

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 June 2009 (18.06.2009)

PCT

(10) International Publication Number
WO 2009/074606 A1

(51) International Patent Classification:
C10L 1/14 (2006.01) *C10L 10/06* (2006.01)
C10L 10/00 (2006.01) *C10L 10/18* (2006.01)

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(21) International Application Number:
PCT/EP2008/067223

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:
10 December 2008 (10.12.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
07122864.7 11 December 2007 (11.12.2007) EP

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments



WO 2009/074606 A1

(54) Title: HYDROCARBYLPHENOLS AS INTAKE VALVE CLEAN-UP BOOSTERS

(57) Abstract: The present invention relates to a fuel additive composition comprising polyisobutenyl monoamines or polyamines as nitrogen-containing dispersants, synthetic or mineral carrier oils which are substantially free of nitrogen, and hydrocarbylphenols with long-chain hydrocarbyl residues. Furthermore, it relates to a gasoline fuel composition comprising a minor amount of this fuel additive composition. Furthermore, it relates to the use of such long-chain hydrocarbylphenol as an intake valve clean-up booster in internal combustion engines operated with gasoline containing the above detergents and the carrier oils.

Hydrocarbylphenols as Intake Valve Clean-up Boosters

Description

5 The present invention relates to a novel fuel additive composition comprising nitrogen-containing dispersants selected from polyisobutenyl monoamines and polyisobutenyl polyamines, carrier oils which are substantially free of nitrogen and which are selected from synthetic carrier oils and mineral carrier oils, and hydrocarbylphenols with at least one long-chain hydrocarbyl residue. Furthermore, the present invention relates to a
10 gasoline fuel composition comprising a minor amount of the said fuel additive composition. Furthermore, the present invention relates to the use of such long-chain hydrocarbylphenols as an intake valve clean-up booster in internal combustion engines operated with gasoline containing the above detergents and the above carrier oils.

15 Technical Background

Carburettors and inlet systems of automobile engines, and also injection systems for fuel proportioning, are subjected to increasing load due to contamination caused by dust particles from the air, unburned hydrocarbon residues from the combustion chamber and crankcase ventilation, and exhaust gas recycle passed to the intake system.
20

These residues shift the air-to-fuel ratio during idling and in the lower partial load region, so that the mixture becomes richer and combustion less complete and consequently the content of unburned or partly burned hydrocarbons in the exhaust gas increases and the gasoline consumption rises.
25

It is known that these drawbacks may be avoided through the use of fuel additives for cleaning the valves and carburettors or injection systems of Otto engines (cf. e.g.: M. Rossenbeck in "Katalysatoren, Tenside, Mineralöladditive", edited by J. Falbe, U. Hasserodt, page 223, G. Thieme Verlag, Stuttgart 1978).
30

For trouble-free running, modern Otto engines require automotive fuels having a complex set of properties which can only be guaranteed when use is made of appropriate gasoline additives. Such fuels usually consist of a complex mixture of chemical compounds and are characterized by physical parameters.
35

Fuel additives are i.a. used in order to avoid formation of deposits in the intake system and the intake valves of engines (keep-clean effect). On the other hand, fuel additives may be used in order to remove deposits already formed at the valves and in the intake system (clean-up effect).
40

Hydrocarbylphenols such as 4-polyisobutenylphenols with or without further short-chain alkyl substituents in the 2- and/or 6-position are generally known as additives in fuels,

e.g. from WO 05/073152 and WO 02/26840. When carrying sterically hindered residues, the said hydrocarbylphenols especially function as antioxidants.

5 WO 01/23440 relates to fuel additives and gasoline fuel formulations effective in reducing intake valve deposits. The components for these fuel additives are amines having at least one polyolefin group, polyetheramines, and optionally hydrocarbylphenols. Example 6 in Table 1 of this document discloses an additive concentrate comprising 35 ptb (about 140 ppm) of N-poly(butene)ethylenediamine (Mn about 1300) as the amine component, 35 ptb (about 140 ppm) of polyetheramine made by reductive amination of 4-alkylphenol initiated polyoxypropylene monool, and 17.5 ptb (about 70 ppm) of polyisobutene phenol (molecular weight equals 1000), the said additive concentrate resulting in an intake valve deposit clean-up effect of 46 % reduction of deposit after build-up.

15 EP 0 878 532 A1 relates to a gasoline fuel composition comprising about 50 to about 800 ppm of an additive composition comprising polyether alcohols, long-chain hydrocarbylphenols, and optionally nitrogen-containing dispersants such as acylated amines, hydrocarbyl-substituted amines, e.g. polybutene amines, Mannich dispersants or polyetheramines. Example 6 in Table 1 of this document discloses an additive concentrate comprising 120 ppm of polyisobutenylphenol, 120 ppm of a Emkarox AF-20 (a polypropylene oxide monool), 40 ppm of polybutenyl amine based detergent, and 40 ppm of acylated amine dispersant, the said additive concentrate resulting in an intake valve deposit effect of 35 mg in the 2.3L Ford engine.

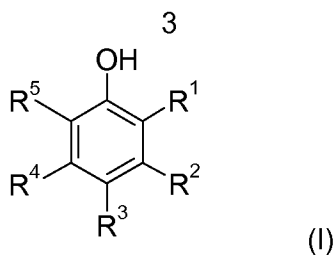
25 The interrelationship between gasoline fuels and appropriate fuel additives in fuel compositions may still be unsatisfactory as regards their intake valve clean-up performance. It is, therefore, an object of the present invention to provide improved fuel additive formulations which allow an efficient control of deposits formed in the engine, especially an improved intake valve clean-up performance.

30

Brief Description of the Invention

It has now been observed that a fuel additive composition comprising:

- 35 (A) at least one nitrogen-containing dispersant selected from polyisobutenyl monoamines and polyisobutenyl polyamines,
- (B) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils, and
- 40 (C) at least one hydrocarbylphenol of formula I



wherein at least one of R¹ to R⁵ is a C₆-C₂₀₀-hydrocarbyl residue and the others are C₁-C₅-hydrocarbyl residues and/or hydrogen,

5

improves the intake valve clean-up performance of gasoline fuels significantly. Therefore, the said fuel additive composition is a first subject matter of the instant invention.

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

A third subject matter of the instant invention is the use of a hydrocarbylphenol (C) of formula I as set above as an intake valve clean-up booster in internal combustion engines operated with a liquid fuel in the gasoline boiling range containing minor amounts of (A) at least one nitrogen-containing dispersant selected from polyisobutenyl monoamines and polyisobutenyl polyamines and (B) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils.

20 Details Description of the Invention and Preferred Embodiments

The nitrogen-containing dispersant (Component A)

The polyisobutenes which are suitable for preparing the polyisobutenyl monoamines and polyisobutenyl polyamines used in the present invention include polyisobutenes which comprise at least about 20%, preferably at least 50% and more preferably at least 70% of the more reactive methylvinylidene isomer. Suitable polyisobutenes include those prepared using BF₃ catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high percentage of the total composition is for example described in US-A 4,152,499 and US-A 4,605,808.

Examples of suitable polyisobutenes having a high alkylvinylidene content include Ultravis® 30, a polyisobutene having a number average molecular weight of about 1300 and a methylvinylidene content of about 74%, and Ultravis® 10, a 950 molecular weight polyisobutene having a methylvinylidene content of about 76%, both available from British Petroleum. Another example of a suitable polyisobutene having a number average molecular weight of about 1000 and a high methylvinylidene content is Glisopal® 1000, available from BASF Aktiengesellschaft.

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

5

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

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

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

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

25 Particularly preferred polyisobutenyl polyamines include polyisobutenyl ethylene diamine and polyisobutenyl amine. The polyisobutenyl group is substantially saturated.

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

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

A polyamine finding use within the scope of the present invention as amine component for the polyisobutenyl polyamines may be a polyalkylene polyamine, including substituted polyamines, e.g., alkyl and hydroxyalkyl-substituted polyalkylene polyamine.

Among the polyalkylene polyamines, those containing 2-12 amino nitrogen atoms and 2-24 carbon atoms should be mentioned, in particular C2 -C3 alkylene polyamines. Preferably, the alkylene group contains from 2 to 6 carbon atoms, there being preferably from 2 to 3 carbon atoms between the nitrogen atoms. Such groups are exemplified by ethylene, 1,2-propylene, 2,2-dimethylpropylene, trimethylene, 1,3,2-hydroxy-propylene.

10

Examples of such polyamines include ethylene diamine, diethylene triamine, di(trimethylene) triamine, 1,2-propylene diamine, 1,3-propylene diamine, dipropylene triamine, triethylene tetraamine, tripropylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, hexamethylene diamine, and dimethylaminopropylene diamine.

15

Such amines encompass isomers such as branched-chain polyamines and previously-mentioned substituted polyamines, including hydroxy- and hydrocarbyl-substituted polyamines.

20

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

25

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

30

Alternatively, the amine component for the polyisobutenyl monoamines may be derived from a monoamine having the formula HNR^6R^7 wherein R^6 and R^7 are independently selected from the group consisting of hydrogen and hydrocarbyl of 1 to about 20 carbon atoms and, when taken together, R^6 and R^7 may form one or more 5- or 6-membered rings containing up to about 20 carbon atoms. Preferably, R^6 is hydrogen and R^7 is a hydrocarbyl group having 1 to about 10 carbon atoms. More preferably, R^6 and R^7 are hydrogen. The hydrocarbyl groups may be straight-chain or branched and may be aliphatic, alicyclic, aromatic or combinations thereof. The hydrocarbyl groups may also contain one or more oxygen atoms.

35

40

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

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

Cyclic secondary amines may also be employed to form the polyisobutenyl monoamines or polyisobutenyl polyamines used in the instant invention. In such cyclic compounds, R⁶ and R⁷ of the formula hereinabove, when taken together, form one or more 5- or 6-membered rings containing up to about 20 carbon atoms. The ring containing the amine nitrogen atom is generally saturated, but may be fused to one or more saturated or unsaturated rings. The rings may be substituted with hydrocarbyl groups of from 1 to about 10 carbon atoms and may contain one or more oxygen atoms.

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

The number average molecular weight of the polyisobutenyl monoamines or polyisobutenyl polyamines used in the instant invention is usually in the range of from 500 to 2500, typically about 550, about 750, about 1000 or about 1300. A preferred range for the number average molecular weight of the polyisobutenyl monoamines or polyisobutenyl polyamines is from 550 to 1000. As already stated for the polyisobutene precursors, the polyisobutenyl monoamines or polyisobutenyl polyamines are mostly not pure single products, but rather mixtures of compounds having number average molecular weights as indicated above. Usually, the range of molecular weights will be relatively narrow having a maximum near the indicated molecular weight.

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

The carrier oil (Component B)

The fuel-soluble, nonvolatile carrier oil of component (B) is to be used as a necessary part of the fuel additive composition of the instant invention, in order to achieve the
5 desired improvement in intake valve clean-up performance. The carrier oil is a chemically inert hydrocarbon-soluble liquid vehicle. The carrier oil of component (B) may be a synthetic oil or a mineral oil; for the instant invention, a refined petroleum oil is also understood to be a mineral oil.

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

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

20

When employed in fuel additive compositions or fuel additive concentrates, such as in the instant fuel additive composition, carrier oils will generally be present in amounts ranging from about 10 to about 60 weight percent, preferably from 20 to 40 weight percent (referring to the amount of all components in the composition or concentrate, respectively, including possible solvents).
25

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

Examples for synthetic carrier oils which can be used for the instant invention are olefin
35 polymers with a number average molecular weight of from 400 to 1800, based on poly-alpha-olefins or poly-internal-olefins, especially those based on polybutene or on polyisobutene (hydrogenated or nonhydrogenated). Further examples for suitable synthetic carrier oils are polyesters, polyalkoxylates, polyethers, alkylphenol-initiated polyethers, and carboxylic acids of long-chain alkanols.

40

Examples for suitable polyethers which can be used for the instant invention are compounds containing polyoxy-C₂-C₄-alkylene groups, especially polyoxy-C₃-C₄-alkylene groups, which can be obtained by reacting C₁-C₃₀-alkanols, C₂-C₆₀-alkandiols,

C₁-C₃₀-alkylcyclohexanols or C₁-C₃₀-alkylphenols with 1 to 30 mol ethylene oxide and/or propylene oxide and/or butylene oxides per hydroxyl group, especially with 1 to 30 mol propylene oxide and/or butylene oxides per hydroxyl group. This type of compounds is described, for example, in EP-A 310 875, EP-A 356 725, EP-A 700 985 and
5 US-A 4,877,416.

Typical examples for suitable polyethers are tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates, polyisobutenol butoxylates and polyisobutenol propoxylates.
10

Hydrocarbyl-terminated poly(oxyalkylene) polymers which may be employed in the present invention as component (B), are monohydroxy compounds, i.e., alcohols, and are often termed monohydroxy polyethers, or polyalkylene glycol monohydrocarbylethers, or "capped" poly(oxyalkylene).
15

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

In general, the poly(oxyalkylene) polymers are mixtures of compounds that differ in polymer chain length. However, their properties closely approximate those of the poly-
40 mer represented by the average composition and molecular weight.

Examples of carboxylic esters of long-chain alkanols are esters of mono-, di- and tri-carboxylic acids with long-chain alkanols or polyhydric alcohols such as described e.g.

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

Examples for particularly useful synthetic carrier oils are alcohol-initiated polyethers containing about 5 to 35, e.g. 5 to 30 C₃-C₆-alkylenoxide units, such as propylenoxide, n-butylenoxide and iso-butylenoxide units or mixtures thereof. Non-limiting examples
10 for alcoholic starters are long-chain alkanols or phenols substituted by long-chain alkyl groups, where the alkyl group preferably is linear or branched C₆-C₁₈-alkyl. Preferred examples for the alcoholic starters are tridecanol and nonylphenol.

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

Preferably, synthetic carrier oils are used. Preferred synthetic carrier oils are alkanol alkoxyates, in particular alkanol propoxyates and alkanol butoxyates.

20 In an especially preferred embodiment, carrier oil component (B) comprises at least one polyether obtained from C₁-C₃₀-alkanols, especially C₆-C₁₈-alkanols, or C₂-C₆₀-alkandiols, especially C₈-C₂₄-alkandiols, and from 1 to 30 mol, especially 5 to 30 mol, in sum, of propylene oxide and/or butylene oxides. Other synthetic carrier oils and/or mineral carrier oils may be present in component (B) in minor amounts.

25 The hydrocarbylphenol (Component C)

Phenol compounds useful as starting materials for preparing the long-chain hydrocarbylphenols of component (C) are typically phenol (C₆H₅OH), xyenols, cresols, and
30 other monohydric phenols. Preferably, phenols carrying already one or more C₁-C₅-hydrocarbon residues are suitable starting materials, in case one or more C₁-C₅-hydrocarbon residues are desired in hydrocarbylphenol component (C) of formula I.

Numerous methods are known for preparing hydrocarbyl-substituted phenols, also
35 considered suitable for preparing instant hydrocarbylphenols of formula I. Techniques for alkylating phenols, such as for the above-listed phenols as starting materials for the instant long-chain hydrocarbylphenols (C), are well known to those skilled in the art. One particularly suitable technique is the Friedel-Crafts reaction, wherein an olefin (e.g. a polymer containing an olefinic bond, or halogenated or hydrohalogenated analogs
40 thereof) is reacted with a phenol in the presense of a Lewis acid catalyst (e.g.: boron trifluoride and its complexes with ethers, phenols or hydrogen fluoride; aluminium chloride; aluminium bromide; zinc dichloride; etc.). Other equally appropriate and conven-

ient techniques for attaching long-chain hydrocarbyl groups to aromatic rings of phenols will occur readily to those skilled in the art.

“Hydrocarbyl residue” for R^1 to R^5 in formula I shall mean a residue which is essentially
5 composed of carbon and hydrogen, however, it can contain in small amounts heteroatoms, especially oxygen and/or nitrogen, and/or functional groups, e.g. hydroxyl groups and/or carboxylic groups, to an extent which does not distort the predominantly hydrocarbon character of the residue. Hydrocarbyl residues are preferably alkyl, alkenyl, alkynyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups. Especially preferred hydrocarbyl residues for R^1 to R^5 in formula I are linear or branched alkyl or alkenyl groups.
10

The hydrocarbylphenol of formula I may exhibit one long-chain hydrocarbyl residue, preferably for R^1 or more preferably for R^3 , or two such long-chain hydrocarbyl residues, preferably for R^1 and R^3 , or three of them, preferably for R^1 and R^3 and R^5 . The
15 said long-chain hydrocarbyl residue, which is preferably a linear or branched alkyl group or which is preferably a residue derived from an oligomer or a polymer or a copolymer of a C_2 - C_6 olefin such as ethylene, propylene, 1,2-butylene, isobutylene or 2,3-butylene, has 6 to 200, preferably 8 to 170, more preferably 12 to 140, most preferably 16 to 100 carbon atoms. Such oleophilic long-chain hydrocarbyl residues provide advantageous properties to the hydrocarbylphenols, i.e. high solubility for gasoline
20 fuels and low volatility.

In one especially preferred embodiment, the at least one C_6 - C_{200} -hydrocarbyl residue in formula I of component (C) is a polyisobutenyl residue with 12 to 100 carbon atoms.
25 For the polyisobutene starting material for component (C) applies the same as stated above for the polyisobutene starting material for component (A).

In another especially preferred embodiment, the at least one C_6 - C_{200} -hydrocarbyl residue in formula I of component (C) is a linear or branched alkyl residue with 6 to 12 carbon atoms. Examples of such alkyl residues are n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, iso-nonyl, n-decyl, 2-propylheptyl, n-undecyl and n-dodecyl.
30

Other suitable C_6 - C_{200} -hydrocarbyl residues are cyclohexyl, methylcyclohexyl, phenyl, tolyl, xylyl or benzyl.
35

The C_1 - C_5 -hydrocarbyl residues, if any, are usually short-chain alkyl groups, e.g. methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec.-butyl, tert.-butyl, n-pentyl or tert.-pentyl.
40

Typical examples for hydrocarbylphenol of formula I suitable as component (C) for the instant invention are: 4-polyisobutenylphenol, 2,4-bis(polyisobutenyl)phenol, 2-methyl-4-polyisobutenylphenol, 2-iso-propyl-4-polyisobutenylphenol, 2-tert.-butyl-4-polyisobutenylphenol, 2,6-dimethyl-4-polyisobutenylphenol, 2,6-di-iso-propyl-4-polyisobutenyl-

phenol and 2,6-di-tert.-butyl-4-polyisobutenylphenol. The polyisobutenyl residues in the above list are typically composed of 3, 4 or 5 isobutene units (molecular weight of 167, 223 or 279, respectively) or, in the alternative, have typically a number average molecular weight of about 950 or about 1000, corresponding to 68 carbon atoms or
5 72 carbon atoms, respectively.

The fuel additive composition

The instant fuel additive composition may be formulated as a concentrate, using an
10 inert stable oleophilic (i.e., dissolves in fuel) organic solvent boiling in the range of about 65°C to 205°C. Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene or higher-boiling aromatics or aromatic thin-
ners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcar-
binol, n-butanol, 2-ethylhexanol, and the like, in combination with hydrocarbon sol-
15 vents, are also suitable for use in such concentrate. In the concentrate, the amount of the instant fuel additive composition will be ordinarily at least 10% by weight to about 90% by weight, as for example 40 to 85 weight percent or 50 to 80 weight percent.

In gasoline fuels, other fuel additives may be employed with the additives of the pre-
20 sent invention, including, for example, oxygenates, such as tert.-butyl methyl ether, antiknock agents, such as methylcyclopentadienyl manganese tricarbonyl, and other dispersants/detergents, such as various hydrocarbyl amines, or succinimides. Preferably, polyetheramines, i.e. hydrocarbyl poly(oxyalkylene) amines, are excluded from the instant fuel additive composition. A list of suitable other detergent additives is for ex-
25 ample given in WO 00/47698 or in EP-A 1 155 102.

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

In an especially preferred embodiment, the weight ratio of dispersant component (A) to hydrocarbylphenol component (C) is in the range of from 0.3 : 1 to less than 2 : 1, thus provided the best improvement of intake valve clean-up performance of gasoline fuels.

35 An interaction between all three components (A), (B) and (C) is necessary to achieve the desired improvement in intake valve clean-up performance. In the instant fuel additive composition, the hydrocarbylphenol (C) may exhibit a synergistic effect in this respect when used in combination with components (A) and (B) of the instant fuel additive composition.

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The fuel composition

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

The proper concentration of the instant fuel additive composition necessary in order to achieve the desired intake valve clean-up performance varies depending upon the type of fuel employed, and may also be influenced by the presence of other detergents, dispersants and other additives, etc. Generally, however, from 200 to 10.000 weight ppm, especially from 400 to 2800 weight ppm, of the instant fuel additive composition per part of base fuel is needed to achieve the best results.

In an especially preferred embodiment, dispersant component (A) is present in the instant fuel composition at a level of from more than 50 to 3000 ppm, especially from 100 to 800 ppm, carrier oil component (B) at a level of from 50 to 2000 ppm, especially from 100 to 800 ppm, and hydrocarbylphenol component (C) at a level of from 100 to 3000 ppm, especially from 200 to 1200 ppm (all ppm values refer to the weight).

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

The aromatics content of the gasoline is preferably not more than 50 volume % and more preferably not more than 45 volume %. Preferred ranges for the aromatics content are from 1 to 42 volume % and particularly from 5 to 40 volume %.

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

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

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

The gasoline has an oxygen content of not more than 45 weight %, preferably from 0 to 2.7 weight %, and most preferably from 0.1 to 2.7 weight % (first type) or most preferably from 2.7 to 45 weight % (second type). The gasoline of the second type mentioned

above is a mixture of lower alcohols such as methanol or especially ethanol, which derive preferably from natural source like plants, with mineral oil based gasoline, i.e. usual gasoline produced from crude oil. An example for such gasoline is "E 85", a mixture of 85 volume % of ethanol with 15 volume % of mineral oil based gasoline.

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The content of alcohols, especially lower alcohols, and ethers in a gasoline of the first type mentioned in the above paragraph is normally relatively low. Typical maximum contents are for methanol 3 volume %, for ethanol 5 volume %, for isopropanol 10 volume %, for tert.-butanol 7 volume %, for isobutanol 10 volume %, and for ethers containing 5 or more carbon atoms in the molecule 15 volume %.

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For example, a gasoline which has an aromatics content of not more than 38 volume % and at the same time an olefin content of not more than 21 volume %, a sulfur content of not more than 50 ppm by weight, a benzene content of not more than 1.0 volume % and an oxygen content of from 0.1 to 2.7 weight % may be applied.

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

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

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

25 Experimental Part

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

30 Example 1:

1.1. In a test engine of the type M 102 E, a first test run for intake valve deposits ("IVD") according to standard procedure CEC F-05-A-93 was carried through using a commercially available 100 RON gasoline from a German refinery containing no fuel additives ("dirty-up" run). As a result, deposits of 136 mg/valve on average were found.

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1.2. A second test run for IVD in the same engine (without cleaning of the intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 100 RON gasoline, however, now containing 1250 ppm by weight of a fuel additive package comprising a polyisobutenyl monoamine (Glissopal® 1000) dispersant, a polyether carrier oil (based on a blockwise propoxylated and butoxylated C₁₃-alkanol) and a hydrocarbon solvent ("clean-up" run), the dosage

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for the polyisobutenyl amine being 280 ppm by weight (polymer content) and for the polyether 260 ppm by weight (each per part of the gasoline base fuel). As a result, deposits of 29 mg/valve on average were found. According to the formula:

5 clean-up effect [%] = $100 \times (\text{IVD after dirty-up} - \text{IVD after clean-up}) / \text{IVD after dirty-up}$

a clean-up effect of 79 % was determined for the use of dispersant plus carrier oil.

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1.3. A third test run for IVD in the same engine (starting with clean intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 100 RON gasoline, now containing no fuel additives again (second "dirty-up" run). As a result, deposits of 129 mg/valve on average were found.

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1.4 A fourth test run for IVD in the same engine (without cleaning of the intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 100 RON gasoline, however, now containing 1250 ppm by weight of the same fuel additive package as under 1.2. above plus 1000 ppm by weight of 2-tert.-butyl-4-polyisobutenylphenol, the polyisobutenyl residue consisting of 4 isobutene units (each per part of the gasoline base fuel) (second "clean-up" run). As a result, deposits of 5 mg/valve on average were found. According to the formula under 1.2. above, a clean-up effect of 96 % was determined for the use of dispersant plus carrier oil plus hydrocarbylphenol.

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1.5 A fifth test run for IVD in the same engine (starting with clean intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 100 RON gasoline, however, now containing 600 ppm by weight (per part of the gasoline base fuel) of 2-tert.-butyl-4-polyisobutenylphenol, the polyisobutenyl residue consisting of 4 isobutene units. No other fuel additive was present. As a result, deposits of 178 mg/valve on average were found, showing that the hydrocarbylphenol itself has no detergency effect but acts only synergistically with the fuel additive package.

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35 Example 2:

2.1. In a test engine of the type M 102 E, a first test run for IVD according to standard procedure CEC F-05-A-93 was carried through using a commercially available 95 RON gasoline from a German refinery containing no fuel additives ("dirty-up" run). As a result, deposits of 155 mg/valve on average were found.

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- 2.2. A second test run for IVD in the same engine (without cleaning of the intake valves) according to standard procedure CEC F-05-A-93 was carried through using a commercially available 100 RON gasoline from a German refinery, containing 1250 ppm by weight of a fuel additive package comprising a polyisobutenyl monoamine (Glissopal® 1000) dispersant, a polyether carrier oil (based on a blockwise propoxyated and butoxylated C₁₃-alkanol) and a hydrocarbon solvent (“clean-up” run), the dosage for the polyisobutenyl amine being 280 ppm by weight (polymer content) and for the polyether 260 ppm by weight (each per part of the gasoline base fuel). As a result, deposits of 23 mg/valve on average were found. According to the formula under 1.2. above, a clean-up effect of 85 % was determined for the use of dispersant plus carrier oil.
- 2.3. A third test run for IVD in the same engine (starting with clean intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 95 RON gasoline as under 2.1. above, containing no fuel additives again (second “dirty-up” run). As a result, deposits of 189 mg/valve on average were found.
- 2.4. A fourth test run for IVD in the same engine (without cleaning of the intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 100 RON gasoline as under 2.2. above, however, now containing 1250 ppm by weight of the same fuel additive package as under 1.2. above plus 600 ppm by weight of 2-tert.-butyl-4-polyisobutenylphenol, the polyisobutenyl residue consisting of 4 isobutene units (each per part of the gasoline base fuel) (second “clean-up” run). As a result, deposits of 9 mg/valve on average were found. According to the formula under 1.2. above, a clean-up effect of 95 % was determined for the use of dispersant plus carrier oil plus hydrocarbylphenol.

Example 3:

- 3.1. In a test engine of the type M 102 E, a first test run for IVD according to standard procedure CEC F-05-A-93 was carried through using a commercially available 95 RON gasoline from a German refinery (but different from the 95 RON gasoline used in Example 1) containing no fuel additives (“dirty-up” run). As a result, deposits of 132 mg/valve on average were found.
- 3.2. A second test run for IVD in the same engine (without cleaning of the intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 95 RON gasoline, however, now containing 835 ppm by weight of a fuel additive package comprising a polyisobutenyl monoamine (Glissopal® 1000) dispersant, a polyether carrier oil (based on a mixture of propoxyated and butoxylated C₁₃-alkanols) and a hydrocarbon solvent (“clean-up” run), the dosage for the polyisobutenyl amine being 280 ppm by weight (polymer content) and for

the polyether 260 ppm by weight (each per part of the gasoline base fuel). As a result, deposits of 34 mg/valve on average were found. According to the formula under 1.2. above, a clean-up effect of 74 % was determined for the use of dispersant plus carrier oil.

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3.3. A third test run for IVD in the same engine (starting with clean intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 95 RON gasoline, now containing no fuel additives again (second "dirty-up" run). As a result, deposits of 151 mg/valve on average were found.

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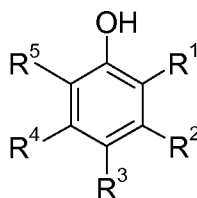
3.4 A fourth test run for IVD in the same engine (without cleaning of the intake valves) according to standard procedure CEC F-05-A-93 was carried through using the same 95 RON gasoline, however, now containing 835 ppm by weight of the same fuel additive package as under 1.2. above plus 250 ppm by weight of 4-iso-nonylphenol (each per part of the gasoline base fuel) (second "clean-up" run). As a result, deposits of 24 mg/valve on average were found. According to the formula under 1.2. above, a clean-up effect of 84 % was determined for the use of dispersant plus carrier oil plus hydrocarbylphenol.

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Hydrocarbylphenols as Intake Valve Clean-up Boosters

Claims

- 5 1. A fuel additive composition comprising:
- (A) at least one nitrogen-containing dispersant selected from polyisobutenyl monoamines and polyisobutenyl polyamines,
- 10 (B) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils, and
- (C) at least one hydrocarbylphenol of formula I



(I)

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wherein at least one of R¹ to R⁵ is a C₆-C₂₀₀-hydrocarbyl residue and the others are C₁-C₅-hydrocarbon residues and/or hydrogen.

- 20 2. The fuel additive composition according to Claim 1, wherein the at least one C₆-C₂₀₀-hydrocarbyl residue in formula I of component (C) is a polyisobutenyl residue with 12 to 100 carbon atoms.
3. The fuel additive composition according to Claim 1, wherein the at least one C₆-C₂₀₀-hydrocarbyl residue in formula I of component (C) is a linear or branched alkyl residue with 6 to 12 carbon atoms.
- 25 4. The fuel additive composition according to Claims 1 to 3, wherein carrier oil component (B) comprises at least one polyether obtained from C₁-C₃₀-alkanols or C₂-C₆₀-alkandiols and from 1 to 30 mol, in sum, of propylene oxide and/or butylene oxides.
- 30 5. The fuel additive composition according to Claims 1 to 4, wherein dispersant component (A) is a polyisobutenyl monoamine with a number average molecular weight of from 550 to 1000.
- 35

6. The fuel additive composition according to Claims 1 to 5, wherein the weight ratio of dispersant component (A) to hydrocarbylphenol component (C) is in the range of from 0.3 : 1 to less than 2 : 1.
- 5 7. A fuel composition comprising a major amount of a liquid fuel in gasoline boiling range and a minor amount of a fuel additive composition according to Claims 1 to 6.
- 10 8. The fuel composition according to Claims 7, wherein dispersant component (A) is present at a level of from more than 50 to 3000 ppm, carrier oil component (B) at a level of from 50 to 2000 ppm, and hydrocarbylphenol component (C) at a level of from 100 to 3000 ppm.
- 15 9. The use of a hydrocarbylphenol (C) of formula I as set out in Claim 1 as an intake valve clean-up booster in internal combustion engines operated with a liquid fuel in the gasoline boiling range containing minor amounts of (A) at least one nitrogen-containing dispersant selected from polyisobutenyl monoamines and polyisobutenyl polyamines and (B) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/067223

A. CLASSIFICATION OF SUBJECT MATTER		
INV. C10L1/14	C10L10/00	C10L10/06 C10L10/18
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C10L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search 6 April 2009		Date of mailing of the international search report 06/05/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer de La Morinerie, B

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