.

Test methods suitable for examination of each of the above-designated applications are known to those skilled in the art, or are described in the experimental which follows, to which explicit and general reference is hereby made.

A2) General definitions

In the absence of statements to the contrary, the following general definitions apply:

"Hydrocarbyl" can be interpreted widely and comprises both long-chain and short-chain, straight-chain and branched hydrocarbyl radicals having 1 to 50 carbon atoms, which may optionally additionally comprise heteroatoms, for example O, N, NH, S, in the chain thereof. A specific group of hydrocarbyl radicals comprises both long-chain and short-chain, straight-chain or branched alkyl radicals having 1 to 50 carbon atoms.

"Long-chain" hydrocarbyl radicals are straight-chain or branched hydrocarbyl radicals and have 7 to 50 or 8 to 50 or 8 to 40 or 10 to 20 carbon atoms, which may optionally additionally comprise heteroatoms, for example O, N, NH, S, in the chain thereof. In addition, the radicals may be mono- or polyunsaturated and have one or more noncumulated, for example 1 to 5, such as 1, 2 or 3, C-C double bonds or C-C triple bonds, especially 1, 2 or 3 double bonds. They may be of natural or synthetic origin. They may also have a number-average molecular weight (M_n) of 85 to 20 000, for example 113 to 10 000, or 200 to 10 000 or 350 to 5000, for example 350 to 3000, 500 to 2500, 700 to 2500, or 800 to 1500. In that case, they are more particularly formed essentially from C_{2-6} , especially C_{2-4} , monomer units such as ethylene, propylene, n- or isobutylene or mixtures thereof, where the different monomers may be copolymerized in random distribution or as blocks. Such long-chain hydrocarbyl radicals are also referred to as polyalkylene radicals or poly- C_{2-6} - or poly- C_{2-4} -alkylene radicals. Suitable long-chain hydrocarbyl radicals and the preparation thereof are also described, for example, in WO 2006/135881 and the literature cited therein. A specific group of long-chain hydrocarbyl radicals comprises straight-chain or branched alkyl radicals ("long-chain" alkyl radicals) having 8 to 50, for example 8 to 40 or 8 to 30 or 10 to 20, carbon atoms.

"Short-chain hydrocarbyl" or "low molecular weight hydrocarbyl" is especially straight-chain or branched alkyl or alkenyl, optionally interrupted by one or more, for example 2, 3 or 4, heteroatom groups such as -O- or -NH-, or optionally mono- or polysubstituted, for example di-, tri- or tetrasubstituted.

"Hydrocarbylene" represents straight-chain or singly or multiply branched bridging groups having 1 to 10 carbon atoms, optionally interrupted by one or more, for example 2, 3 or 4, heteroatom groups such as -O- or -NH-, or optionally mono- or polysubstituted, for example di-, tri- or tetrasubstituted.

"Alkyl" or "lower alkyl" represents especially saturated, straight-chain or branched hydrocarbon radicals having 1 to 4, 1 to 5, 1 to 6, or 1 to 7, carbon atoms, for example methyl, ethyl, n-propyl, 1-methylethyl, n-butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, n-pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl,

1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl; and also n-heptyl, and the singly or multiply
5 branched analogs thereof.

"Long-chain alkyl" especially represents saturated, straight-chain or branched hydrocarbyl radicals having 8 to 50, for example 8 to 40 or 8 to 30 or 10 to 20, carbon atoms, such as octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl,
10 hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, hencosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, squalyl, constitutional isomers, especially singly or multiply branched isomers and higher homologs thereof.

15 "Alkenyl" represents mono- or polyunsaturated, especially monounsaturated, straight-chain or branched hydrocarbon radicals having 2 to 4, 2 to 6 or 2 to 7 carbon atoms and a double bond in any position, for example C₂-C₆-alkenyl such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl,
20 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl,
25 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl.
35

- "Alkylene" represents straight-chain or mono- or polybranched hydrocarbon bridging groups having 1 to 10 carbon atoms, for example C₁-C₇-alkylene groups selected from -CH₂-, -(CH₂)₂-, -(CH₂)₃-, -CH₂-CH(CH₃)-, -CH(CH₃)-CH₂-, -(CH₂)₄-, -(CH₂)₂-CH(CH₃)-,
 5 -CH₂-CH(CH₃)-CH₂-, (CH₂)₄-, -(CH₂)₅-, -(CH₂)₆-, -(CH₂)₇-, -CH(CH₃)-CH₂-CH₂-CH(CH₃)- or -CH(CH₃)-CH₂-CH₂-CH₂-CH(CH₃)- or C₁-C₄-alkylene groups selected from -CH₂-, -(CH₂)₂-, -(CH₂)₃-, -CH₂-CH(CH₃)-,
 -CH(CH₃)-CH₂-, -(CH₂)₄-, -(CH₂)₂-CH(CH₃)-, -CH₂-CH(CH₃)-CH₂-.
 10 "Alkenylene" represents the mono- or polyunsaturated, especially monounsaturated, analogs of the above alkylene groups having 2 to 10 carbon atoms, especially C₂-C₇-alkenylenes or C₂-C₄-alkenylene, such as -CH=CH-, -CH=CH-CH₂-, -CH₂-CH=CH-,
 -CH=CH-CH₂-CH₂-, -CH₂-CH=CH-CH₂-, -CH₂-CH₂-CH=CH-, -CH(CH₃)-CH=CH-,
 -CH₂-C(CH₃)=CH-.
 15 "Cycloalkyl" represents carbocyclic radicals having 3 to 20 carbon atoms, for example C₃-C₁₂-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl and cyclododecyl; preference is given to cyclopentyl, cyclohexyl, cycloheptyl, and also cyclopropylmethyl, cyclopropylethyl,
 20 cyclobutylmethyl, cyclobutylethyl, cyclopentylmethyl, cyclopentylethyl, cyclohexylmethyl or C₃-C₇-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclopropylmethyl, cyclopropylethyl, cyclobutylmethyl, cyclopentylethyl, cyclohexylmethyl, where the bond to the rest of the molecule may be via any suitable carbon atom.
 25 "Aryl" represents mono- or polycyclic, preferably mono- or bicyclic, optionally substituted aromatic radicals having 6 to 20, for example 6 to 10, ring carbon atoms, for example phenyl, biphenyl, naphthyl such as 1- or 2-naphthyl, tetrahydronaphthyl, fluorenyl, indenyl and phenanthrenyl. These aryl radicals may optionally bear 1, 2, 3, 4,
 30 5 or 6 identical or different substituents.
 "Substituents" for radicals specified herein are especially, unless stated otherwise, selected from keto groups, -COOH, -COO-alkyl, -OH, -SH, -CN, amino, -NO₂, alkyl, or alkenyl groups.
 35

"Mn" represents the number-average molecular weight and is determined in a conventional manner; more particularly, such statements relate to Mn values determined by gel permeation chromatography.

5 **A3) Tertiary amines of the formula (3)**

Tertiary amines of the formula (3) are compounds known per se, as described, for example, in EP-A-2 033 945.

10 The tertiary amine reactant (3) preferably bears a segment of the formula $NR_a R_b$ where one of the radicals has an alkyl group having 8 to 40 carbon atoms and the other an alkyl group having up to 40 and more preferably 8 to 40 carbon atoms. The R_c radical is especially a short-chain C_1 - C_6 -alkyl radical, such as a methyl, ethyl or propyl group. R_a and R_b may be straight-chain or branched, and/or may be the same or different. For example, R_a and R_b may be a straight-chain C_{12} - C_{24} -alkyl group.
15 Alternatively, only one of the two radicals may be long-chain (for example having 8 to 40 carbon atoms), and the other may be a methyl, ethyl or propyl group.

Appropriately, the $NR_a R_b$ segment is derived from a secondary amine, such as dioctadecylamine, dicocoamine, hydrogenated ditallowamine and methylbehenylamine.
20 Amine mixtures as obtainable from natural materials are likewise suitable. One example is a secondary hydrogenated tallowamine where the alkyl groups are derived from hydrogenated tallow fat, and contain about 4% by weight of C_{14} , 31% by weight of C_{16} and 59% by weight of C_{18} -alkyl groups. Corresponding tertiary amines of the formula (3) are sold, for example, by Akzo Nobel under the Armeen® M2HT or
25 Armeen® M2C name.

The tertiary amine reactant (3) may also take such a form that the R_a , R_b and R_c radicals have identical or different long-chain alkyl radicals, especially straight-chain or branched alkyl groups having 8 to 40 carbon atoms.

30

Further nonlimiting examples of suitable amines are:

N,N-dimethyl-N-(2-ethylhexyl)amine, N,N-dimethyl-N-(2-propylheptyl)amine, dodecyl-dimethylamine, hexadecyldimethylamine, oleyldimethylamine, cocoyldimethylamine,
35 dicocoylmethylamine, tallowdimethylamine, ditallowmethylamine, tridodecylamine,

trihexadecylamine, trioctadecylamine, soyadimethylamine, tris(2-ethylhexyl)amine, and Alamine 336 (tri-n-octylamine).

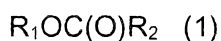
A4) Quaternizing agents:

- 5 Useful quaternizing agents in principle include all compounds suitable as such. The quaternizing agent is especially selected from alkylene oxides, optionally in combination with acid; aliphatic or aromatic carboxylic esters such as, more particularly, dialkyl carboxylates; alkanooates; cyclic nonaromatic or aromatic carboxylic esters; alkyl sulfates; alkyl halides; alkylaryl halides; dialkyl carbonates; and mixtures thereof.

10 Suitable examples are alkyl esters, derived from carboxylic acids, whose pK_a is less than 3.5. Examples are especially alkyl esters derived from oxalic acid, phthalic acid, salicylic acid, maleic acid, malonic acid and citric acid.

15 In a particular embodiment, however, the at least one quaternizable tertiary nitrogen atom is quaternized with at least one quaternizing agent selected from

20 a) compounds of the general formula 1

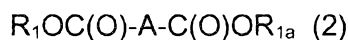


in which

- 25 R_1 is a lower alkyl radical and R_2 is an optionally substituted monocyclic aryl or cycloalkyl radical, where the substituent is selected from OH, NH_2 , NO_2 , $C(O)OR_3$; $R_{1a}OC(O)-$ in which R_{1a} is as defined above for R_1 , and R_3 is H or R_1 ;

or

30 b) compounds of the general formula 2



in which

- 35 R_1 and R_{1a} are each independently a lower alkyl radical and

A is an optionally mono- or polysubstituted hydrocarbylene (such as, more particularly, an optionally mono- or polysubstituted C₁-C₇-alkylene or C₂-C₇-alkenylene); where suitable substituents, for example, are selected from OH, NH₂, NO₂, or C(O)OR₃, especially OH and C(O)OR₃, where R₃ is as defined above.

5

Particularly suitable compounds of the formula 1 are those in which

R₁ is a C₁-, C₂- or C₃-alkyl radical and

R₂ is a substituted phenyl radical, where the substituent is HO- or an ester radical of the formula R_{1a}OC(O)- which is in the para, meta or especially ortho position to the

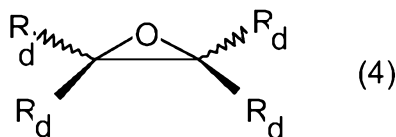
10 R₁OC(O)- radical on the aromatic ring.

Especially suitable quaternizing agents are the lower alkyl esters of salicylic acid, such as methyl salicylate, ethyl salicylate, n- and i-propyl salicylate, and n-, i- or tert-butyl salicylate.

15 Abovementioned esters are typically used in the presence of acids, especially in the presence of free protic acids such as, in particular, with C₁₋₁₂-monocarboxylic acids such as formic acid, acetic acid or propionic acid, or C₂₋₁₂-dicarboxylic acids such as oxalic acid or adipic acid; or else in the presence of sulfonic acids such as benzenesulfonic acid or toluenesulfonic acid, or aqueous mineral acids such as sulfuric
20 acid or hydrochloric acid.

c) In a further particular embodiment, the at least one quaternizable tertiary nitrogen atom is quaternized with at least one quaternizing agent selected from epoxides, especially hydrocarbyl epoxides.

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where the R_d radicals present therein are the same or different and are each H or a hydrocarbyl radical, where the hydrocarbyl radical has at least 1 to 10 carbon atoms.

30 These are especially aliphatic or aromatic radicals, for example linear or branched C₁₋₁₀-alkyl radicals, or aromatic radicals such as phenyl or C₁₋₄-alkylphenyl.

Examples of suitable hydrocarbyl epoxides include aliphatic and aromatic alkylene oxides such as, more particularly, C₂₋₁₂-alkylene oxides such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, 2-methyl-1,2-propene oxide (isobutene oxide), 1,2-pentene oxide, 2,3-pentene oxide, 2-methyl-1,2-butene oxide, 3-methyl-1,2-butene oxide, 1,2-hexene oxide, 2,3-hexene oxide, 3,4-hexene oxide, 2-methyl-1,2-pentene oxide, 2-ethyl-1,2-butene oxide, 3-methyl-1,2-pentene oxide, 1,2-decene oxide, 1,2-dodecene oxide or 4-methyl-1,2-pentene oxide; and aromatic-substituted ethylene oxides such as optionally substituted styrene oxide, especially styrene oxide or 4-methylstyrene oxide.

In the case of use of epoxides as quaternizing agents, these are used in the presence or in the absence of free acids, especially in the presence or absence of free protic acids, such as, in particular, with C₁₋₁₂-monocarboxylic acids such as formic acid, acetic acid or propionic acid, or C₂₋₁₂-dicarboxylic acids such as oxalic acid or adipic acid; or else in the presence or absence of sulfonic acids such as benzenesulfonic acid or toluenesulfonic acid, or aqueous mineral acids such as sulfuric acid or hydrochloric acid. The quaternization product thus prepared is thus either "acid-containing" or "acid-free" in the context of the present invention.

A5) Preparation of inventive additives:

a) Quaternization

The quaternization is performed in a manner known per se.

(1) To perform the quaternization, the tertiary amine is admixed with at least one compound of the above formula 1 or 2, especially in the stoichiometric amounts required to achieve the desired quaternization. It is possible to use, for example, 0.1 to 5.0, 0.2 to 3.0 or 0.5 to 2.5 equivalents of quaternizing agent per equivalent of quaternizable tertiary nitrogen atom. More particularly, however, about 1 to 2 equivalents of quaternizing agent are used in relation to the tertiary amine, in order to fully quaternize the tertiary amine group.

Typical working temperatures here are in the range from 50 to 180°C, for example 90 to 160°C or 100 to 140°C. The reaction time may be in the region of a few minutes or a

few hours, for example about 10 minutes up to about 24 hours. The reaction can be effected at a pressure of about 0.1 to 20 bar, for example 1 to 10 or 1.5 to 3 bar, but especially at about standard pressure.

- 5 If required, the reactants can be initially charged for the quaternization in a suitable inert organic aliphatic or aromatic solvent or a mixture thereof. Typical examples are, for example, solvents of the Solvesso series, toluene or xylene, or ethylhexanol. The quaternization can, however, also be performed in the absence of a solvent.
- 10 To perform the quaternization, the addition of catalytically active amounts of an acid may be appropriate. Preference is given to aliphatic monocarboxylic acids, for example C₁-C₁₈-monocarboxylic acids such as, more particularly, lauric acid, isononanoic acid or 3,3,5-trimethylhexanoic acid or neodecanoic acid, but also aliphatic dicarboxylic acids or polybasic aliphatic carboxylic acids with a carbon atom number in the range
- 15 specified above. The quaternization can also be performed in the presence of a Lewis acid. The quaternization can, however, also be performed in the absence of any acid.

- (2) The quaternization with an epoxide of the formula (4) is likewise effected in a manner known per se. When the boiling temperature of one component of the reaction
- 20 mixture, especially of the epoxide, at standard pressure is above the reaction temperature, the reaction is appropriately performed in an autoclave.

- For example, in an autoclave, a solution of the tertiary amine is admixed with the organic acid (for example acetic acid) in the required stoichiometric amounts. It is
- 25 possible to use, for example, 0.1 to 2.0, 0.2 to 1.5 or 0.5 to 1.25 equivalents of acid per equivalent of quaternizable tertiary nitrogen atom. More particularly, however, approximately equimolar proportions of the acid are used. This is followed by sufficient purging with N₂, and establishment of a suitable initial pressure, and metered addition of the epoxide (e.g. propylene oxide) in the stoichiometric amounts required at a
- 30 temperature between 20°C and 180°C. It is possible to use, for example, 0.1 to 4.0, 0.2 to 3 or 0.5 to 2 equivalents of epoxide per equivalent of quaternizable tertiary nitrogen atom. More particularly, however, about 1 to 2 equivalents of epoxide are used in relation to the tertiary amine, in order to fully quaternize the tertiary amine group. This is followed by stirring over a suitably long period of a few minutes up to about 24 hours,

for example about 10 h, at a temperature between 20°C and 180°C (e.g. 50°C), cooling, for example to about 20 to 50°C, purging with N₂ and emptying of the reactor.

5 The reaction can be effected at a pressure of about 0.1 to 20 bar, for example 1 to 10 or 1.5 to 5 bar. However, the reaction can also be effected at standard pressure. An inert gas atmosphere is particular appropriate, for example nitrogen.

10 If required, the reactants can be initially charged for the quaternization in a suitable inert organic aliphatic or aromatic solvent or a mixture thereof. Typical examples are, for example, solvents of the Solvesso series, toluene or xylene, or 2-ethylhexanol. The quaternization can, however, also be performed in the absence of a solvent.

15 The quaternization can be performed in the presence of a protic solvent, optionally also in combination with an aliphatic or aromatic solvent. Suitable protic solvents especially have a dielectric constant (at 20°C) of greater than 7. The protic solvent may comprise one or more OH groups, and may also be water. Suitable solvents may also be alcohols, glycols and glycol ethers. More particularly, suitable protic solvents may be those specified in WO 2010132259. Especially suitable solvents are methanol, ethanol, n-propanol, isopropanol, all isomers of butanol, all isomers of pentanol, all isomers of
20 hexanol, 2-ethylhexanol, 2-propylheptanol, and also mixtures of different alcohols. The presence of a protic solvent can positively influence the conversion and the reaction rate of the quaternization.

b) Workup of the reaction mixture

25 The reaction end product thus formed can theoretically be purified further, or the solvent can be removed. Optionally, excess reagent, for example excess epoxide, can be removed. This can be accomplished, for example, by introducing nitrogen at standard pressure or under reduced pressure. In order to improve the further processability of the products, however, it is also possible to add solvents after the
30 reaction, for example solvents of the Solvesso series, 2-ethylhexanol, or essentially aliphatic solvents. However, this is usually not absolutely necessary, and so the reaction product can be used without further purification as an additive, optionally after blending with further additive components (see below).

35 B) Further additive components

The fuel additized with the inventive quaternized additive is a gasoline fuel or especially a middle distillate fuel, in particular a diesel fuel.

- 5 The fuel may comprise further customary additives to improve efficacy and/or suppress wear.

10 In the case of diesel fuels, these are primarily customary detergent additives, carrier oils, cold flow improvers, lubricity improvers, corrosion inhibitors, demulsifiers, dehazers, antifoams, cetane number improvers, combustion improvers, antioxidants or stabilizers, antistats, metallocenes, metal deactivators, dyes and/or solvents.

15 In the case of gasoline fuels, these are in particular lubricity improvers (friction modifiers), corrosion inhibitors, demulsifiers, dehazers, antifoams, combustion improvers, antioxidants or stabilizers, antistats, metallocenes, metal deactivators, dyes and/or solvents.

Typical examples of suitable coadditives are listed in the following section:

20 B1) Detergent additives

The customary detergent additives are preferably amphiphilic substances which possess at least one hydrophobic hydrocarbon radical with a number-average molecular weight (M_n) of 85 to 20 000 and at least one polar moiety selected from:

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(Da) mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties;

30

(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;

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(Dd) carboxyl groups or the alkali metal or alkaline earth metal salts thereof;

(De) sulfonic acid groups or the alkali metal or alkaline earth metal salts thereof;

5 (Df) polyoxy-C₂- to C₄-alkylene moieties terminated by hydroxyl groups, mono- or polyamino groups, at least one nitrogen atom having basic properties, or by carbamate groups;

(Dg) carboxylic ester groups;

10 (Dh) moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; and/or

(Di) moieties obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines.

15 The hydrophobic hydrocarbon radical in the above detergent additives, which ensures the adequate solubility in the fuel, has a number-average molecular weight (M_n) of 85 to 20 000, preferably of 113 to 10 000, more preferably of 300 to 5000, even more preferably of 300 to 3000, even more especially preferably of 500 to 2500 and especially of 700 to 2500, in particular of 800 to 1500. As typical hydrophobic
20 hydrocarbon radicals, especially in conjunction with the polar, especially polypropenyl, polybutenyl and polyisobutenyl radicals with a number-average molecular weight M_n of preferably in each case 300 to 5000, more preferably 300 to 3000, even more preferably 500 to 2500, even more especially preferably 700 to 2500 and especially 800 to 1500 into consideration.

25

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

Additives comprising mono- or polyamino groups (Da) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or on high-reactivity (i.e. having
30 predominantly terminal double bonds) or conventional (i.e. having predominantly internal double bonds) polybutene or polyisobutene having $M_n = 300$ to 5000, more preferably 500 to 2500 and especially 700 to 2500. Such additives based on high-reactivity polyisobutene, which can be prepared from the polyisobutene which may comprise up to 20% by weight of n-butene units by hydroformylation and reductive
35 amination with ammonia, monoamines or polyamines such as

dimethylaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine, are known especially from EP-A 244 616. When polybutene or polyisobutene having predominantly internal double bonds (usually in the β and γ positions) are used as starting materials in the preparation of the additives, a possible 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 the abovementioned polyamines. Corresponding additives based on polypropene are described more particularly in WO-A 94/24231.

Further particular 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 more particularly in WO-A 97/03946.

Further particular 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 more particularly in DE-A 196 20 262.

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 more particularly in WO-A 96/03367 and in WO-A 96/03479. These reaction products are generally mixtures of pure nitropolyisobutenes (e.g. α,β -dinitropolyisobutene) and mixed hydroxynitropolyisobutenes (e.g. α -nitro- β -hydroxypolyisobutene).

Additives comprising hydroxyl groups in combination with mono- or polyamino groups (Dc) are especially 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 more particularly in EP-A 476 485.

35

Additives comprising carboxyl groups or their alkali metal or alkaline earth metal salts (Dd) are preferably copolymers of C₂- to C₄₀-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 more particularly 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.

Additives comprising sulfonic acid 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 more particularly 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.

Additives comprising polyoxy-C₂-C₄-alkylene moieties (Df) are preferably polyethers or polyetheramines which are obtainable by reaction of C₂- to C₆₀-alkanols, C₆- to C₃₀-alkanediols, mono- or di-C₂- to C₃₀-alkylamines, C₁- to C₃₀-alkylcyclohexanols or C₁- to C₃₀-alkylphenols with 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, monoamines or polyamines. Such products are described more particularly 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 properties. Typical examples thereof are tridecanol butoxylates or isotridecanol butoxylates, isononylphenol butoxylates and also 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 tricarboxylic acids with long-chain alkanols or polyols, especially those having a minimum viscosity of 2 mm²/s at 100°C, as described more particularly 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, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol. Such products also satisfy carrier oil properties.

5 Additives comprising moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or especially imido groups (Dh) are preferably corresponding derivatives 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 $M_n =$
10 preferably 300 to 5000, more preferably 300 to 3000, even more preferably 500 to 2500, even more especially preferably 700 to 2500 and especially 800 to 1500, with maleic anhydride by a thermal route in an ene reaction or via the chlorinated polyisobutene. 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
15 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, carboximides 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. In the presence of
20 imido moieties D(h), the further detergent additive in the context of the present invention is, however, used only up to a maximum of 100% of the weight of compounds with betaine structure. Such fuel additives are common knowledge and are described, for example, in documents (1) and (2). They are preferably the reaction products of alkyl- or alkenyl-substituted succinic acids or derivatives thereof with amines and more
25 preferably the reaction products of polyisobutenyl-substituted succinic acids or derivatives thereof with amines. Of particular interest in this context are reaction products with aliphatic polyamines (polyalkyleneimines) such as especially ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine and hexaethyleneheptamine, which have an imide structure.

30

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
35 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 more particularly in EP-A 831 141.

- 5 One or more of the detergent additives mentioned can be added to the fuel in such an amount that the dosage of these detergent additives is preferably 25 to 2500 ppm by weight, especially 75 to 1500 ppm by weight, in particular 150 to 1000 ppm by weight.

B2) Carrier oils

- 10 Carrier oils additionally used may be of mineral or synthetic nature. 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
15 oil" (vacuum distillate cut having a boiling range of from about 360 to 500 °C, obtainable from natural mineral oil which has been catalytically hydrogenated under high pressure and isomerized and also deparaffinized). Likewise suitable are mixtures of the abovementioned mineral carrier oils.
- 20 Examples of suitable synthetic carrier oils are polyolefins (polyalphaolefins or polyinternalolefins), (poly)esters, (poly)alkoxylates, polyethers, aliphatic polyetheramines, alkylphenol-started polyethers, alkylphenol-started polyetheramines and carboxylic esters of long-chain alkanols.
- 25 Examples of suitable polyolefins are olefin polymers having $M_n = 400$ to 1800, in particular based on polybutene or polyisobutene (hydrogenated or unhydrogenated).

- Examples of suitable polyethers or polyetheramines are preferably compounds comprising polyoxy- C_2 - to C_4 -alkylene moieties which are obtainable by reacting C_2 - to
30 C_{60} -alkanols, C_6 - to C_{30} -alkanediols, mono- or di- C_2 - to C_{30} -alkylamines, C_1 - to C_{30} -alkylcyclohexanols or C_1 - to C_{30} -alkylphenols with 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, monoamines or polyamines. Such products are described more particularly in EP-A
35 310 875, EP-A 356 725, EP-A 700 985 and US-A 4 877 4,877,416. For example, the

polyetheramines used may be poly-C₂- to C₆-alkylene oxide amines or functional derivatives thereof. Typical examples thereof are tridecanol butoxylates or isotridecanol butoxylates, isononylphenol butoxylates and also polyisobutenol butoxylates and propoxylates, and also the corresponding reaction products with ammonia.

5

Examples of carboxylic esters of long-chain alkanols are more particularly esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, as described more particularly in DE-A 38 38 918. The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids; 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, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, isononanol, isodecanol and isotridecanol, for example di(n- or isotridecyl) phthalate.

15 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 452 328 and EP-A 548 617.

Examples of particularly suitable synthetic carrier oils are alcohol-started polyethers having about 5 to 35, preferably about 5 to 30, more preferably 10 to 30 and especially 20 15 to 30 C₃- to C₆-alkylene oxide units, for example propylene oxide, n-butylene oxide and isobutylene oxide units, or mixtures thereof, per alcohol molecule. 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 especially a straight-chain or branched C₆- to C₁₈-alkyl radical. Particular examples include tridecanol and 25 nonylphenol. Particularly preferred alcohol-started polyethers are the reaction products (polyetherification products) of monohydric aliphatic C₆- to C₁₈-alcohols with C₃- to C₆-alkylene oxides. Examples of monohydric aliphatic C₆-C₁₈-alcohols are hexanol, heptanol, octanol, 2-ethylhexanol, nonyl alcohol, decanol, 3-propylheptanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, octadecanol and the 30 constitutional and positional isomers thereof. The alcohols can be used either in the form of the pure isomers or in the form of technical grade mixtures. A particularly preferred alcohol is tridecanol. Examples of C₃- to C₆-alkylene oxides are propylene oxide, such as 1,2-propylene oxide, butylene oxide, such as 1,2-butylene oxide, 2,3-butylene oxide, isobutylene oxide or tetrahydrofuran, pentylene oxide and hexylene 35 oxide. Particular preference among these is given to C₃- to C₄-alkylene oxides, i.e.

propylene oxide such as 1,2-propylene oxide and butylene oxide such as 1,2-butylene oxide, 2,3-butylene oxide and isobutylene oxide. Especially butylene oxide is used.

5 Further suitable synthetic carrier oils are alkoxyated alkylphenols, as described in DE-A 10 102 913.

Particular carrier oils are synthetic carrier oils, particular preference being given to the above-described alcohol-started polyethers.

10 The carrier oil or the mixture of different carrier oils is added to the fuel in an amount of preferably 1 to 1000 ppm by weight, more preferably of 10 to 500 ppm by weight and especially of 20 to 100 ppm by weight.

B3) Cold flow improvers

15

Suitable cold flow improvers are in principle all organic compounds which are capable of improving the flow performance of middle distillate fuels or diesel fuels under cold conditions. For the intended purpose, they must have sufficient oil solubility. More particularly, useful cold flow improvers for this purpose are the cold flow improvers (middle distillate flow improvers, MDFIs) typically used in the case of middle distillates of fossil origin, i.e. in the case of customary mineral diesel fuels. However, it is also possible to use organic compounds which partly or predominantly have the properties of a wax antissettling additive (WASA) when used in customary diesel fuels. They can also act partly or predominantly as nucleators. It is also possible to use mixtures of organic compounds effective as MDFIs and/or effective as WASAs and/or effective as nucleators.

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The cold flow improver is typically selected from

(K1) copolymers of a C₂- to C₄₀-olefin with at least one further ethylenically unsaturated monomer;

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(K2) comb polymers;

(K3) polyoxyalkylenes;

(K4) polar nitrogen compounds;

(K5) sulfocarboxylic acids or sulfonic acids or derivatives thereof; and

35 (K6) poly(meth)acrylic esters.

It is possible to use either mixtures of different representatives from one of the particular classes (K1) to (K6) or mixtures of representatives from different classes (K1) to (K6).

5

Suitable C₂- to C₄₀-olefin monomers for the copolymers of class (K1) are, for example, those having 2 to 20 and especially 2 to 10 carbon atoms, and 1 to 3 and preferably 1 or 2 carbon-carbon double bonds, especially having one carbon-carbon double bond. In the latter case, the carbon-carbon double bond may be arranged either terminally (α -olefins) or internally. However, preference is given to α -olefins, particular preference to α -olefins having 2 to 6 carbon atoms, for example propene, 1-butene, 1-pentene, 1-hexene and in particular ethylene.

10

In the copolymers of class (K1), the at least one further ethylenically unsaturated monomer is preferably selected from alkenyl carboxylates, (meth)acrylic esters and further olefins.

15

When further olefins are also copolymerized, they are preferably higher in molecular weight than the abovementioned C₂- to C₄₀-olefin base monomer. When, for example, the olefin base monomer used is ethylene or propene, suitable further olefins are especially C₁₀- to C₄₀- α -olefins. Further olefins are in most cases only additionally copolymerized when monomers with carboxylic ester functions are also used.

20

Suitable (meth)acrylic esters are, for example, esters of (meth)acrylic acid with C₁- to C₂₀-alkanols, especially C₁- to C₁₀-alkanols, in particular with methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol and decanol, and structural isomers thereof.

25

Suitable alkenyl carboxylates are, for example, C₂- to C₁₄-alkenyl esters, for example the vinyl and propenyl esters, of carboxylic acids having 2 to 21 carbon atoms, whose hydrocarbon radical may be linear or branched. Among these, preference is given to the vinyl esters. Among the carboxylic acids with a branched hydrocarbon radical, preference is given to those whose branch is in the α position to the carboxyl group, and the α -carbon atom is more preferably tertiary, i.e. the carboxylic acid is what is

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called a neocarboxylic acid. However, the hydrocarbon radical of the carboxylic acid is preferably linear.

- 5 Examples of suitable alkenyl carboxylates are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl neopentanoate, vinyl hexanoate, vinyl neononanoate, vinyl neodecanoate and the corresponding propenyl esters, preference being given to the vinyl esters. A particularly preferred alkenyl carboxylate is vinyl acetate; typical copolymers of group (K1) resulting therefrom are ethylene-vinyl acetate copolymers ("EVAs"), which are some of the most frequently used.
- 10 Ethylene-vinyl acetate copolymers usable particularly advantageously and the preparation thereof are described in WO 99/29748.

- 15 Suitable copolymers of class (K1) are also those which comprise two or more different alkenyl carboxylates in copolymerized form, which differ in the alkenyl function and/or in the carboxylic acid group. Likewise suitable are copolymers which, as well as the alkenyl carboxylate(s), comprise at least one olefin and/or at least one (meth)acrylic ester in copolymerized form.

- 20 Terpolymers of a C₂- to C₄₀- α -olefin, a C₁- to C₂₀-alkyl ester of an ethylenically unsaturated monocarboxylic acid having 3 to 15 carbon atoms and a C₂- to C₁₄-alkenyl ester of a saturated monocarboxylic acid having 2 to 21 carbon atoms are also suitable as copolymers of class (K1). Terpolymers of this kind are described in WO 2005/054314. A typical terpolymer of this kind is formed from ethylene, 2-ethylhexyl acrylate and vinyl acetate.

- 25 The at least one or the further ethylenically unsaturated monomer(s) are copolymerized in the copolymers of class (K1) in an amount of preferably 1 to 50% by weight, especially 10 to 45% by weight and in particular 20 to 40% by weight, based on the overall copolymer. The main proportion in terms of weight of the monomer units in the
- 30 copolymers of class (K1) therefore originates generally from the C₂- to C₄₀ base olefins.

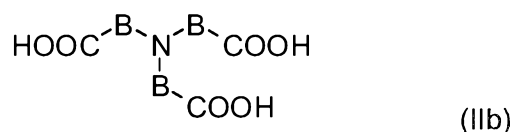
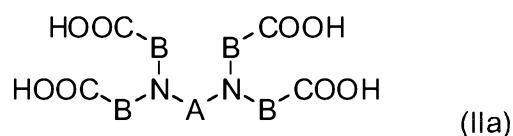
The copolymers of class (K1) preferably have a number-average molecular weight M_n of 1000 to 20 000, more preferably of 1000 to 10 000 and especially of 1000 to 8000.

- Typical comb polymers of component (K2) are, for example, obtainable by the copolymerization of maleic anhydride or fumaric acid with another ethylenically unsaturated monomer, for example with an α -olefin or an unsaturated ester, such as vinyl acetate, and subsequent esterification of the anhydride or acid function with an alcohol having at least 10 carbon atoms. Further suitable comb polymers are copolymers of α -olefins and esterified comonomers, for example esterified copolymers of styrene and maleic anhydride or esterified copolymers of styrene and fumaric acid. Suitable comb polymers may also be polyfumarates or polymaleates. Homo- and copolymers of vinyl ethers are also suitable comb polymers. Comb polymers suitable as components of class (K2) are, for example, also those described in WO 2004/035715 and in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs. 8, pages 117 to 253 (1974)". Mixtures of comb polymers are also suitable.
- Polyoxyalkylenes suitable as components of class (K3) are, for example, polyoxyalkylene esters, polyoxyalkylene ethers, mixed polyoxyalkylene ester/ethers and mixtures thereof. These polyoxyalkylene compounds preferably comprise at least one linear alkyl group, preferably at least two linear alkyl groups, each having 10 to 30 carbon atoms and a polyoxyalkylene group having a number-average molecular weight of up to 5000. Such polyoxyalkylene compounds are described, for example, in EP A 061 895 and also in US 4 491 455. Particular polyoxyalkylene compounds are based on polyethylene glycols and polypropylene glycols having a number-average molecular weight of 100 to 5000. Additionally suitable are polyoxyalkylene mono- and diesters of fatty acids having 10 to 30 carbon atoms, such as stearic acid or behenic acid.
- Polar nitrogen compounds suitable as components of class (K4) may be either ionic or nonionic and preferably have at least one substituent, especially at least two substituents, in the form of a tertiary nitrogen atom of the general formula $>NR^7$ in which R^7 is a C_8 - to C_{40} -hydrocarbyl radical. The nitrogen substituents may also be quaternized, i.e. be in cationic form. An example of such nitrogen compounds is that of ammonium salts and/or amides which are obtainable by the reaction of at least one amine substituted by at least one hydrocarbon radical with a carboxylic acid having 1 to 4 carboxyl groups or with a suitable derivative thereof. The amines preferably comprise at least one linear C_8 - to C_{40} -alkyl radical. Primary amines suitable for preparing the polar nitrogen compounds mentioned are, for example, octylamine, nonylamine,

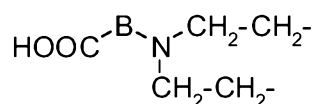
decylamine, undecylamine, dodecylamine, tetradecylamine and the higher linear homologs; secondary amines suitable for this purpose are, for example, dioctadecylamine and methylbehenylamine. Also suitable for this purpose are amine mixtures, especially amine mixtures obtainable on the industrial scale, such as fatty amines or hydrogenated tallamines, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, "Amines, aliphatic" chapter. Acids suitable for the reaction are, for example, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalenedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and succinic acids substituted by long-chain hydrocarbon radicals.

More particularly, the component of class (K4) is an oil-soluble reaction product of poly(C₂- to C₂₀-carboxylic acids) having at least one tertiary amino group with primary or secondary amines. The poly(C₂- to C₂₀-carboxylic acids) which have at least one tertiary amino group and form the basis of this reaction product comprise preferably at least 3 carboxyl groups, especially 3 to 12 and in particular 3 to 5 carboxyl groups. The carboxylic acid units in the polycarboxylic acids have preferably 2 to 10 carbon atoms, and are especially acetic acid units. The carboxylic acid units are suitably bonded to the polycarboxylic acids, usually via one or more carbon and/or nitrogen atoms. They are preferably attached to tertiary nitrogen atoms which, in the case of a plurality of nitrogen atoms, are bonded via hydrocarbon chains.

The component of class (K4) is preferably an oil-soluble reaction product based on poly(C₂- to C₂₀-carboxylic acids) which have at least one tertiary amino group and are of the general formula IIa or IIb



in which the variable A is a straight-chain or branched C₂- to C₆-alkylene group or the moiety of the formula III



(III)

- 5 and the variable B is a C₁- to C₁₉-alkylene group. The compounds of the general formulae IIa and IIb especially have the properties of a WASA.

Moreover, the preferred oil-soluble reaction product of component (K4), especially that of the general formula IIa or IIb, is an amide, an amide-ammonium salt or an ammonium salt in which no, one or more carboxylic acid groups have been converted to amide groups.

Straight-chain or branched C₂- to C₆-alkylene groups of the variable A are, for example, 1,1-ethylene, 1,2-propylene, 1,3-propylene, 1,2-butylene, 1,3-butylene, 1,4-butylene, 2-methyl-1,3-propylene, 1,5-pentylene, 2-methyl-1,4-butylene, 2,2-dimethyl-1,3-propylene, 1,6-hexylene (hexamethylene) and especially 1,2-ethylene. The variable A comprises preferably 2 to 4 and especially 2 or 3 carbon atoms.

C₁- to C₁₉-alkylene groups of the variable B are, for example, 1,2-ethylene, 1,3-propylene, 1,4-butylene, hexamethylene, octamethylene, decamethylene, dodecamethylene, tetradecamethylene, hexadecamethylene, octadecamethylene, nonadecamethylene and especially methylene. The variable B comprises preferably 1 to 10 and especially 1 to 4 carbon atoms.

25 The primary and secondary amines as a reaction partner for the polycarboxylic acids to form component (K4) are typically monoamines, especially aliphatic monoamines. These primary and secondary amines may be selected from a multitude of amines which bear hydrocarbon radicals which may optionally be bonded to one another.

30 These parent amines of the oil-soluble reaction products of component (K4) are usually secondary amines and have the general formula HN(R⁸)₂ in which the two variables R⁸ are each independently straight-chain or branched C₁₀- to C₃₀-alkyl radicals, especially C₁₄- to C₂₄-alkyl radicals. These relatively long-chain alkyl radicals are preferably straight-chain or only slightly branched. In general, the secondary amines mentioned,

with regard to their relatively long-chain alkyl radicals, derive from naturally occurring fatty acids and from derivatives thereof. The two R^8 radicals are preferably the same.

The secondary amines mentioned may be bonded to the polycarboxylic acids by means of amide structures or in the form of the ammonium salts; it is also possible for only a portion to be present as amide structures and another portion as ammonium salts. Preferably only few, if any, free acid groups are present. The oil-soluble reaction products of component (K4) are preferably present completely in the form of the amide structures.

Typical examples of such components (K4) are reaction products of nitrilotriacetic acid, of ethylenediaminetetraacetic acid or of propylene-1,2-diaminetetraacetic acid with in each case 0.5 to 1.5 mol per carboxyl group, especially 0.8 to 1.2 mol per carboxyl group, of dioleamine, dipalmitamine, dicocoamine, distearyamine, dibehenylamine or especially ditallowamine. A particularly preferred component (K4) is the reaction product of 1 mol of ethylenediaminetetraacetic acid and 4 mol of hydrogenated ditallowamine.

Further typical examples of component (K4) include the N,N-dialkylammonium salts of 2-N',N'-dialkylamidobenzoates, for example the reaction product of 1 mol of phthalic anhydride and 2 mol of ditallowamine, the latter being hydrogenated or unhydrogenated, and the reaction product of 1 mol of an alkenylspirobis lactone with 2 mol of a dialkylamine, for example ditallowamine and/or tallowamine, the latter two being hydrogenated or unhydrogenated.

Further typical structure types for the component of class (K4) are cyclic compounds with tertiary amino groups or condensates of long-chain primary or secondary amines with carboxylic acid-containing polymers, as described in WO 93/18115.

Sulfocarboxylic acids, sulfonic acids or derivatives thereof suitable as cold flow improvers of the component of class (K5) are, for example, the oil-soluble carboxamides and carboxylic esters of ortho-sulfobenzoic acid, in which the sulfonic acid function is present as a sulfonate with alkyl-substituted ammonium cations, as described in EP-A 261 957.

Poly(meth)acrylic esters suitable as cold flow improvers of the component of class (K6) are either homo- or copolymers of acrylic and methacrylic esters. Preference is given to copolymers of at least two different (meth)acrylic esters which differ with regard to the esterified alcohol. The copolymer optionally comprises another different olefinically unsaturated monomer in copolymerized form. The weight-average molecular weight of the polymer is preferably 50 000 to 500 000. A particularly preferred polymer is a copolymer of methacrylic acid and methacrylic esters of saturated C₁₄- and C₁₅-alcohols, the acid groups having been neutralized with hydrogenated tallamine. Suitable poly(meth)acrylic esters are described, for example, in WO 00/44857.

The cold flow improver or the mixture of different cold flow improvers is added to the middle distillate fuel or diesel fuel in a total amount of preferably 10 to 5000 ppm by weight, more preferably of 20 to 2000 ppm by weight, even more preferably of 50 to 1000 ppm by weight and especially of 100 to 700 ppm by weight, for example of 200 to 500 ppm by weight.

B4) Lubricity improvers

Suitable lubricity improvers or friction modifiers are based typically on fatty acids or fatty acid esters. Typical examples are tall oil fatty acid, as described, for example, in WO 98/004656, and glyceryl monooleate. The reaction products, described in US 6 743 266 B2, of natural or synthetic oils, for example triglycerides, and alkanolamines are also suitable as such lubricity improvers.

B5) Corrosion inhibitors

Suitable corrosion inhibitors are, for example, succinic esters, in particular with polyols, fatty acid derivatives, for example oleic esters, oligomerized fatty acids, substituted ethanolamines, and products sold under the trade name RC 4801 (Rhein Chemie Mannheim, Germany) or HiTEC 536 (Ethyl Corporation).

B6) Demulsifiers

Suitable demulsifiers are, for example, the alkali metal or alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal or alkaline

earth metal salts of fatty acids, and also neutral compounds such as alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylate or tert-pentylphenol ethoxylate, fatty acids, alkylphenols, condensation products of ethylene oxide (EO) and propylene oxide (PO), for example including in the
5 form of EO/PO block copolymers, polyethyleneimines or else polysiloxanes.

B7) Dehazers

Suitable dehazers are, for example, alkoxylated phenol-formaldehyde condensates, for
10 example the products available under the trade names NALCO 7D07 (Nalco) and TOLAD 2683 (Petrolite).

B8) Antifoams

15 Suitable antifoams are, for example, polyether-modified polysiloxanes, for example the products available under the trade names TEGOPREN 5851 (Goldschmidt), Q 25907 (Dow Corning) and RHODOSIL (Rhone Poulenc).

B9) Cetane number improvers

20

Suitable cetane number improvers are, for example, aliphatic nitrates such as 2-ethylhexyl nitrate and cyclohexyl nitrate and peroxides such as di-tert-butyl peroxide.

B10) Antioxidants

25

Suitable antioxidants are, for example substituted phenols, such as 2,6-di-tert-butylphenol and 6-di-tert-butyl-3-methylphenol, and also phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine.

30 B11) Metal deactivators

Suitable metal deactivators are, for example, salicylic acid derivatives such as N,N'-disalicylidene-1,2-propanediamine.

35 B12) Solvents

Suitable solvents are, for example, nonpolar organic solvents such as aromatic and aliphatic hydrocarbons, for example toluene, xylenes, white spirit and products sold under the trade names SHELLSOL (Royal Dutch/Shell Group) and EXXSOL (ExxonMobil), and also polar organic solvents, for example, alcohols such as 2-ethylhexanol, decanol and isotridecanol. Such solvents are usually added to the diesel fuel together with the aforementioned additives and coadditives, which they are intended to dissolve or dilute for better handling.

C) Fuels

The inventive additive is outstandingly suitable as a fuel additive and can be used in principle in any fuels. It brings about a whole series of advantageous effects in the operation of internal combustion engines with fuels. Preference is given to using the inventive quaternized additive in middle distillate fuels, especially diesel fuels.

The present invention therefore also provides fuels, especially middle distillate fuels, with a content of the inventive quaternized additive which is effective as an additive for achieving advantageous effects in the operation of internal combustion engines, for example of diesel engines, especially of direct injection diesel engines, in particular of diesel engines with common rail injection systems. This effective content (dosage) is generally 10 to 5000 ppm by weight, preferably 20 to 1500 ppm by weight, especially 25 to 1000 ppm by weight, in particular 30 to 750 ppm by weight, based in each case on the total amount of fuel.

Middle distillate fuels such as diesel fuels or heating oils are preferably mineral oil raffinates which typically have a boiling range from 100 to 400°C. These are usually distillates having a 95% point up to 360°C or even higher. These may also be what is called "ultra low sulfur diesel" or "city diesel", characterized by a 95% point of, for example, not more than 345°C and a sulfur content of not more than 0.005% by weight or by a 95% point of, for example, 285°C and a sulfur content of not more than 0.001% by weight. In addition to the mineral middle distillate fuels or diesel fuels obtainable by refining, those obtainable by coal gasification or gas liquefaction ["gas to liquid" (GTL) fuels] or by biomass liquefaction ["biomass to liquid" (BTL) fuels] are also suitable. Also

suitable are mixtures of the aforementioned middle distillate fuels or diesel fuels with renewable fuels, such as biodiesel or bioethanol.

5 The qualities of the heating oils and diesel fuels are laid down in detail, for example, in DIN 51603 and EN 590 (cf. also Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Volume A12, p. 617 ff.).

10 In addition to the use thereof in the abovementioned middle distillate fuels of fossil, vegetable or animal origin, which are essentially hydrocarbon mixtures, the inventive quaternized additive can also be used in mixtures of such middle distillates with biofuel oils (biodiesel). Such mixtures are also encompassed by the term "middle distillate fuel" in the context of the present invention. They are commercially available and usually comprise the biofuel oils in minor amounts, typically in amounts of 1 to 30% by weight, especially of 3 to 10% by weight, based on the total amount of middle distillate of fossil, vegetable or animal origin and biofuel oil.

15 Biofuel oils are generally based on fatty acid esters, preferably essentially on alkyl esters of fatty acids which derive from vegetable and/or animal oils and/or fats. Alkyl esters are typically understood to mean lower alkyl esters, especially C₁-C₄-alkyl esters, which are obtainable by transesterifying the glycerides which occur in vegetable and/or animal oils and/or fats, especially triglycerides, by means of lower alcohols, for
20 example ethanol or in particular methanol ("FAME"). Typical lower alkyl esters based on vegetable and/or animal oils and/or fats, which find use as a biofuel oil or components thereof, are, for example, sunflower methyl ester, palm oil methyl ester ("PME"), soya oil methyl ester ("SME") and especially rapeseed oil methyl ester
25 ("RME").

The middle distillate fuels or diesel fuels are more preferably those having a low sulfur content, i.e. having a sulfur content of less than 0.05% by weight, preferably of less than 0.02% by weight, more particularly of less than 0.005% by weight and especially
30 of less than 0.001% by weight of sulfur.

Useful gasoline fuels include all commercial gasoline fuel compositions. One typical representative which shall be mentioned here is the Eurosuper base fuel to EN 228, which is customary on the market. In addition, gasoline fuel compositions of the

specification according to WO 00/47698 are also possible fields of use for the present invention.

5 The inventive quaternized additive is especially suitable as a fuel additive in fuel compositions, especially in diesel fuels, for overcoming the problems outlined at the outset in direct injection diesel engines, in particular in those with common rail injection systems.

10 The invention is now illustrated in detail by the working examples which follow. Especially the test methods specified hereinafter form part of the general disclosure of the application and are not restricted to the specific working examples.

Experimental:

15 **Reagents used:**

N-methyl-N,N-ditallowamine: Armeen® M2HT from Akzo Nobel, CAS 61788-63-4, total amine value 103-110 mg KOH/g.

Solvent Naphtha Heavy from Exxon Mobil, CAS 64742-94-5.

20 dimethyl oxalate from Aldrich, CAS 553-90-2

lauric acid from Aldrich, CAS 143-07-7

3,5,5-trimethylhexanoic acid from BASF, CAS 3302-10-1

methyl salicylate from Aldrich, CAS 119-36-8

2-ethylhexanol from BASF, CAS 104-76-7

25 acetic acid from Aldrich, CAS 64-19-7

A. General test methods

Engine test

30

1. XUD9 test - determination of flow restriction

The procedure was according to the standard stipulations of CEC F-23-1-01.

2. DW10 test - determination of power loss as a result of injector deposits in the common rail diesel engine

2.1. DW10-KC - keep-clean test

- 5 The keep-clean test is based on CEC test procedure F-098-08 Issue 5. This is done using the same test setup and engine type (PEUGEOT DW10) as in the CEC procedure.

Change and special features:

- 10 In the tests, cleaned injectors were used. The cleaning time in the ultrasound bath in water + 10% Superdecontamine (Intersciences, Brussels) at 60°C was 4 h.

Test run times:

- The test run time was 12 h without shutdown phases. The one-hour test cycle from
15 CEC F-098-08, shown in figure 2, was run through 12 times.

Performance determination:

- The initial power $P_{0,KC}$ [kW] is calculated from the measured torque at full load 4000/min directly after the test has started and the engine has run hot. The procedure
20 is described in Issue 5 of the test procedure (CEC F-98-08). This is done using the same test setup and the PEUGEOT DW10 engine type.

- The final performance ($P_{end,KC}$) is determined in the 12th cycle in stage 12 (see table, figure 2). Here too, the operation point is full load 4000/min. $P_{end,KC}$ [kW] is calculated
25 from the torque measured.

The power loss in the KC test is calculated as follows:

$$\text{Powerloss}_{KC} [\%] = \left(1 - \frac{P_{end,KC}}{P_{0,KC}} \right) * 100$$

30 2.2. DW10 dirty-up clean-up (DU-CU)

The DU-CU test is based on CEC test procedure F-098-08 Issue 5. The procedure is described in Issue 5 of the test procedure (CEC F-98-08). This is done using the same test setup and the PEUGEOT DW10 engine type.

The DU-CU test consists of two individual tests which are run in succession. The first test serves to form deposits (DU), the second to remove the deposits (CU). After the DU, the power loss is determined. After the end of the DU run, the engine is not
 5 operated for at least 8 hours and is cooled to ambient temperature. Thereafter, the CU fuel is used to start the CU without deinstalling and cleaning the injectors. The deposits and power loss ideally decline over the course of the CU test.

Change and special features:

10 Cleaned injectors were installed in the engine prior to each DU test. The cleaning time in the ultrasound bath at 60°C, in water + 10% Superdecontamine (Intersciences, Brussels), was 4 h.

Test run times:

15 The test run time was 12 h for the DU and 12 h for the CU. The engine was operated in the DU and CU tests without shutdown phases.

The one-hour test cycle from CEC F-098-08, shown in figure 2, was run through 12 times in each case.

20

Performance determination:

The initial power $P_{0,du}$ [kW] is calculated from the measured torque at full load 4000/min directly after the test has started and the engine has run hot. The procedure is likewise described in Issue 5 of the test procedure.

25

The final performance ($P_{end,du}$) is determined in the 12th cycle in stage 12 (see table above). Here too, the operation point is full load 4000/min. $P_{end,du}$ [kW] is calculated from the torque measured.

30 The power loss in the DU is calculated as follows:

$$\text{Powerloss}_{du} [\%] = \left(1 - \frac{P_{end,du}}{P_{0,du}} \right) * 100$$

Clean-up

The initial power $P_{0,du}$ [kW] is calculated from the measured torque at full load 4000/min directly after the test has started and the engine has run hot in the CU. The procedure is likewise described in Issue 5 of the test procedure.

- 5 The final performance ($P_{end,du}$) is determined in the 12th cycle in stage 12 (see table, figure 2). Here too, the operation point is full load 4000/min. $P_{end,du}$ [kW] is calculated from the torque measured.

10 The power loss in the CU test is calculated as follows (negative number for the power loss in the CU test means an increase in performance)

$$\text{Powerloss (DU,CU)}[\%] = \left(\frac{P_{end,du} - p_{end,cu}}{P_{0,du}} \right) * 100$$

15 The fuel used was a commercial diesel fuel from Haltermann (RF-06-03). To artificially induce the formation of deposits at the injectors, 1 ppm by weight of zinc in the form of a zinc didodecanoate solution was added thereto.

3. IDID test - determination of additive action against internal injector deposits

20 The formation of deposits within the injector was characterized on the basis of the deviations in the exhaust gas temperatures of the cylinders at the cylinder outlet when the DW10 engine is cold-started.

To promote the formation of deposits, 1 mg/l of sodium salt of an organic acid, 20 mg/l of dodecenylsuccinic acid and 10 mg/l of water were added to the fuel.

25

The test is conducted as a dirty-up clean-up test (DU-CU).

DU-CU is based on CEC test procedure F-098-08 Issue 5.

- 30 The DU-CU test consists of two individual tests which are run in succession. The first test serves to form deposits (DU), the second to remove the deposits (CU).

After the DU run, after a rest phase of at least eight hours, a cold start of the engine is conducted, followed by idling for 10 minutes.

Thereafter, the CU fuel is used to start the CU without deinstalling and cleaning the injectors. After the CU run over 8 h, after a rest phase of at least eight hours, a cold start of the engine is conducted, followed by idling for 10 minutes. The evaluation is effected by the comparison of the temperature profiles for the individual cylinders after the cold start in the DU and CU runs.

The IDID test indicates the formation of internal deposits in the injector. The characteristic used in this test is the exhaust gas temperature of the individual cylinders. In an injector system without IDIDs, the exhaust gas temperatures of the cylinders increase homogeneously. In the presence of IDIDs, the exhaust gas temperatures of the individual cylinders do not increase homogeneously and deviate from one another.

The temperature sensors are beyond the cylinder head outlet in the exhaust gas manifold. Significant deviation of the individual cylinder temperatures (e.g. $> 20^{\circ}\text{C}$) indicates the presence of internal injector deposits (IDIDs).

The tests (DU and CU) are each conducted with run time 8 h. The one-hour test cycle from CEC F-098-08 (see figure 3) is run through 8 times in each case. In the event of deviations of the individual cylinder temperatures of greater than 45°C from the mean for all 4 cylinders, the test is stopped early.

Alteration and special features: cleaned injectors were installed prior to the start of each DU test. The cleaning time in the ultrasound bath at 60°C , water + 10% Superdecontamine, was 4 h.

B. Preparation examples:

Preparation example 1: N,N-dimethyl-N,N-ditallowammonium methyloxalate was synthesized on the basis of EP 2 033 945

N-Methyl-N,N-ditallowamine (90 g) is admixed with dimethyl oxalate (90 g) and lauric acid (1.8 g). The reaction mixture is heated to 120°C and stirred at this temperature for 4 h. Subsequently, excess dimethyl oxalate is removed at 130°C under reduced

pressure with the aid of a rotary evaporator. This gives 110.8 g of the product as a white wax. ^1H NMR (CDCl_3) confirms the quaternization.

Preparation example 2: N,N-dimethyl-N,N-ditallowammonium salicylate

N-Methyl-N,N-ditallowamine (80 g) is admixed with methyl salicylate (45.4 g) and 3,5,5-trimethylhexanoic acid (0.8 g). The reaction mixture is heated to 160°C and stirred at this temperature for 4 h. After cooling to room temperature, 124 g of the product are obtained as a white wax. ^1H NMR (CDCl_3) confirms the quaternization.

Preparation example 3: N-methyl-N-(2-hydroxypropyl)-N,N-ditallowammonium acetate

In a 2 l autoclave, a solution of N-methyl-N,N-ditallowamine (250 g) in 2-ethylhexanol (250 g) is admixed with acetic acid (100%, 33.5 g). This is followed by purging three times with N_2 , establishment of an initial pressure of approx. 1.3 bar of N_2 and an increase in the temperature to 50°C . Propylene oxide (54 g) is metered in such that the temperature remains between $45\text{--}55^\circ\text{C}$. This is followed by stirring at 50°C for 10 h, cooling to 25°C , purging with N_2 and emptying of the reactor. The product is degassed on a rotary evaporator at 80°C and 20 mbar for 3 h. This gives 549.4 g of the product in 2-ethylhexanol. ^1H NMR (CDCl_3) confirms the quaternization. The sample is adjusted to an active ingredient content of 38% by addition of Solvent Naphtha Heavy.

C. Use examples:

In the use examples which follow, the additives are used either as a pure substance (as synthesized in the above preparation examples) or in the form of an additive package.

Use example 1: determination of additive action on the formation of deposits in diesel engine injection nozzles

a) XUD9 tests

Fuel used: RF-06-03 (reference diesel, Haltermann Products, Hamburg)

The results are summarized in table 1.

Table 1: Results of the XUD9 tests

Ex.	Reference	Dosage ppm active	Flow restriction 0.1 mm needle stroke [%]
#1	according to preparation example 1	30	8.4
#2	according to preparation example 1	15	22.4

5

b) DW10 test

The table below shows the results of the determinations of the relative power loss at 4000 rpm after 12 hours of sustained operation without interruption. The value P0 gives the power after 10 minutes and the value P_{end} the power at the end of the measurement:

10 The test results are shown in table 2.

15 Table 2: Results of the DW10 test

Additive	Dose [mg/kg]	Power loss KC	Power loss DU	Power loss DU-CU
base value	0		4.1%	
according to preparation example 1, keep clean	100	0.4%		
according to preparation example 1, clean-up	100			-4.9%
base value	0		3.8%	
according to preparation example 2, keep clean	100	-0.4 %		

It is found that the inventive additives according to preparation examples 1 and 2 have improved action compared to the base value.

5 c) Action against internal injector deposits (IDID)

Fuel used: RF-06-03 (reference diesel, Haltermann Products, Hamburg)

The test results are shown in appended figures 1 and 2.

10

Figure 1 shows a measurement of the exhaust gas temperatures of the cylinders in the case of use of a fuel without additive; large deviations in the temperature are caused by internal injector deposits.

15

Figure 2 shows the exhaust gas temperatures measured in the same cylinders after treatment with the inventive additive from preparation example 3, dosage 394 mg/kg.

20

The measurements illustrate the action of the inventive additive for dissolution of internal injector deposits. The falls in the exhaust gas temperature caused by the internal injector deposits (fig. 1, cylinders 1 and 4) can be eliminated again by the inventive additive.

25

Reference is made explicitly to the disclosure of the publications cited herein.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

30

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

35

Claims

1. A quaternized nitrogen compound obtainable by reacting a quaternizable
alkylamine comprising at least one quaternizable tertiary amino group with a
quaternizing agent which converts the at least one tertiary amino group to a
quaternary ammonium group,
wherein the quaternizing agent is a hydrocarbyl epoxide, optionally in
combination with a free acid, or a dialkyl carbonate;
and wherein the alkylamine comprises at least one compound of the following
general formula 3



- in which
at least one of the R_a , R_b and R_c radicals is a straight-chain or branched,
saturated or unsaturated C_8 - C_{40} -hydrocarbyl radical having no heteroatoms and
the remaining radicals are identical or different, straight-chain or branched,
saturated or unsaturated C_1 - C_6 -hydrocarbyl radicals; or
in which all R_a , R_b and R_c radicals are identical or different, straight-chain or
branched, saturated or unsaturated C_8 - C_{40} -hydrocarbyl radicals having no
heteroatoms,
and wherein the quaternizable alkylamine is reacted with the quaternizing agent
in the presence of an inert organic aliphatic or aromatic solvent or a mixture
thereof, or wherein the quaternizable alkylamine is reacted with the quaternizing
agent in the absence of a solvent.

2. A process for preparing a quaternized nitrogen compound, comprising the
reaction of a quaternizable alkylamine comprising at least one quaternizable
tertiary amino group with a quaternizing agent which converts the at least one
tertiary amino group to a quaternary ammonium group,
wherein the quaternizing agent is a hydrocarbyl epoxide, optionally in
combination with a free acid, or a dialkyl carbonate;
and wherein the alkylamine comprises at least one compound of the following
general formula 3



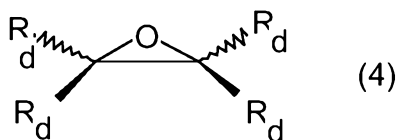
in which

at least one of the R_a , R_b and R_c radicals is a straight-chain or branched, saturated or unsaturated C_8 - C_{40} -hydrocarbyl radical having no heteroatoms and the remaining radicals are identical or different, straight-chain or branched, saturated or unsaturated C_1 - C_6 -hydrocarbyl radicals; or

in which all R_a , R_b and R_c radicals are identical or different, straight-chain or branched, saturated or unsaturated C_8 - C_{40} -hydrocarbyl radicals having no heteroatoms,

and wherein the quaternizable alkylamine is reacted with the quaternizing agent in the presence of an inert organic aliphatic or aromatic solvent or a mixture thereof, or wherein the quaternizable alkylamine is reacted with the quaternizing agent in the absence of a solvent.

3. The quaternized nitrogen compound according to claim 1 or the process according to claim 2, wherein the quaternizing agent comprises an epoxide of the general formula 4



where

the R_d radicals present therein are the same or different and are each H or a hydrocarbyl radical, where the hydrocarbyl radical is an aliphatic or aromatic radical having at least 1 to 10 carbon atoms and the free acid of the quaternizing agent is a free protic acid.

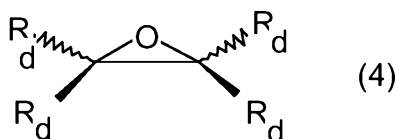
4. The quaternized nitrogen compound or the process according to claim 3, wherein the free protic acid is a C_{1-12} -monocarboxylic acid or -dicarboxylic acid.
5. The quaternized nitrogen compound or the process according to any one of the preceding claims, wherein the quaternizable tertiary amine is a compound of the formula 3 in which at least two of the R_a , R_b and R_c radicals are the same or different and are each a straight-chain or branched C_{10} - C_{20} -alkyl radical and the other radical is C_1 - C_4 -alkyl.

6. The quaternized nitrogen compound or the process according to any one of the preceding claims, wherein the quaternizing agent is selected from lower alkylene oxides in combination with a monocarboxylic acid, alkyl salicylates, dialkyl phthalates and dialkyl oxalates.
7. An additive concentrate comprising, in combination with further diesel fuel additives or gasoline fuel additives or lubricant additives, at least one quaternized nitrogen compound as defined in or prepared according to any one of the preceding claims.
8. A fuel composition or lubricant composition comprising, in a majority of a customary fuel or lubricant, a proportion of at least one reaction product comprising a quaternized nitrogen compound, or of a fraction thereof which comprises a quaternized nitrogen compound and is obtained from the reaction product by purification, wherein the reaction product is obtainable by reacting a quaternizable alkylamine comprising at least one quaternizable tertiary amino group with a quaternizing agent which converts the at least one tertiary amino group to a quaternary ammonium group, wherein the quaternizing agent is an alkyl epoxide, optionally in combination with a free acid, or a dialkyl carbonate; and wherein the alkylamine comprises at least one compound of the following general formula 3



- in which
- at least one of the R_a , R_b and R_c radicals is a straight-chain or branched, saturated or unsaturated C_8 - C_{40} -hydrocarbyl radical having no heteroatoms and the remaining radicals are identical or different, straight-chain or branched, saturated or unsaturated C_1 - C_6 -hydrocarbyl radicals; or
- in which all R_a , R_b and R_c radicals are identical or different, straight-chain or branched, saturated or unsaturated C_8 - C_{40} -hydrocarbyl radicals having no heteroatoms,
- and wherein the quaternizable alkylamine is reacted with the quaternizing agent in the presence of an inert organic aliphatic or aromatic solvent or a mixture thereof, or wherein the quaternizable alkylamine is reacted with the quaternizing agent in the absence of a solvent.

9. The fuel composition or lubricant composition according to claim 8, wherein the quaternizing agent comprises an epoxide of the general formula 4



where

the R_d radicals present therein are the same or different and are each H or a hydrocarbyl radical, where the hydrocarbyl radical is an aliphatic or aromatic radical having at least 1 to 10 carbon atoms and the free acid of the quaternizing agent is a free protic acid.

10. The fuel composition or lubricant composition according to claim 9, wherein the free protic acid is a C_{1-12} -monocarboxylic acid or -dicarboxylic acid.
11. The fuel composition or lubricant composition according to any one of claims 8 to 10, wherein the quaternizable tertiary amine is a compound of the formula 3 in which at least two of the R_a , R_b and R_c radicals are the same or different and are each a straight-chain or branched C_{10} - C_{20} -alkyl radical and the other radical is C_1 - C_4 -alkyl.
12. The fuel composition or lubricant composition according to any one of claims 8 to 11, wherein the quaternizing agent is selected from lower alkylene oxides in combination with a monocarboxylic acid, alkyl salicylates, dialkyl phthalates and dialkyl oxalates.
13. The fuel composition or lubricant composition according to any one of claims 8 to 12, selected from diesel fuels, biodiesel fuels, gasoline fuels, and alkanol-containing gasoline fuels.

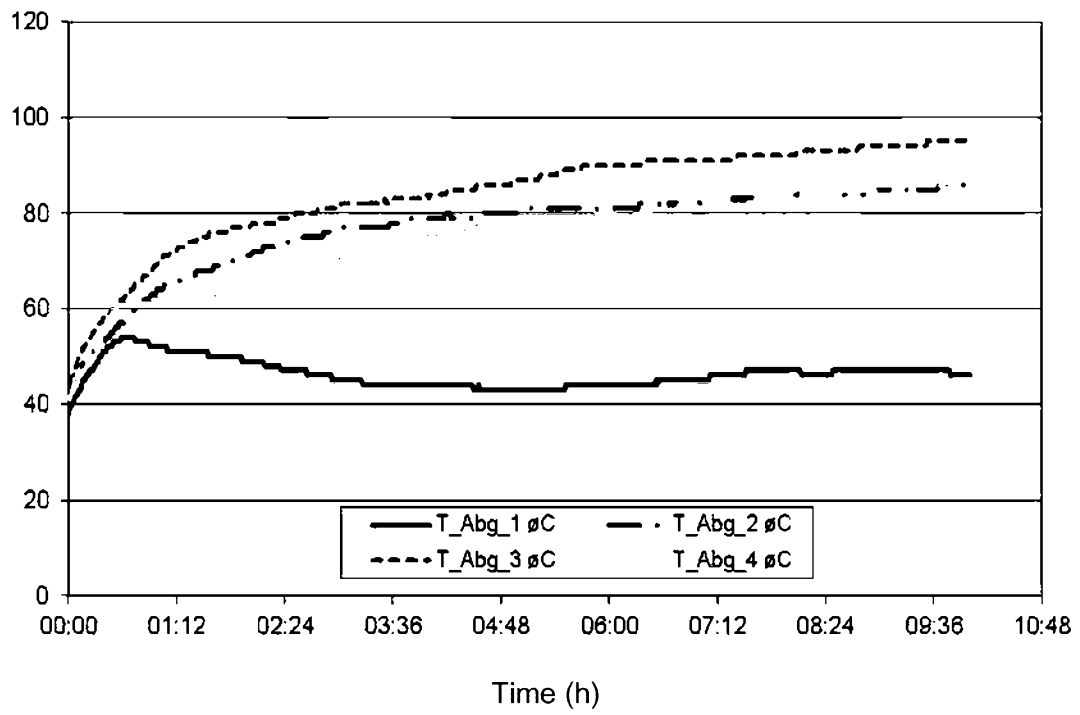


Fig.1

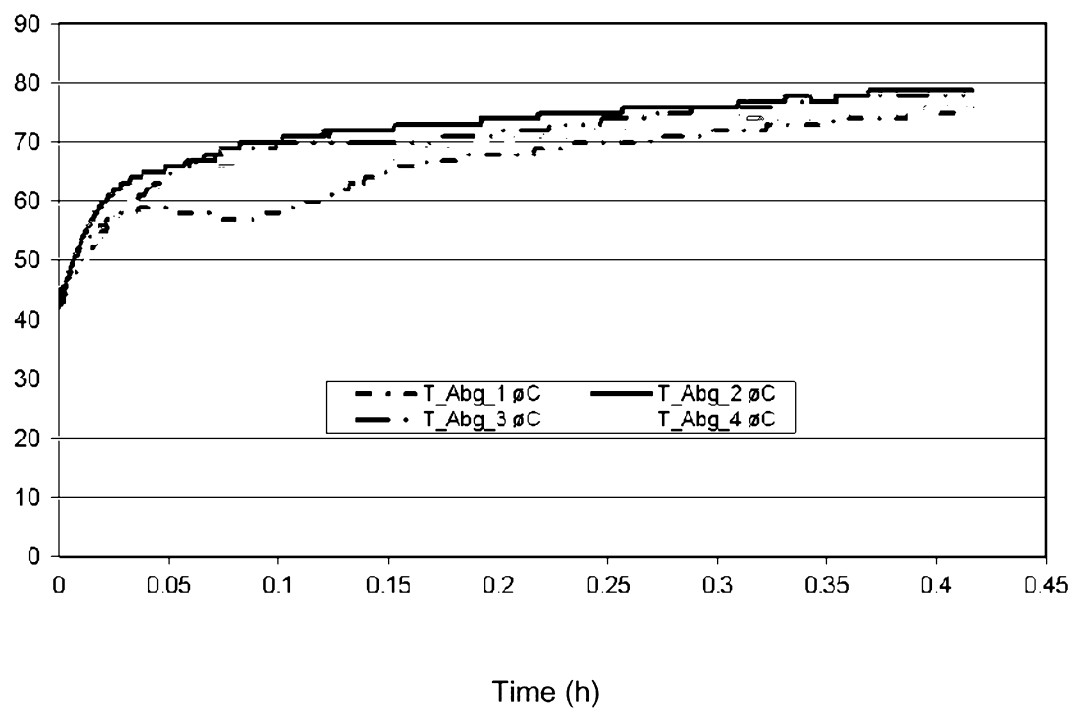


Fig.2

step	duration (minutes)	engine speed (rpm) +/- 20	load (%)	torque (Nm) +/-5	boost air after IC (°C) +/-3
1	2'	1750	(20)	62	45
2	7'	3000	(60)	173	50
3	2'	1750	(20)	62	45
4	7'	3500	(80)	212	50
5	2'	1750	(20)	62	45
6	10'	4000	100	*	50
7	2'	1250	(10)	25	43**
8	7'	3000	100	*	50
9	2'	1250	(10)	25	43**
10	10'	2000	100	*	50
11	2'	1250	(10)	25	43**
12	7'	4000	100	*	50
	Σ= 1 hour				

* for expected range see appendix 06.5

** target only

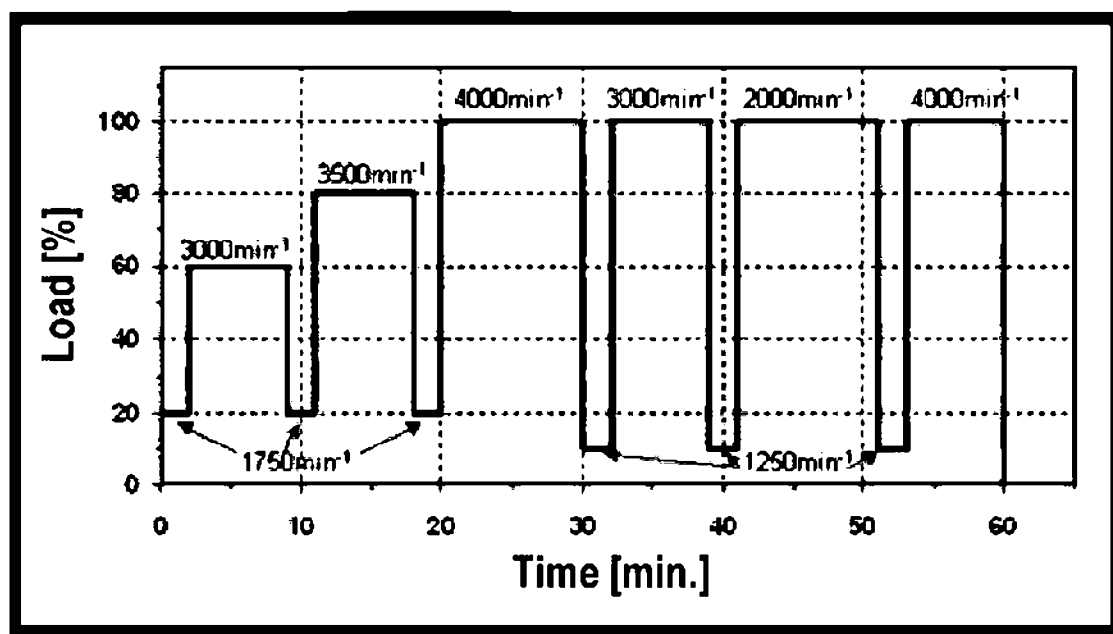


Fig.3