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(54) DEHAZING COMPOSITIONS FOR FUELS

(57) New compositions with improved dehazing properties for fuels.

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Description

[0001] The present application describes new compositions with improved dehazing properties for fuels.

[0002] EP 1609843 A2 describes the use of alkoxylated polyethyleneimines with a molecular weight Mw of more than 55000 as demulsifiers for middle distillates with vegetable or animal fuel oils and water. Furthermore, mixing such alkoxylated polyethyleneimines with other additives, such as paraffin dispersants, alkyl phenol-aldehyde resins, polymeric cold flow improvers and oil-soluble amphiphiles, is generally mentioned in the text, however, not explicitly disclosed.

[0003] Optionally, the middle distillates according to EP 1609843 A2 may further contain alkylphenol-aldehyde resins as paraffin dispersants.

[0004] EP 1609843 A2 does not recognise the demulsifying effect of alkylphenol-aldehyde resins or their synergistic effect in combination with alkoxylated polyethyleneimines as demulsifiers.

[0005] WO 96/22343 describes alkoxylated alkylphenol-aldehyde resins or alkylaryl sulfonates as demulsifiers in fuel oil compositions, however, is silent about alkoxylated polyethyleneimines and does not recognise their synergistic effect.

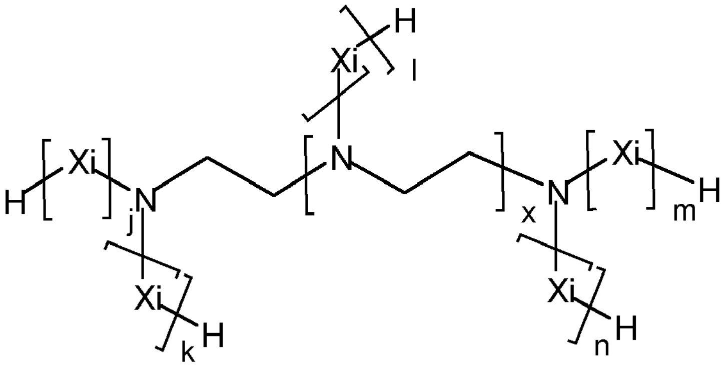
[0006] It was an object of the present invention to develop compositions with improved dehazing properties in fuels, preferably Diesel fuels, especially Diesel fuels containing non-fossil fuel constituents. The terms "dehazing", "demulsification" and "water separation" and their adjectives are used synonomously throughout the text.

[0007] The problem was solved by the use of a composition according to Claim 1.

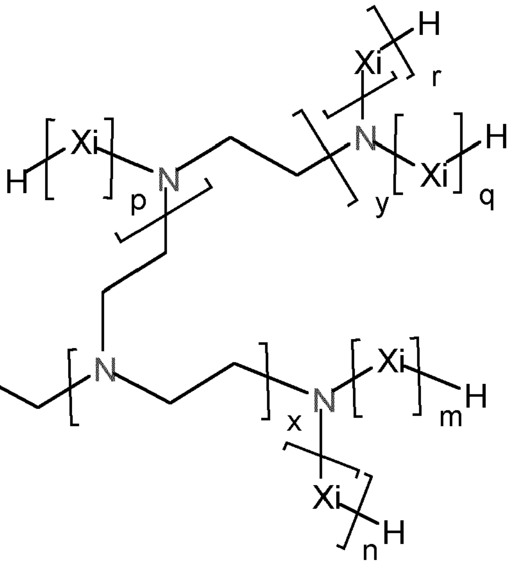
[0008] The inventive demulsifier combinations show good formulability and storage stability. Fuel additive packages containing these demulsifier formulations show good formulability and storage stability as well.

Component (A)

[0009] Component (A) is at least one alkoxylated polyethyleneimine polyethyleneimine of Formula (I)



or Formula (II)



and
in which

> X_i for i = 1 to j, 1 to k, 1 to l, 1 to m, 1 to n, 1 to p, 1 to q, 1 to r or 1 to s is independently selected from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$, $-CH(C_2H_5)-CH_2-O-$ and $-CH(CH_3)-CH(CH_3)-O-$, preferably selected from the group consisting of $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$, $-CH(C_2H_5)-CH_2-O-$ and $-CH(CH_3)-CH(CH_3)-O-$, more preferably selected from the group consisting of $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$ and $-CH(C2H_5)-CH_2-O-$ and most preferably selected from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$, $-CH(C_2H_5)-CH_2-O-$, $-CH_2-CH(CH_3)-O-$ and $-CH(CH_3)-CH_2-O-$, and especially selected from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(CH_3)-O-$ and $-CH(CH_3)-CH_2-O-$,
> x and y are independently zero or a positive integer
> j, k, l, m, n, p, q, and r are independently zero or a positive integer

wherein
with the proviso that

- in formula (II) the sum total of x and y is non-zero
- the sum total of j, k, l, m, n, p, q, and r is non-zero.

[0010] The precursors of the alkoxylated monomeric, oligo- and polyethyleneimines to be used in the context of the present invention are branched, monomeric, oligomeric or polymeric amines in which a nitrogen atom always follows two carbon atoms.

[0011] In formula (I) representing alkoxylated monomeric and oligoethyleneimines typical values for x are zero or 1 to 5, more preferably zero or 1 to 4, even more preferably zero or 1 to 3 and especially zero or 1 or 2.

[0012] Examples of monomeric and oligomeric ethyleneimines are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and pentaethylene hexamine. Above five ethylene imine units these compounds are referred to as polyethylene imines.

[0013] In formula (II) representing alkoxylated polyethyleneimines typical values for x and y are independently of another zero or 1 to 1500, more preferably 10 to 1400, even more preferably 20 to 1300 and especially 30 to 1200.

[0014] The proviso is that in formula (II) the sum total of x and y is non-zero.

[0015] The ratio of primary to secondary to tertiary nitrogen atoms, determined by ^{13}C-NMR spectroscopy, in the polyethyleneimines underlying the alkoxylated polyethyleneimines is preferably, as is typical in the corresponding commercially available products, 1: 0.5 to 1.5 : 0.3 to 0.9, preferably 1 : 0.6 to 1.3 : 0.4 to 0.8, more preferably 1 : 0.7 to 1.3 : 0.4 to 0.8 and especially 1 : 0.9 to 1.1 : 0.5 to 0.7. As polymers, they have a molecular weight distribution. In the context of the present invention, preference is given to using those types of polyethyleneimines whose average molar masses (Mw measured by means of GPC) are less than 55 000 g/mol, preferably less than 50 000, more preferably less than 40 000 and even more preferably less than 30 000 g/mol. Idealised Formulae (I) and (II) illustrate the structure of commercial branched polyethyleneimines, in which the ratio of primary to secondary to tertiary nitrogen atoms on average is about 1:2:1. Preferred polyethyleneimines exhibit the above-mentioned preferred ratio of primary to secondary to tertiary nitrogen atoms.

[0016] The monomeric, oligo- or polyethyleneimines are alkoxylated with C_2- to C_4-alkylene oxides or a mixture of such alkylene oxides, so that the alkoxylated monomeric, oligo- or polyethyleneimine has a preferred degree of alkoxylation, i.e. the sum total of j, k, l, m, n, p, q, and r, of from 2 to 200 alkylene oxide units, preferably from 5 to 180, more preferably from 10 to 150, most preferably 15 to 100 and especially 20 to 50.

[0017] The degree of alkoxylation per free NH group, i.e. each of the parameters j, k, l, m, n, p, q, and r is independently of another zero or a positive integer with the proviso that the sum total of j, k, l, m, n, p, q, and r is non-zero. Preferred values of parameters j, k, l, m, n, p, q, and r are independently of another zero or 1 to 50, more preferably zero or 1 to 40, even more preferably 1 to 35 and especially from 2 to 30.

[0018] In particular, the alkoxylated monomeric, oligo- or polyethyleneimines used are prepared by sequential alkoxylation of ethylene oxide, propylene oxide, 1-butene oxide, 2-butene oxide and/or iso butylene oxide, preferably ethylene oxide, propylene oxide, and/or 1-butene oxide, more preferably ethylene oxide, and/or propylene oxide, under alkaline catalysis.

[0019] Preference is given to those alkoxylated monomeric, oligo- or polyethyleneimines which are prepared by alkoxylation first with propylene oxide (PO) and subsequently with ethylene oxide (EO).

[0020] Alkoxylation with two or more different alkylene oxide, preferably with two different alkylene oxides, may occur statistically or blockwise, preferably statistically.

[0021] The compounds (A) generally have a weight average molecular weight Mw of 2,000 to 5,000,000 g/mol, preferably 3000 to 4,500,000, more preferably 4000 to 3,000,000, even more preferably 5000 to 2,500,000, and most preferably 6000 to less than 2,000,000 g/mol, measured by means of gel permeation chromatography (GPC) against polyethylene glycol in tetrahydrofuran.

[0022] In one embodiment of the present invention compound (A) exhibits a weight average molecular weight M_w determined by gel permeation chromatography of less than 55000 g/mol, preferably less than 50000, more preferably less than 45000, even more preferably less than 40000, most preferably less than 35000 and especially less than 30000 g/mol.

[0023] In another embodiment of the present invention compound (A) exhibits a weight average molecular weight M_w determined by gel permeation chromatography of more than 55000 g/mol, preferably more than 100000, more preferably more than 200000 and especially more than 500000 g/mol.

[0024] An important determining parameter for the polymers (A) is their relative solubility number (RSN) determined according to the method as described by J. Wu, Y. Xu, T. Dabros and H. Hamza, Colloids and Surface A: Physicochem. Eng. Aspects 232 (2004) 229-237.

[0025] Water is added to 30 ml of a solvent mixture which consists of toluene and ethyl glycol dimethyl ether (EGDE) in a ratio of 2.6:97.4 and in which 1 g of the sample of (A) is present as a clear solution, until a persistent opacity occurs.

[0026] The relative solubility number of the compounds (A) is preferably between 4 ml and 50 ml, in particular between 5 ml and 35 ml

[0027] Water separation is usually achieved at lower levels of compound (A) compared with the disclosure of EP 1609843 A2.

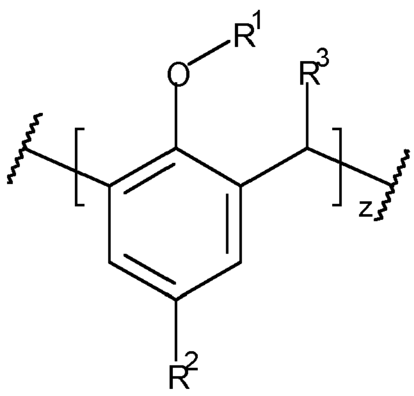
[0028] The alkoxylated monomeric, oligo- or polyethyleneimines (A) are added to the fuel together with mixtures with (B) in amounts of from 0.1 to 100 ppm by weight, preferably from 0.5 to 50 ppm by weight and more preferably from 1 to 10 ppm by weight.

[0029] They may be used as such or else dissolved or dispersed in solvents, for example aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, for example toluene, xylene, ethylbenzene, decane, pentadecane, benzine fractions, kerosene, naphtha, diesel, heating oil, isoparaffins or commercial solvent mixtures such as Solvent Naphtha, ®Shellsol AB, ®Solvesso 150, ®solvesso 200, ®Exxsol, ®Isopar and ®Shellsol D types, preferably as naphthalene depleted qualities. Furthermore, long chain alcohols, preferably alkanols with 6 or more, preferably 8 to 20 carbon atoms may be used as solvents. Preferred examples are 2-ethylhexanol or 2-propylheptanol. They are preferably dissolved in fuel oil of animal or vegetable origin based on fatty acid alkyl esters. The inventive additives preferably contain 1 - 80 %, especially 10 - 70%, in particular 25 - 60%, of solvent.

[0030] The polymers (A) may be added to the fuel which is or will be additized in accordance with processes disclosed in the prior art. When more than one compound (A) is to be used, such components may be introduced into the fuel together or separately in any combination.

Component (B)

[0031] Component (B) of the mixture according to the invention is at least one alkylphenol-aldehyde resin having a repeating structural unit of formula (III)



in which

R^1 is hydrogen or a group $-[-X_i-]_s-H$
R^2 is a linear or branched C_4- to C_{24}-alkyl group

R^3 is hydrogen or a C_1- to C_4-alkyl group,
X_i has the meaning mentioned above,
z is a positive integer of 10 to 80, preferably from 15 to 75, more preferably from 20 to 70 and especially from 25 to 65, and
s is a positive integer of 3 to 30, preferably 5 to 10.

[0032] Alkylphenol-aldehyde resins are known in principle and are described, for example, in Römpp Chemie Lexikon, 9th edition, Thieme Verlag 1988-92, volume 4, p. 3351 ff.

[0033] The alkyl or alkenyl radicals of the alkylphenol have 4 - 24, preferably 6 - 24, more preferably 8 - 22, in particular 9 - 18 carbon atoms. They may be linear or preferably branched, in which case the branch may contain secondary and also tertiary structural elements. The alkyl or alkenyl radicals are preferably n- and isohexyl, n- and isooctyl, n- and isononyl, n- and isodecyl, n- and isododecyl, tetradecyl, hexadecyl, octadecyl, eicosyl and also tripropenyl, tetrapropenyl, pentapropenyl and polyisobutenyl up to C_{24}. The alkylphenol-aldehyde resin may also contain up to 20 mol% of phenol units and/or alkyl phenols having short alkyl chains, for example butylphenol. For the alkylphenolaldehyde resin, the same or different alkylphenols may be used.

[0034] The aldehyde in the alkylphenol-aldehyde resin has from 1 to 10, preferably from 1 to 4 carbon atoms and may bear further functional groups. It is preferably an aliphatic aldehyde, more preferably formaldehyde or acetaldehyde, even more preferably formaldehyde.

[0035] The number average molecular weight Mn of the alkylphenol-aldehyde resins is preferably 1000 - 50000 g/mol, in particular 5000 - 15000 g/mol. This preferably corresponds to a degree of condensation z of from 10 to 80, preferably from 15 to 75, more preferably from 20 to 70 and especially from 25 to 65.

[0036] The alkyl phenol-aldehyde resins are prepared in a known manner by basic catalysis to form condensation products of the resol type, or by acidic catalysis to form condensation products of the novolak type.

[0037] The condensates obtained in both ways are suitable for the inventive compositions. Preference is given to condensation in the presence of acidic catalysts. To prepare the alkyl phenol-aldehyde resins, an alkylphenol having 6 - 24, preferably 8 - 22, in particular 9 - 18, carbon atoms per alkyl group, or mixtures thereof, and at least one aldehyde are reacted with one another, and about 0.5 - 2 mol, preferably 0.7 - 1.3 mol and in particular equimolar amounts of aldehyde are used per mole of alkyl phenol compound.

[0038] Suitable alkylphenols are in particular n- and isohexylphenol, n- and isooctylphenol, n- and isononylphenol, n- and isodecylphenol, n- and isododecylphenol, tetradecylphenol, hexadecylphenol, octadecylphenol, eicosylphenol, tripropenylphenol, tetrapropenylphenol and poly(isobutenyl)phenol up to C_{24}.

[0039] The alkylphenols are preferably para-substituted. The alkylphenols may bear one or more alkyl radicals. They are substituted by more than one alkyl group preferably to an extent of at most 5 mol%, in particular to an extent of at most 20 mol% and especially at most 40 mol%. Preferably at most 40 mol%, in particular at most 20 mol% of the alkylphenols used bear an alkyl radical in the ortho-position. The alkylphenols are especially not substituted by tertiary alkyl groups in the ortho-position to the hydroxyl group.

[0040] The aldehyde may be a mono- or dialdehyde and bear further functional groups such as -COOH. Particularly suitable aldehydes are formaldehyde, acetaldehyde, butyraldehyde, glutaraldehyde and glyoxalic acid, preference is given to formaldehyde. The formaldehyde may be used in the form of paraformaldehyde or in the form of a preferably 20 - 40% by weight aqueous formalin solution. It is also possible to use corresponding amounts of trioxane.

[0041] The reaction of alkyl phenol and aldehyde is effected typically in the presence of alkaline catalysts, for example alkali metal hydroxides or alkylamines, or of acidic catalysts, for example inorganic or organic acids such as hydrochloric acid, sulfuric acid, phosphoric acid, sulfonic acid, sulfamido acids or haloacetic acids, and in the presence of an organic solvent which forms an azeotrope with water, for example toluene, xylene, higher aromatics or mixtures thereof. The reaction mixture is heated to a temperature of from 90 to 200°C, preferably 100 - 160°C, and the water of reaction formed is removed by azeotropic distillation during the reaction.

[0042] Solvents which do not release any protons under the conditions of the condensation may remain in the products after the condensation reaction. The resins may be used directly or after neutralization of the catalyst, optionally also after further dilution of the solution with aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, for example benzine fractions, kerosene, decane, pentadecane, toluene, xylene, ethylbenzene or solvents such as ®Solvent Naphtha, ®Shellsol AB, ®Solvesso iSO, ®Solvesso 200, ®Exxsol, ®ISOPAR and ®Shellsol D types.

[0043] Components (B) do not necessarily need to be obtained from reaction of a phenol with an aldehyde but may also be obtained from reaction of acetylene with the respective alkylphenols. In this case in formula (III) R^3 is methyl. A preferred example of such resins is Koresin®, a resin marketed by BASF, and which is obtainable by reacting acetylene and para tertiary butyl phenol.

[0044] The alkyl phenol and aldehyde resins may be alkoxylated with ethylene oxide, propylene oxide, 1-butene oxide, 2-butene oxide and/or iso butylene oxide, pref-erably ethylene oxide, propylene oxide, and/or 1-butene oxide, more preferably ethylene oxide, and/or propylene oxide as described in the prior art.

[0045] The amount of alkoxylate groups in component (B) is from 10 to 75 wt%.

Component (C)

[0046] In a preferred embodiment the composition according to the invention further comprises at least one alkyl-, aryl- or alkylaryl sulfonate or sulfate (C), preferably a sulfonate, more preferably an alkyl- or alkylaryl sulfonate, and especially an alkylaryl sulfonate.

[0047] The alkyl group for example comprises 6 to 24, preferably 8 to 20, more preferably 10 to 18 carbon atoms and can be linear or branched.

[0048] Examples are n- and isohexyl, n- and isooctyl, 2-ethylhexyl, n- and isononyl, n- and isodecyl, 2-propylheptyl, n- and isododecyl, tetradecyl, hexadecyl, octadecyl, eicosyl and also tripropenyl, tetrapropenyl, pentapropenyl and polyisobutenyl up to C_{24}.

[0049] Aryl groups comprise 6 to 12 carbon atoms.

[0050] Examples are phenyl or naphthyl.

[0051] Alkylaryl groups for example comprise 7 to 30 carbon atoms, preferably 10 to 24, more preferably 14 to 22 carbon atoms.

[0052] Examples are n- and isohexylphenyl, n- and isooctylphenyl, 2-ethylhexylphenyl, n- and isononylphenyl, n- and isodecylphenyl, 2-propylheptylphenyl, n- and isododecylphenyl, tetradecylphenyl, hexadecylphenyl, and octadecylphenyl.

[0053] The alkyl substituent is preferably mainly located in para position of the aryl ring.

[0054] The counter ions of the sulfates or sulfonates may be sodium, potassium, ammonium or magnesium, preferably sodium or potassium and very preferably sodium.

[0055] Preferred sulfates are sodium dodecyl sulfate, potassium dodecyl sulfate, ammonium dodecyl sulfate, sodium tetradecyl sulfate, sodium hexadecyl sulfate, and mixtures thereof.

[0056] Preferred sulfonates are sodium n-decyl benzene sulfonate, sodium iso-decyl benzene sulfonate, sodium n-dodecyl benzene sulfonate, sodium iso-dodecyl benzene sulfonate, sodium n-tetradecyl benzene sulfonate, sodium iso-tetradecyl benzene sulfonate, and mixtures thereof, especially sodium-n-alkyl (C_{10}-C_{13}) benzene sulphonate.

[0057] The weight ratio of the components (A) : (B) : (C) in the compositions according to the invention is 0.1 - 100 : 0.1 - 100 : 0 - 0.5, preferably 0.5 - 75 : 0.5 - 75 : 0 - 0.5, and especially 1 - 50 : 1 - 50 : 0.1 - 0.5

Fuels

[0058] The inventive mixtures can be added either to middle distillate fuels entirely of fossil origin, i.e. those that have been obtained from mineral oil, or to fuels which, as well as the proportion based on mineral oil, comprise a proportion of biodiesel, in order to improve the properties thereof. In both cases, a distinct improvement of water separation is observed using the compositions according to the invention.

[0059] The present invention also provides fuels, especially those with a biodiesel content, comprising the inventive mixtures.

[0060] In general, the fuels or fuel additive concentrates also comprise, as further additives in amounts customary therefor, flow improvers (as described above), further paraffin dispersants, conductivity improvers, anticorrosion additives, lubricity additives, antioxidants, metal deactivators, antifoams, demulsifiers, detergents, cetane number improvers, solvents or diluents, dyes or fragrances or mixtures thereof. The aforementioned further additives are familiar to those skilled in the art and therefore need not be explained any further here. Especially detegents are present which tend to deteriorate the water separation behavior of fuels since they usually act as emulsifiers.

[0061] In the context of the present invention, fuel oils shall be understood to mean middle distillate fuels of fossil, vegetable or animal origin, biofuel oils ("biodiesel") and mixtures of such middle distillate fuels and biofuel oils.

[0062] Middle distillate fuels (also called "middle distillates" for short hereinafter) are especially understood to mean fuels which are obtained by distilling crude oil as the first process step and boil within the range from 120 to 450°C. Such middle distillate fuels are used especially as diesel fuel, heating oil or kerosene, particular preference being given to diesel fuel and heating oil. Preference is given to using low-sulfur middle distillates, i.e. those which comprise less than 350 ppm of sulfur, especially less than 200 ppm of sulfur, in particular less than 50 ppm of sulfur. In special cases they comprise less than 10 ppm of sulfur; these middle distillates are also referred to as "sulfur-free". They are generally crude oil distillates which have been subjected to refining under hydrogenating conditions and therefore comprise only small proportions of polyaromatic and polar compounds. They are preferably those middle distillates which have 90% distillation points below 370°C, especially below 360°C and in special cases below 330°C.

[0063] Low-sulfur and sulfur-free middle distillates may also be obtained from relatively heavy mineral oil fractions which cannot be distilled under atmospheric pressure. Typical conversion processes for preparing middle distillates from heavy crude oil fractions include: hydrocracking, thermal cracking, catalytic cracking, coking processes and/or visbreaking. Depending on the process, these middle distillates are obtained in low-sulfur or sulfur-free form, or are subjected to refining under hydrogenating conditions.

[0064] The middle distillates preferably have aromatics contents of below 30% by weight, preferably below 25% by weight, and especially below 20% by weight. The content of normal paraffins is between 5% by weight and 50% by weight, preferably between 10 and 35% by weight.

[0065] In the context of the present invention, middle distillate fuels shall also be understood here to mean those fuels which can either be derived indirectly from fossil sources such as mineral oil or natural gas, or else are produced from biomass via gasification and subsequent hydrogenation. A typical example of a middle distillate fuel which is derived indirectly from fossil sources is the GTL ("gas-to-liquid") diesel fuel obtained by means of Fischer-Tropsch synthesis. A middle distillate is prepared from biomass, for example, via the BTL ("biomass-to-liquid") process, and can be used as fuel either alone or in a mixture with other middle distillates. The middle distillates also include hydrocarbons which are obtained by the hydrogenation of fats and fatty oils. They comprise predominantly n-paraffins.

[0066] The qualities of the heating oils and diesel fuels are laid down in more detail, for example, in DIN 51603 and EN 590 (cf. also Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, volume A12, p. 617 ff.).

[0067] In addition to its use in the middle distillate fuels of fossil, vegetable or animal origin mentioned, which are essentially hydrocarbon mixtures, the inventive copolymer can also be used in biofuel oils and in mixtures of the middle distillates mentioned with biofuel oils, in order to improve cold flow characteristics. Mixtures of this kind 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.

[0068] 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 preferably understood to mean lower alkyl esters, especially C_1- to C_4-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 example ethanol or in particular methanol ("FAME"). Typical lower alkyl esters which are based on vegetable and/or animal oils and/or fats and find use as a biofuel oil or components thereof are, for example, HVO (hydrogenated vegetable oil), sunflower methyl ester, palm oil methyl ester ("PME"), soya oil methyl ester ("SME") and especially rapeseed oil methyl ester ("RME").

(D) Deposit control additives (Diesel fuels)

[0069] In one preferred embodiment of the present application the Diesel fuel contains at least one Deposit Control Agent for removal of deposits, especially quaternary ammonium salts as Deposit Control Agents.

[0070] Preferred examples of such quaternary ammonium salts are disclosed in WO 06/135881, WO 10/132259, WO 12/004300, WO 13/000997, and WO 14/195464, the content of these references is hereby incorporated by reference.

[0071] In another embodiment of the present invention, fuel may be a gasoline.

[0072] The term "gasoline" includes blends of distillate hydrocarbon fuels with oxygenated compounds such as ethanol, as well as the distillate fuels themselves.

[0073] Suitable gasolines are e.g. those described in Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, 1990, volume A16, page 719 ff.

[0074] Suitable gasolines are e.g. those having an aromatics content of not more than 60% by volume, e.g. not more than 42% by volume or not more than 35% by volume and/or a sulfur content of not more than 2000 ppm by weight, e.g. not more than 150 ppm by weight or not more than 10 ppm by weight.

[0075] In a preferred embodiment, the aromatics content of the gasoline is e.g. from 10 to 50% by volume, e.g. from 30 to 42% by volume, in particular from 32 to 40% by volume or not more than 35% by volume.

[0076] In another preferred embodiment, the sulfur content is e.g. of from 2 to 500 ppm by weight, e.g. of from 5 to 100 or not more than 10 ppm by weight.

[0077] In another preferred embodiment, the olefin content of the gasoline can be up to 50% by volume, e.g. from 6 to 21% by volume, in particular from 7 to 18% by volume.

[0078] In another preferred embodiment, the gasoline has a benzene content of not more than 5% by volume, e.g. from 0.5 to 1.0% by volume, in particular from 0.6 to 0.9% by volume.

[0079] In another preferred embodiment, the gasoline has an oxygen content of not more than 30% by weight, e.g. up to 10% by weight or from 1.0 to 3.7% by weight, and in particular from 1.2 to 2.7% by weight.

[0080] Particular preference is given to a gasoline which has an aromatics content of not more than 38% by volume or preferably not more than 35% by volume, and at the same time an olefin content of not more than 21% by volume, a sulfur content of not more than 50 or 10 ppm by weight, a benzene content of not more than 1.0% by volume and an oxygen content of from 1.0 to 2.7% by weight.

[0081] The amount of alcohols and ethers contained in the gasoline may vary over wide ranges. Typical maximum contents are e.g. methanol 15% by volume, ethanol 85% by volume, isopropanol 20% by volume, tert-butanol 15% by volume, isobutanol 20% by volume and ethers containing 5 or more carbon atoms in the molecule 30% by volume.

[0082] The summer vapor pressure of the gasoline (at 37°C) is usually not more than 70kPa, in particular not more than 60kPa.

[0083] The research octane number (RON) of the gasoline is usually from 75 to 105. A usual range for the corresponding motor octane number (MON) is from 65 to 95.

[0084] The above characteristics are determined by conventional methods (DIN EN 228).

[0085] The fuel may comprise further customary additives to improve its features.

[0086] In the case of gasoline fuels, these are in particular lubricity improvers (friction modifiers), corrosion inhibitors, combustion improvers, antioxidants or stabilizers, antistats, metallocenes, metal deactivators, dyes and/or solvents.

[0087] In a preferred embodiment the gasoline fuel comprises at least one deposit control additive.

(D) Deposit control additives (gasoline)

[0088] The customary deposit control 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:

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

(Df) polyoxy-C_2- to C_4-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;

(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.

[0089] The hydrophobic hydrocarbon radical in the above deposit control additives, which ensures 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 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.

[0090] Examples of the above groups of deposit control 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 predominantly terminal double bonds) or conventional (i.e. having predominantly internal double bonds) polybutene or polyisobutene with 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 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.

[0091] 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.

[0092] 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.

[0093] Additives comprising polyoxy-C_2-C_4-alkylene moieties (Df) are preferably polyethers or polyetheramines which are obtainable by reaction of C_2- to 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 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.

[0094] 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 mm^2/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.

[0095] 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 = 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 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 imido moieties D(h), the further deposit control 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 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.

[0096] Additives comprising moieties (Di) obtained by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and mono- or polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. The polyisobutenyl-substituted phenols may originate from conventional or high-reactivity polyisobutene having M_n = 300 to 5000. Such "polyisobutene Mannich bases" are described more particularly in EP-A 831 141.

[0097] One or more of the deposit control additives mentioned can be added to the fuel in such an amount that the dosage of these deposit control additives is preferably 25 to 2500 ppm by weight, especially 75 to 1500 ppm by weight, in particular 150 to 1000 ppm by weight.

[0098] The other further additives mentioned above are, incidentally, familiar to those skilled in the art and therefore need not be elucidated here any further.

[0099] The examples which follow are intended to elucidate the present invention without restricting it.

Examples

Materials:

[0100]

Component A: Polyethyleneimine with average molar mass of 25000 g/mol according to GPC and a ratio of primary/secondary/tertiary amines of 1/1,1/0,7 according to ^{13}C-NMR, propoxylated and ethoxylated (95 wt% propylene oxide and 5 wt% ethylene oxide) to a hydroxyl value of 38 mg KOH/g. Weight averaged molecular weight M_w is 1.5 million g/mol, determined by gel permeation chromatography (GPC), tetrahydrofurane as eluent, polystyrene standard. Relative solubility number (RSN): 8 ml (determined according to the method as described by J. Wu, Y. Xu, T. Dabros and H. Hamza, Colloids and Surface A: Physicochem. Eng. Aspects 232 (2004) 229-237.)

Component B: Ethoxylated Novolac resin obtained from condensation of isononylphenol with formaldehyde and subsequent ethoxylation up to an ethylene oxide-content of 60 wt-%. GPC (solvent THF against polystyrene standard): M_n 11630 g/mol, M_w 20370 g/mol, (determined by gel permeation chromatography, tetrahydrofurane as eluent, polystyrene standard) hydroxyl value (according to DIN 53240-1 potentiometric) 99 mg KOH/g. RSN 18.5 ml.

Component C: Polyethyleneimine with average molar mass of 25000 g/mol according to GPC and a ratio of primary/secondary/tertiary amines of 1/1,1/0,7 according to ^{13}C-NMR, propoxylated to a hydroxyl value of 32 mg KOH/g. RSN 6 ml. M_w 4.4 million g/mol (GPC as described above).

[0101] Deposit Control Additive 1 (DCA1): Quaternary ammonium compound preparatory example 6 from WO 2014/195464.
Deposit Control Additive 2 (DCA2): Quaternary ammonium compound example 3 from WO 2010/132259.
Defoamer: silicone component TP-645 from Momentive Performance Materials Inc.
LAS: Sodium-n-alkyl (C10-C13) benzene sulphonate; Disponil® LDBS 55 (BASF SE)
Reference diesel fuel: Unadditized B7 diesel fuel compliant to EN 590 (fuel F) and B0 diesel fuel RF-79-07 batch 9 from Haltermann (fuel G).

[0102] Component H is an ethylene diamine alkoxylated with 67 propylene oxide (PO) und 73 ethylene oxide (EO) (block) using potassium hydroxide (KOH) as catalyst, neutralized with neodecanoic acid. RSN 34 ml, M_n 8900 g/mol, M_w 9800 g/mol.

[0103] The effectiveness of the demulsifiers was evaluated according to ASTM D 1094-07. In this test 80 ml of the fuel is shaken with 20 ml pH 7 phosphate buffer using a standardized technique at room temperature. The change in volume of the aqueous layer, the appearance of the interface and the degree of separation are taken as the water reaction of the fuel.

[0104] Interface Conditions according to ASTM:

Rating	Appearance
1	Clear and clean
1b	Clear bubbles covering not more than an estimated 50 % of the interface and no shreds, lace, or film at the interface
2	Shred, lace, or film at interface
3	Loose lace or slight scum, or both
4	Tight lace or heavy scum, or both

[0105] Separation according to ASTM:

Rating	Appearance
(1)	Complete absence of all emulsions and/or precipitates within either layer or upon the fuel layer.
(2)	Same as (1), except small air bubbles or small water droplets in the fuel layer.
(3)	Emulsions and/or precipitates within either layer or upon the fuel layer, and/or droplets in the water layer or adhering to the cylinder walls, excluding the walls above the fuel layer.

The change of volume of the aqueous layer is determined after 5 minutes ($V_{aq.}$ 5 min.), in addition the times needed for separation of 15 ml (t(15 ml)) and the total 20 ml (t(20 ml)) aqueous layer are reported. In all cases the reported dosages of additives refer to active material. Separation rating and interface rating was done after 5 minutes. In all cases except for examples 1, 12 and 23 (without demulsifier compounds) the interface rating was 4, the separation rating for the aqueous phase was 2 and the separation rating for the fuel layer was 3. For examples 1, 12 and 23 the interface rating was 4, the separation rating for the aqueous phase was 3 and the separation rating for the fuel layer was 3.

[0106] As can be seen from examples 1, 12 and 23 the fuels containing solely DCA tend to form quite stable emulsions. The employed silicone defoamer already shows demulsifying properties (compare examples 1 and 2, or 12 and 13, respectively). The inventive demulsifier combinations further increase the demulsification tendency leading to improved or equally good water separation after 5 minutes (increased $V_{aq.}$ 5 min.) for a fixed combination of fuel, DCA and defoamer compared to the comparative examples.

Ex.	Type	A	B	C	H	LAS	Defoamer	DCA 1	DCA 2	Fuel	VAQ 5 min	t (15mL)	t (20mL)
1	comp							65		F	0	205	n.d.
2	comp						3	65		F	12	07:02	16:05

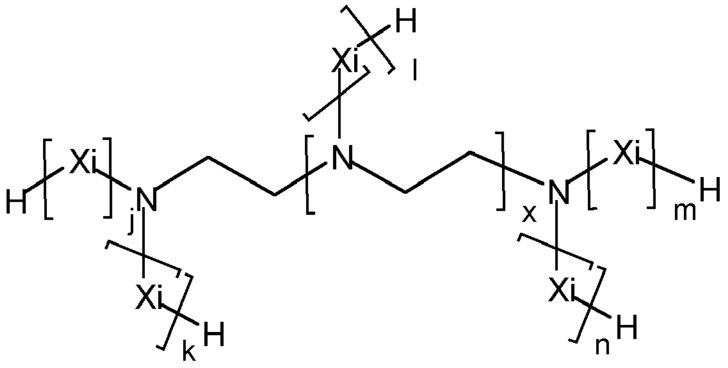
(continued)

Ex.	Type	A	B	C	H	LAS	Defoamer	DCA 1	DCA 2	Fuel	VAQ 5 min	t (15mL)	t (20mL)
3	inv	1	1			0.03	3	65		F	14	05:14	08:04
4	comp		2			0.03	3	65		F	12	07:13	15:44
5	comp			2			3	65		F	12	07:40	21:04
6	comp							65		G	0	>120	n.d.
7	comp						3	65		G	9.5	09:56	19:40
8	inv	1	1			0.03	3	65		G	16	04:49	07:48
9	inv	1	1				3	65		G	11	07:30	11:56
10	inv		1	1			3	65		G	13.5	06:15	15:55
11	comp			2			3	65		G	10	09:37	20:29
12	comp								60	F	0	>120	n.d.
13	comp						3		60	F	0	>120	n.d.
14	inv	1	1			0.03	3		60	F	11	08:51	20:13
15	inv		1	1			3		60	F	10	06:34	13:06
16	inv.		1		1		3	65		F	13.5	6:13	16:04
17	inv.		1		1	0.03	3	65		F	14	5:15	14:52
18	inv.		1		1		3	65		G	11	8:22	16:11
19	inv.		1		1	0.03	3	65		G	11.5	8:15	16:11
20	inv.		1		1	0.03	3		60	G	14	5:30	20:05

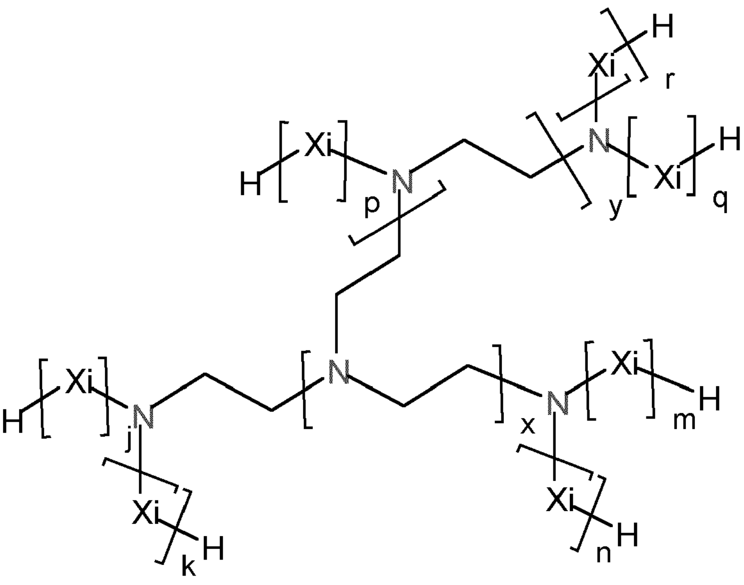
Claims

1. Use of a composition of

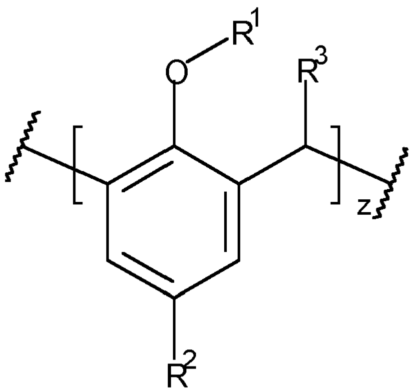
(A) at least one alkoxylated polyethyleneimine of Formula (I)



or Formula (II)



and
(B) at least one alkoxylated alkylphenol-aldehyde resin having a repeating structural unit of Formula (III)



in which

X_i for i = 1 to j, 1 to k, 1 to l, 1 to m, 1 to n, 1 to p, 1 to q, 1 to r or 1 to s is independently selected from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$, $-CH(C_2H_5)-CH_2-O-$ and $-CH(CH_3)-CH(CH_3)-O-$, preferably selected from the group consisting of $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$, $-CH(C_2H_5)-CH_2-O-$ and $-CH(CH_3)-CH(CH_3)-O-$, more preferably selected from the group consisting of $-CH_2-CH(CH_3)-O-$, $-CH(CH_3)-CH_2-O-$, $-CH_2-C(CH_3)_2-O-$, $-C(CH_3)_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$ and $-CH(C_2H_5)-CH_2-O-$ and most preferably selected from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(C_2H_5)-O-$, $-CH(C_2H_5)-CH_2-O-$, $-CH_2-CH(CH_3)-O-$ and $-CH(CH_3)-CH_2-O-$, and especially selected from the group consisting of $-CH_2-CH_2-O-$, $-CH_2-CH(CH_3)-O-$ and $-CH(CH_3)-CH_2-O-$,
x and y are independently zero or a positive integer
z is a positive integer of 10 to 80
j, k, l, m, n, p, q, and r are independently zero or a positive integer
R^1 is hydrogen or a group $-[-X_i-]_s-H$
R^2 is a linear or branched C_4- to C_{24}-alkyl group
R^3 is hydrogen or a C_1- to C_4-alkyl group,

wherein
s is a positive integer of 3 to 30,
with the proviso that

- in formula (II) the sum total of x and y is non-zero,
- the sum total of j, k, l, m, n, p, q, and r is non-zero,

for demulsification of mixtures of fuels and water.

2. Use according to Claim 1, wherein the composition further comprises at least one alkyl-, aryl- or alkylaryl sulfonate or sulfate (C).

3. Use according to any of the preceding claims, wherein the weight average molecular weight Mw determined by gel permeation chromatography of the at least one alkoxylated polyethyleneimine (A) is less than 55000 g/mol.

4. Use according to any of the preceding claims, wherein the fuel is a Diesel fuel, optionally with oils of vegetable or animal origin.

5. Use according to Claim 4, wherein the Diesel contains up to 30 wt% of at least one fatty acid alkyl ester.

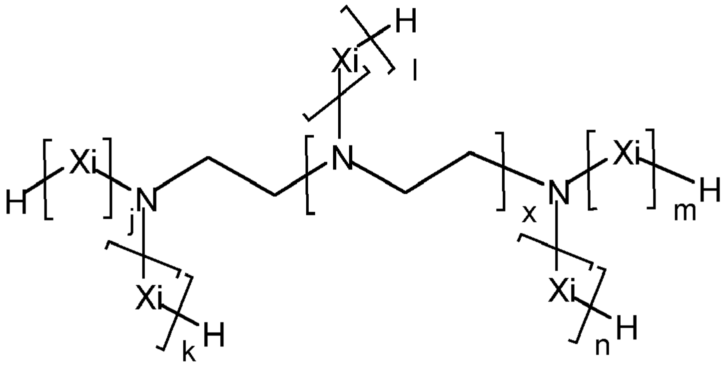
6. Use according to Claim 4 or 5, wherein the Diesel fuel further comprises at least one quaternary ammonium salt as deposit control additive (DCA) as component (D).

7. Use according to any of the preceding claims, wherein the weight ratio of the components (A) : (B) : (C) is 0.1 - 100 : 0.1 - 100 : 0 - 0.5.

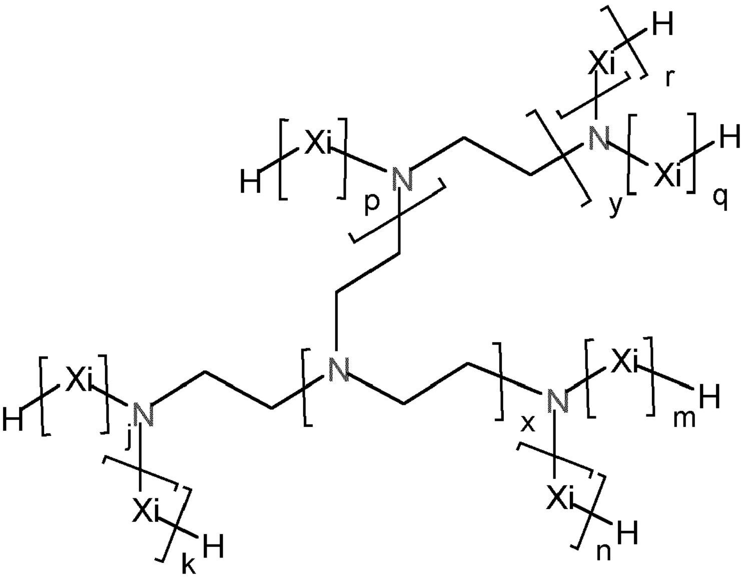
8. Use according to any of the preceding claims, wherein the amount of alkoxylate groups in component (B) is from 10 to 75 wt%.

9. Demulsifying composition comprising

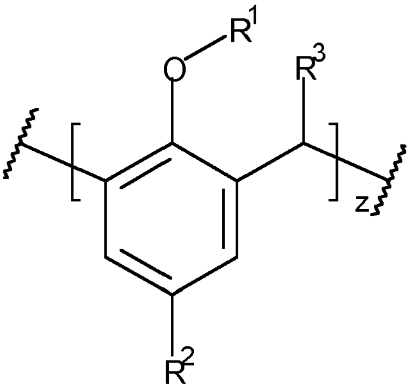
(A) at least one alkoxylated polyethyleneimine of Formula (I)



or Formula (II)



(B) at least one alkoxylated alkylphenol-aldehyde resin having a repeating structural unit of Formula (III)



and
(C) at least one alkyl-, aryl- or alkylaryl sulfonate or sulfate

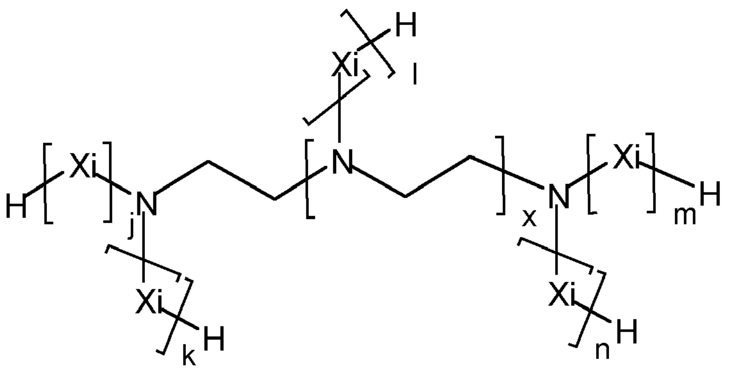
wherein the variables are defined as in Claim 1.

10. Fuel, preferably Diesel fuel, optionally with oils of vegetable or animal origin, comprising at least one composition according to Claim 9.

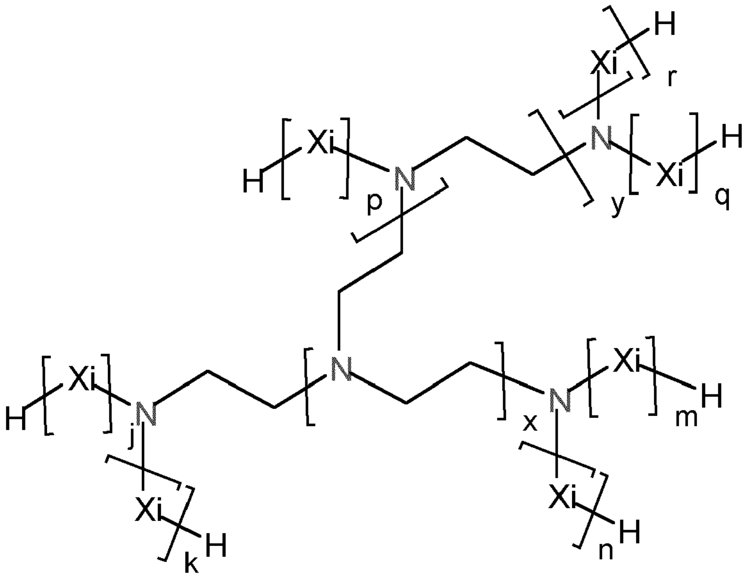
11. Diesel fuel according to Claim 10, further comprising at least one deposit control additive (DCA) as component (D).

12. Demulsifying composition comprising

(A) at least one alkoxylated polyethyleneimine with a molecular weight Mw less than 55000 g/mol of Formula (I)

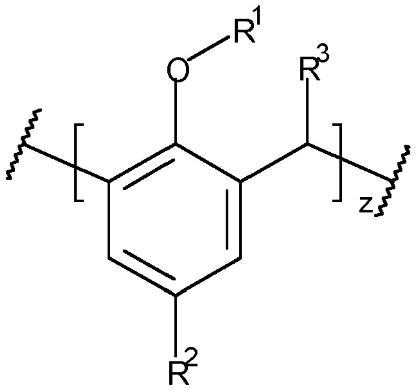


or Formula (II)



and

(B) at least one alkoxylated alkylphenol-aldehyde resin having a repeating structural unit of Formula (III)



wherein the variables are defined as in Claim 1.

13. Fuel, preferably Diesel fuel, optionally with oils of vegetable or animal origin, comprising at least one composition according to Claim 12.

14. Diesel fuel according to Claim 13, further comprising at least one deposit control additive (DCA) as component (D).

15. Gasoline fuel according to Claim 13, further comprising at least one deposit control additive possessing at least one hydrophobic hydrocarbon radical with a number-average molecular weight (Mn) of 85 to 20 000 and at least one polar moiety selected from the group consisting of

(Da) mono- or polyamino groups having up to 6 nitrogen atoms, at least one nitrogen atom having basic properties;
(Df) polyoxy-C_2- to C_4-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;
(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.

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EUROPEAN SEARCH REPORT

Application Number
EP 20 18 8966

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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X Y	DE 27 19 978 A1 (BASF AG) 16 November 1978 (1978-11-16) * page 3 - page 4; claim 1 * * page 6, paragraph 5 - page 8, paragraph 2 *	1,3,7,8, 12 3,7,8, 12-15	
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Y	EP 2 540 808 A1 (BASF SE [DE]) 2 January 2013 (2013-01-02) * paragraph [0162] - paragraph [0169]; claims 13,15,16 *	6,14,15	**TECHNICAL FIELDS SEARCHED (IPC)** C10L

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	15 January 2021	Pöllmann, Klaus

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X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 20 18 8966

15-01-2021

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