(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 December 2024 (12.12.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/254098 A1

(51) International Patent Classification:
C08G 65/26 (2006.01) *C10L 10/18* (2006.01)
C10L 1/238 (2006.01)

(21) International Application Number:
PCT/US2024/032471

(22) International Filing Date:
05 June 2024 (05.06.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/471,611 07 June 2023 (07.06.2023) US

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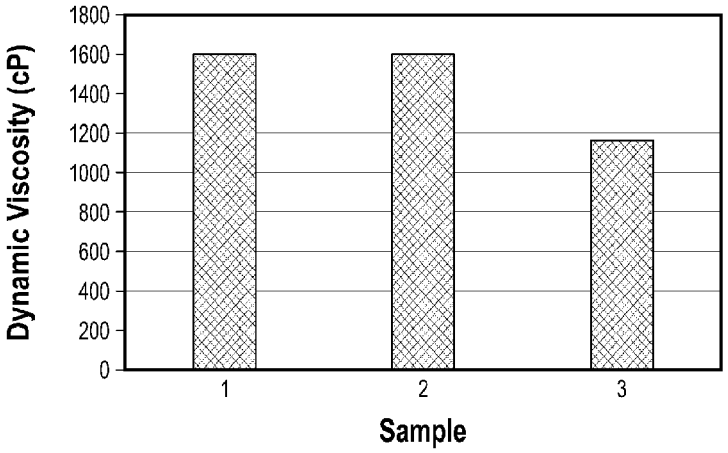
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ,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

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

Published:
— *with international search report (Art. 21(3))*

(54) Title: NAPHTHYL GLYCIDYL ETHER-MODIFIED POLYETHERAMINES AND USE THEREOF



FIGURE

(57) Abstract: A composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of: (a) a polyoxyalkylene monoamine; and (b) naphthyl glycidyl ether; and, its use in a variety of applications, including, but not limited to, as a dispersant or as a deposit control additive.

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NAPHTHYL GLYCIDYL ETHER-MODIFIED POLYETHERAMINES AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This Application claims priority to United States Provisional Application No. 63/471,611 filed June 7, 2023. The Noted application is incorporated herein by reference.

FIELD

[0002] The present disclosure generally relates to a naphthyl glycidyl ether-modified polyetheramine obtained from the reaction of naphthyl glycidyl ether and a polyoxyalkylene monoamine. The naphthyl glycidyl ether-modified polyetheramine may be used in various applications, such as a dispersant for soot, asphaltene, pigments, graphene and carbon nanotubes, or as a deposit control additive in a fuel composition.

BACKGROUND

[0003] During combustion of fuel and notably of gasoline in an engine, the carbonaceous products tend to form carbonaceous particles (soot) which inhibit the performance of the engine. One particular technique that has been used to control soot is to add a deposit control additive to the fuel before combustion. One type of deposit control additive that is generally used is a polyetheramine. Typically, polyetheramines are single molecule additives in which both amine functionality and polyether functionality are present in the same molecule. State of the art polyetheramines can be found in US Pat. Nos. 4,191,537, 4,261,704, 5,752,991, 4,985,047, 5,112,364, 4,609,377, 6,372,000, 6,217,624, 6,548,461, 4,747,851, 5,527,364, 5,660,601, 6,224,642, and 6,548,461.

[0004] In spite of the above, there is a continuing need to develop new, versatile polyetheramines capable of controlling soot and which also may exhibit effective

dispersing properties in connection other materials such as graphene, asphaltene, pigments, and carbon nanotubes.

SUMMARY

[0005] The present disclosure generally provides a composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of a polyoxyalkylene monoamine and naphthyl glycidyl ether. The naphthyl glycidyl ether-modified polyetheramine may be used in various applications, such as a dispersant for various materials including, but not limited to, soot, graphene, asphaltene, pigments, and carbon nanotubes.

[0006] In another embodiment, the naphthyl glycidyl ether-modified polyetheramine may be used as a deposit control additive and added to a fuel composition to form an additized fuel composition.

[0007] In still other embodiments, the present disclosure provides methods of controlling deposits in an engine and improving the performance of the engine by combusting the additized fuel composition in the engine.

BRIEF DESCRIPTION OF THE DRAWING

[0008] The Figure depicts a graph showing the relative dynamic viscosities of Samples 1-3.

DETAILED DESCRIPTION

[0009] The present disclosure is generally directed to a composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained from the reaction of a polyoxyalkylene amine and naphthyl glycidyl ether. It has been surprisingly found that the naphthyl

glycidyl ether-modified polyetheramine of the present disclosure may be effectively used as a dispersant for soot, as well as asphaltenes, pigments, graphene, and carbon nanotubes and as a deposit control additive in a fuel composition. For example, because the naphthyl glycidyl ether-modified polyetheramine has an amine group, it is capable of anchoring to functional groups, like carboxylic acid groups that exist on the surfaces of soot, thereby stabilizing it as smaller, dispersible structures and therefore reducing its tendency to agglomerate. Additionally, it's known soot can also include fused aromatic ring structures. Accordingly, the anchoring force between the naphthyl glycidyl ether-modified polyetheramine of the present disclosure and soot may be greatly enhanced since the naphthyl group can form very strong van der walls forces with the fused aromatic ring structures.

[0010] The following terms shall have the following meanings:

[0011] The term "comprising" and derivatives thereof are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step or procedure, except those that are not essential to operability and the term "consisting of", if used, excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

[0012] The articles "a" and "an" are used herein to refer to one or to more than one (i.e. to at least one) of the grammatical objects of the article. The phrases "in one embodiment", "according to one embodiment" and the like generally mean the particular feature, structure, or characteristic following the phrase is included in at least one embodiment of the present disclosure, and may be included in more than one embodiment of the present disclosure. Importantly, such phrases do not necessarily refer to the same aspect. If the specification states a component or feature "may", "can", "could", or "might" be included or have a characteristic, that particular component or feature is not required to be included or have the characteristic.

[0013] The term “about” as used herein can allow for a degree of variability in a value or range, for example, it may be within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0014] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but to also include all of the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range such as from 1 to 6, should be considered to have specifically disclosed sub-ranges, such as, from 1 to 3, from 2 to 4, from 3 to 6, etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[0015] The terms “preferred” and “preferably” refer to embodiments that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or

more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the present disclosure.

[0016] The term "soot" means a deep black powdery or flaky substance comprising very small particles of carbon or heavy hydrocarbons. Gas-phase soot contains polycyclic aromatic hydrocarbons (PAH). Soot is produced by the incomplete burning of organic matter, such as hydrocarbon based fuels. The soot particles may be mixed with metal oxides and with minerals and may be coated with sulfuric acid.

[0017] The term "major amount" is understood to mean an amount greater than or equal to 50 wt.%, for example from about 60 wt.% to about 99.5 wt. %, or from about 70 wt.% to about 99 wt.%, or from about 80 wt.% to about 98 wt.% relative to the total weight of the composition. Moreover, as used herein, the term "minor amount" is understood to mean an amount less than 50 wt.%, for example from about 0.1 wt.% to about 40 wt.%, or from about 1 wt.% to about 30 wt.%, or from about 5 wt.% to about 20 wt.%, relative to the total weight of the composition.

[0018] The term "alkyl" refers to a monovalent radical of an alkane. Suitable alkyl groups can have, for example, up to about 40 carbon atoms, or up to 24 carbon atoms, or up to 20 carbon atoms, or up to 16 carbon atoms, or up to 12 carbon atoms, or up to 10 carbon atoms, or up to 8 carbon atoms, or up to 6 carbon atoms, or up to 4 carbon atoms, or up to 3 carbon atoms. In some embodiments, the alkyl group may have, for example, between 1 and 40 carbon atoms, or between 2 and 30 or between 3 and 24 carbon atoms or between 8 and 14 carbon atoms. The alkyl groups may be linear, branched, cyclic, or a combination thereof.

[0019] "Controlling deposits", "deposit control" or the like as used herein is intended to cover one or more of: reducing existing deposits ("clean-up"); reducing deposit formation ("keep-clean"); and modifying deposits so as to reduce their negative effects. Deposits may include, but is not limited to, soot.

[0020] Where substituent groups are specified by their conventional chemical formula, written from left to right, they equally encompass the chemically identical substituents that would result from writing the structure from right to left, for example, $-CH_2O-$ is equivalent to $-OCH_2-$.

[0021] The term "optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0022] According to one embodiment, the naphthyl glycidyl ether-modified polyetheramine may be obtained by the reaction of: (a) a polyoxyalkylene monoamine and (b) naphthyl glycidyl ether.

[0023] In one embodiment, the polyoxyalkylene monoamine is a compound containing one amino group that is attached to the terminus of a polyether backbone. The amino group may be a primary ($-NH_2$) or a secondary (-NH-) amino group. In one embodiment, the amino group is a primary amino group. As further discussed below, the polyether backbone is based on, i.e., further defined by, alkylene oxide groups, such as propylene oxide (PO), ethylene oxide (EO), butylene oxide (BO) and mixtures thereof. In mixed structures, the ratios can be in any desired ratio and may be arranged in blocks (for e.g., repeating or alternating) or randomly distributed. In one non-limiting example, in a mixed EO/PO structure, the ratio of EO:PO can range from about 1:1 to about 1:50 and vice-

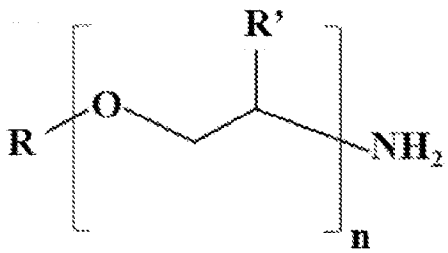
versa. As such, the polyoxyalkylene monoamine may substantially define a polyethylene oxide, polypropylene oxide, and/or a polybutylene oxide. The molecular weights of the polyoxyalkylene monoamines can vary and may range up to a molecular weight of about 6,000 Daltons. According to one embodiment, the molecular weight of the polyoxyalkylene monoamine may be between about 500 Daltons and about 6000 Daltons. In another particular embodiment, the polyoxyalkylene monoamine may have a molecular weight between about 600 Daltons and about 3000 Daltons.

[0024] Additionally, in some embodiments where the naphthyl glycidyl ether-modified polyetheramine of the present disclosure is prepared for use in highly polar systems, such as aqueous media, the polyoxyalkylene monoamine that is used in forming the naphthyl glycidyl ether-modified polyetheramine (a) can include a sufficiently higher fraction (for e.g., a higher amount) of polar groups (i.e., polyethylene oxides) than apolar groups (i.e., polypropylene and/or butylene oxides) in order to achieve a level of water solubility sufficient for the particular area of use. For example, the polyoxyalkylene monoamine may contain greater than 50% by weight, or greater than 60% by weight, or greater than 75% by weight or greater than 90% by weight ethylene oxide. Similarly, in the case of forming the naphthyl glycidyl ether-modified polyetheramine for use in non-polar systems, the polyoxyalkylene monoamine can include a sufficiently high fraction (e.g., a higher amount) of apolar groups than polar groups, such as greater than 50% by weight or greater than 60% by weight or greater than 75% by weight or greater than 90% by weight of propylene oxide and/or butylene oxide.

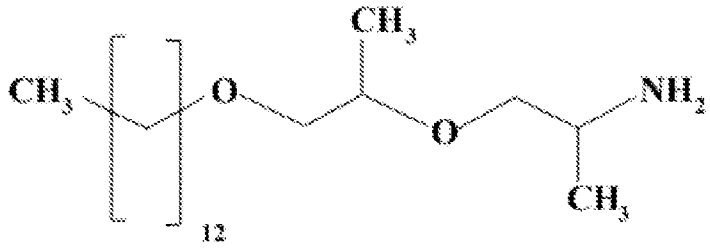
[0025] The polyoxyalkylene monoamine may generally be prepared by reacting a monohydric initiator, for e.g., an alcohol, with ethylene and/or propylene oxide and/or

butylene oxide. This reaction is followed by conversion of the resulting terminal hydroxyl group to an amine, thereby providing a polyether backbone which includes propylene oxide (PO), ethylene oxide (EO), butylene oxide (BO) or mixtures thereof, and a terminal amino group, for e.g., a terminal primary amino group or a terminal secondary amino group, preferably a primary amino group. According to one embodiment, the alcohol may be an aliphatic alcohol having 1-35 carbon atoms or aromatic alcohol having from 6-35 carbon atoms, both of which may be further substituted with moieties such as alkyl, aryl, arylalkyl and alkaryl substituents. In another embodiment, the alcohol is an alkanol having 1-18 carbon atoms, or 1-10 carbon atoms, such as lower alkyl derived alkanols including, for e.g., methanol, ethanol, propanol, butanol, isopropanol and butanol. In another embodiment, the alcohol may be an alkylphenol where the alkyl substituent is a straight or branched chain alkyl of from 1-24 carbon atoms, such as from 4-16 carbon atoms, or an aryl substituted phenol including mono- di- and tri-phenyl-phenol, or an alkaryl phenol, or an arylalkylphenol such as tri-strylphenol, or naphthol, or an alkyl substituted naphthol.

[0026] According to one particular embodiment, the polyoxyalkylene monoamine is a compound having a general formula:



where R is a C_1-C_{40} alkyl group or a C_1-C_{40} alkyl phenol group; each R' is independently hydrogen, methyl, or ethyl; and n is an integer from about 1 to about 50. Particular examples include, but are not limited to compounds having the formulae:



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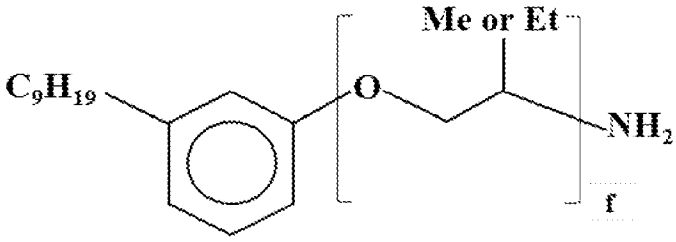

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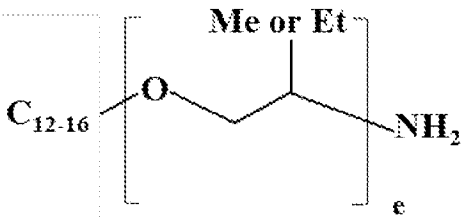


; and

$$CH_3\text{-}[OCH_2CH_2]_a\text{-}[OCH_2CH(CH_3)]_b\text{-}NH_2$$

where Me is methyl and Et is ethyl; f is an integer from about 13 to about 14; e is an integer from about 2 to about 3; a is an integer from 1 to about 45; and b is an integer from 1 to about 30. In some embodiments, the ratio of a/b may range from about 1/9 to about 41/4, for e.g., about 1/9, or about 6/29, or about 19/3, or about 33/10 or about 41/4. Such polyoxyalkylene monoamines included within the above formulas include JEFFAMINE® M-600, M-1000, M-2005, M-2070, FL-1000, C-100; XTJ-435; XTJ-436 amines and SURFONAMINE® B-60, B-100, L-100, L-200 and L-207 amines.

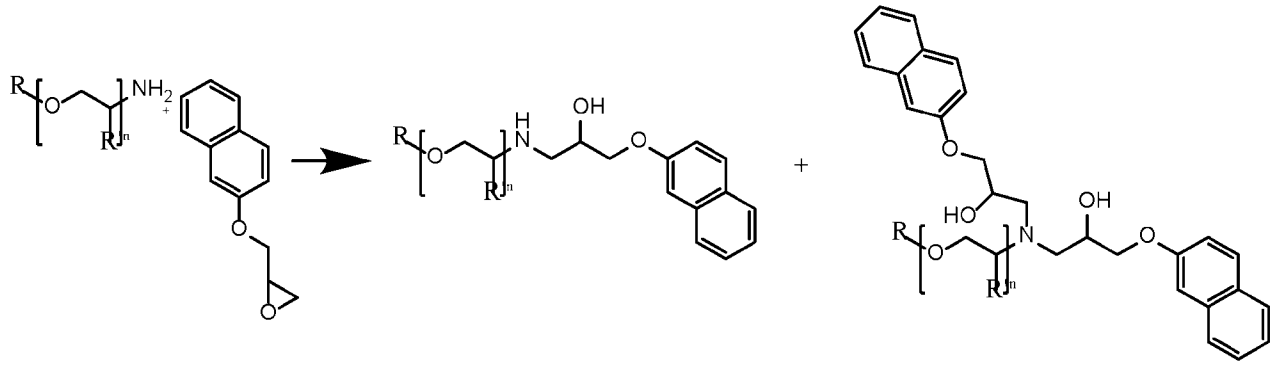
[0041] The polyoxyalkylene amine is reacted with naphthyl glycidyl to form the naphthyl glycidyl ether-modified polyetheramine of the present disclosure. In one embodiment, the naphthyl glycidyl ether is 1-napthyl glycidyl ether. In another embodiment, the naphthyl glycidyl ether is 2-naphthyl glycidyl ether. In still another embodiment, the naphthyl glycidyl ether is a mixture of 1-naphthyl glycidyl ether and 2-naphthyl glycidyl ether.

[0042] The naphthyl glycidyl ether-modified polyetheramine can be reacted by contacting naphthyl glycidyl ether and the polyoxyalkylene monoamine at temperatures between about 50°-300°C. For example, the reaction may take place at a temperature ranging between about 150°-200°C. The reaction may also take place at pressures ranging between about 1-2000 psi. Reaction times may vary from about 30 minutes to about 6 hours. Means for removing water of condensation can also be employed. In some embodiments, the naphthyl glycidyl ether and polyoxyalkylene monoamine may be reacted at a molar ratio (naphthyl glycidyl ether:polyoxyalkylene monoamine) of between about 0.9:1.1 to about 1.1:0.9, or about 0.95:1.05 to about 1.05:0.95 or about 1:1.

[0043] As discussed above, water generated during the reaction as well as unreacted reactant(s) may be removed from the composition by known methods after completion of the reaction. Thus, in some embodiments, the composition may include at least 80 wt.%, or at least 85 wt.%, or at least 90 wt.%, or at least 95 wt.% or at least 99 wt.%, based on the total weight of the composition, of the naphthyl glycidyl ether-modified polyetheramine.

[0044] According to another embodiment, the naphthyl glycidyl ether is reacted with the polyoxyalkylene monoamine as discussed above to produce a naphtyl glycidyl ether-

modified polyetheramine comprising a mixture of a mono addup compound and a di addup compound as follows:



mono addup di addup

where R, R' and n are defined as above. In some embodiments, the composition comprises at least 50 wt.% of the mono addup compound, where the wt.% is based on the total weight of the mono addup compound and the di addup compound. In still another embodiment, the composition comprises at least 60 wt.%, or at least 70 wt.%, or at least 80 wt.% or at least 90 wt.% or at least 95 wt.% of the mono addup compound, where the wt.% is based on the total weight of the composition.

[0045] According to another embodiment, the composition comprising the naphthyl glycidyl ether-modified polyetheramine of the present disclosure may further be diluted in water and/or a solvent(s) to form an aqueous or non-aqueous composition having a desired strength. Thus, in one embodiment there is provided an aqueous or non-aqueous composition containing the naphthyl glycidyl ether-modified polyetheramine of the present disclosure and water and/or other solvent and optionally one or more auxiliaries described below. The amount of water and/or solvent present may be, for instance, from about 0.5% by weight to about 50% by weight, based on the total weight of the aqueous or non-aqueous composition. Accordingly, the amount of the naphthyl glycidyl ether-modified

polyetheramine (and optional auxiliaries) contained in the aqueous or non-aqueous composition may range from about 50 wt.% up to about 99.5 wt.%, based on the total weight of the aqueous or non-aqueous composition.

[0046] As described above, water may be added to the composition, and in some embodiments, the water is de-ionized water. In other embodiments a solvent may be added to the composition in addition to or in place of water. Examples of such solvents include, but are not limited to, hydrocarbons (for e.g., pentane or hexane), halocarbons (for e.g., Freon 113), ethers (for e.g., ethylether (Et_2O), tetrahydrofuran ("THF") or diglyme (diethyleneglycol dimethyl ether)), nitriles (for e.g., CH_3CN), or aromatic compounds (for e.g., benzotrifluoride). Still further exemplary solvents include lactates, pyruvates, and diols. Solvents can also include, but are not limited to, acetone, 1,4-dioxane, 1,3-dioxolane, ethyl acetate, cyclohexanone, acetone, 1-methyl-2-pyrodidianone (NMP), and methyl ethyl ketone. Other solvents, include dimethylformamide, dimethylacetamide, N-methyl pyrrolidone, ethylene carbonate, propylene carbonate, glycerol and derivatives, naphthalene and substituted versions, acetic acid anhydride, propionic acid and propionic acid anhydride, dimethyl sulfone, benzophenone, diphenyl sulfone, phenol, m-cresol, dimethyl sulfoxide, diphenyl ether, terphenyl, and the like. Still further solvents include propylene glycol propyl ether (PGPE), 3-heptanol, 2-methyl-1-pentanol, 5-methyl-2-hexanol, 3-hexanol, 2-heptanol, 2-hexanol, 2,3-dimethyl-3-pentanol, propylene glycol methyl ether acetate (PGMEA), ethylene glycol, isopropyl alcohol (IPA), n-butyl ether, propylene glycol n-butyl ether (PGBE), 1-butoxy-2-propanol, 2-methyl-3-pentanol, 2-methoxyethyl acetate, 2-butoxyethanol, 2-ethoxyethyl acetoacetate, 1-pentanol, and propylene glycol methyl ether. The solvents above may be used alone or in combination.

[0047] Known auxiliaries may also be added to the composition depending upon the application. These auxiliaries may include, but are not limited to, customary detergent additives, carrier oils, cold flow improvers, lubricity improvers, corrosion inhibitors, demulsifiers, dehazers, antifoams, cetane number improvers, combustion improvers, antioxidants or stabilizers, antistats, metallocenes, metal deactivators, dyes, solvents, oxygenates, antiknock agents colorants, pigments, enzymes, wetting agents, antifoaming agents, buffering agents, pH adjusting agents, thickening agents, emulsifiers, anti-streaking agents, builders, chelating or sequestering agents, hydrotopes, anti-microbial agents, perfumes, herbicides, pesticides, fungicides, anti-wear additives, viscosity index improvers, pour point depressants, solid carriers or fillers, protective colloids, adhesion agents, humectants, repellents, attractants, feeding stimulants, compatibilizers, bactericides, anti-freezing agents, crystallization inhibitors, tackifiers, binders, preservatives, clarifiers, fertilizers, UV stabilizers, salts, weighting agents, gravel particulates, gases, crosslinkers, thermodynamic hydrate inhibitors, kinetic hydrate inhibitors, clay stabilizing agents and mixtures thereof.

[0048] According to another embodiment, there is provided a packaged product comprising: a) a container having at least an outlet; and b) the composition comprising the naphthyl glycidyl ether-modified polyetheramine.

[0049] According to another embodiment, the packaged product of the present disclosure comprises a container having a closure means, such as a lid, cover, cap, or plug to seal the container. In still another embodiment, the sealed container also has a nozzle or pour spout. The sealed container may have the shape of a cylinder, oval, round, rectangle, canister, tub, square or jug and contains the composition of the present disclosure.

[0050] In yet another embodiment, the container may be made from any material, such as steel, glass, aluminum, cardboard, tin-plate, plastics including, but not limited to, high density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), oriented polypropylene (OPP), polyethylene (PE) or polyamide and including mixtures, laminates or other combinations of these.

[0051] The composition comprising the naphthyl glycidyl ether-modified polyetheramine may be useful in a variety of applications, including, but not limited to, as a deposit control additive in a fuel composition. Other applications may include, but are not limited to, use as dispersant for soot, graphene, asphaltene, pigments, carbon nanotubes, organic and inorganic pigments, dyestuffs, and color brighteners.

[0052] According to one embodiment, the composition of the present disclosure is used as a deposit control additive for a fuel composition. In such embodiments, the fuel composition, which includes the composition comprising the naphthyl glycidyl ether-modified polyetheramine and a fuel, is used in fueling a fuel combustion system, such as a liquid fuel engine and/or for spark ignited engine. The type of fuel combustion system is not overly limited and includes, but is not limited to, a V engine, an inline engine, an opposed engine, and a rotary engine. The engine may be naturally aspirated, boosted, E-boosted, supercharged, or a turbocharged engine. The engine may be a carbureted or fuel injected gasoline engine. As such, the engine may have a carburetor or injectors (including piezo injectors).

[0053] In one embodiment, the engine may be a gasoline direct injection ("GDI") engine (spray or wall guided, or combinations thereof), a port fuel injection ("PFI") engine, a homogeneous charge compression ignition ("HCCI") engine, stoichiometric burn or lean

burn engine, spark controlled compression ignition ("SPCCI") engine, variable compression, Miller cycle or Atkinson cycle engine, or a combination thereof, such as an engine that contains both GDI and PFI injectors in the same engine. Suitable GDI/PFI engines includes 2-stroke or 4-stroke engines fueled with gasoline, a mixed gasoline/alcohol or any of the fuel compositions known to those skilled in the art.

[0054] In yet other embodiments, any of the above engines may be equipped with a catalyst or device for treating exhaust emissions, such as reducing NO_x. In other embodiments, the engine may be a flexible-fuel engine able to operate on more than one fuel type, typically, gasoline and ethanol or gasoline and methanol. In yet other embodiments, any of the above engine types may be in a hybrid vehicle that also includes an electric motor.

[0055] In some embodiments, the fuel composition may include the composition comprising the naphthyl glycidyl ether-modified polyetheramine in a minor amount and the fuel in a major amount. In still further embodiments, the composition comprising the naphthyl glycidyl ether-modified polyetheramine may be added directly to the fuel composition or it may be added to the fuel composition as a component of a fuel additive concentrate which includes some amount of fuel, carrier oil or a solvent and optionally one or more performance additives.

[0056] Fuels suitable for use are not overly limited and may include, for example, a gasoline as defined by ASTM specification D4814, a diesel fuel, as defined by ASTM specification D975, a biodiesel fuel, or any combination thereof. The fuel may further be leaded or unleaded motor and aviation gasolines and so-called reformulated gasolines which contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents, such as alcohols, ethers and other suitable oxygen-containing organic

compounds. Suitable oxygenates include, for example, methanol, ethanol, isopropanol, t-butanol, mixed C_1 to C_5 alcohols, methyl tertiary butyl ether, tertiary amyl methyl ether, ethyl tertiary butyl ether, mixed ethers, trans-esterified oils and/or fats from plants and animals such as rapeseed methyl ester and soybean methyl ester, and nitromethane. Oxygenates, when used, will normally be present in the fuel in an amount below about 25% by volume, for example in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5% by volume.

[0057] The fuel can also include heavier fuel oils, such as number 5 and number 6 fuel oils, which are also referred to as residual fuel oils, heavy fuel oils, and/or furnace fuel oils. Such fuels may be used alone or mixed with other, typically lighter, fuels to form mixtures with lower viscosities. Bunker fuels are also included, which are generally used in marine engines. These types of fuels have high viscosities and may be solids at ambient conditions, but are liquid when heated and supplied to the engine it is fueling. Other fuels known as alternative fuels may also be used. These fuels will include fuels such as 100% ethanol, hydrated ethanol, 70%-85% ethanol known as "E85".

[0058] The fuel is generally present in the fuel composition in a major amount which, in some embodiments, may be greater than about 90 wt.%, or greater than about 95 wt.%, or in other embodiments greater than about 97 wt.%, or greater than about 99.5 wt.%, or greater than about 99.9 wt.%, or even greater than about 99.99 wt.%, based on the total weight of the fuel composition.

[0059] The composition comprising the naphthyl glycidyl ether-modified polyetheramine is generally present in the fuel composition in a minor amount that may be generally less than about 10 wt.%, or less than about 1 wt.%, or less than about 0.5 wt.% or even less

than about 0.1 wt.% (1000 ppmw) (parts per million by weight), or less than about 0.07 wt.% (700 ppmw), or less than about 0.05 wt.% (500 ppmw), or less than about 0.04 wt.% (400 ppmw), or less than about 0.03 wt.% (300 ppmw), or less than about 0.025 wt.% (250 ppmw), or less than about 0.02 wt.% (200 ppmw), or less than about 0.01 wt.% (100 ppmw), based on the total weight of the fuel composition.

[0060] In other embodiments, the amount of the composition comprising the naphthyl glycidyl ether-modified polyetheramine in the fuel composition may be at least about 0.1 ppmw (parts per million weight), based on the total weight of the fuel composition. In another embodiment, the amount of the composition comprising the naphthyl glycidyl ether-modified polyetheramine present in the fuel composition of the present disclosure may be at least about 1 ppmw, or at least about 5 ppmw, or at least about 10 ppmw, or at least about 20 ppmw, or at least about 30 ppmw, or at least about 40 ppmw, or at least about 50 ppmw, or at least about 60 ppmw, or at least about 70 ppmw, or at least about 80 ppmw, or at least about 90 ppmw, or at least about 100 ppmw, or at least about 1000 ppmw, based on the total weight of the fuel composition.

[0061] In one embodiment, the composition comprising the naphthyl glycidyl ether-modified polyetheramine is part of a fuel additive concentrate. Such fuel additive concentrates are compositions that may optionally contain one or more performance additives as well as some amount of fuel, a carrier oil, or a solvent of some type. The fuel additive concentrate can then be added to other compositions as a convenient way to handle and deliver the composition comprising the naphthyl glycidyl ether-modified polyetheramine, resulting in the final fuel composition described above. The fuel additive concentrate may, in general, contain the composition comprising the naphthyl glycidyl

ether-modified polyetheramine in an amount of about 0.001 wt.% to about 99 wt.%, or about 0.5 wt.% to about 80 wt.%, or about 0.75 wt.% to about 70 wt.%, or about 1 wt.% to about 60 wt.%, or about 5 wt.% to about 50 wt.% or about 10 wt.% to about 40 wt.%, based on the total weight of the fuel additive concentrate.

[0062] The additional performance additives can include, but are not limited to: an antioxidant (for e.g., in an amount of about 8-100 mg/kg of fuel additive concentrate) such as a hindered phenol or derivative thereof and/or a diarylamine or derivative thereof; a corrosion inhibitor (for e.g., in an amount of about 5-100 mg/kg of fuel additive concentrate); and/or a detergent/dispersant additive, such as an additional polyetheramine or nitrogen containing detergent, including but not limited to PIB amine detergents/dispersants, succinimide detergents/dispersants, and other quaternary salt detergents/dispersants including quaternary ammonium imide salts, that is a detergent containing an imide group and a quaternary ammonium salt.

[0063] Other additional performance additives may also include: a cold flow improver such as an esterified copolymer of maleic anhydride and styrene and/or a copolymer of ethylene and vinyl acetate; a foam inhibitor and/or antifoam agent such as a silicone fluid; a demulsifier such as a polyalkoxylated alcohol; a lubricity agent such as a fatty carboxylic acid; a metal deactivator such as an aromatic triazole or derivative thereof, including but not limited to benzotriazole; and/or a valve seat recession additive such as an alkali metal sulfosuccinate salt.

[0064] The additional performance additives may also include a biocide; an antistatic agent, a deicer, a fluidizer such as a mineral oil and/or poly(alpha-olefin) and/or polyether,

and a combustion improver (for e.g., in an amount of about 8-150 mg/kg fuel additive concentrate) such as an octane or cetane improver.

[0065] The total amount of the additional performance additives present in the fuel additive concentrate may be less than about 50 wt.%, or less than about 20 wt.%, or less than about 10 wt.%, or less than about 1 wt.%, based on the total weight of the fuel additive concentrate. In other embodiments, the total amount of the additional performance additives present in the fuel additive concentrate may be at least about 0.001 wt.%, or at least about 0.5 wt.%, or at least about 2.5 wt.%, or at least about 5 wt.% or at least 15 wt.%, based on the total weight of the fuel additive concentrate. In still other embodiments, the total amount of the additional performance additives present in the fuel additive concentrate may be between about 0.001-60 wt.%, or between about 0.1-50 wt.%, or between about 1-40 wt.%, based on the total weight of the fuel additive concentrate.

[0066] The additional performance additives can each be added directly to the fuel additive concentrate and/or the fuel composition, but they are generally mixed with the composition comprising the naphthyl glycidyl ether-modified polyetheramine to form the fuel additive concentrate, which is then mixed with fuel to result in a fuel composition.

[0067] The fuel additive concentrate may also include a carrier oil, such as a mineral carrier oil or a synthetic carrier oil. Suitable mineral carrier oils are the fractions obtained in crude oil processing, such as brightstock or base oils having viscosities, for example, from the SN 500 to 2000 class, but also aromatic hydrocarbons, paraffinic hydrocarbons and alkoxyalkanols. Likewise useful is a fraction which is obtained in the refining of mineral oil and is known as "hydrocrack oil" (vacuum distillate cut having a boiling range from about 360° to 500°C, obtainable from natural mineral oil which has been catalytically

hydrogenated and isomerized under high pressure and also deparaffinized). Likewise suitable are mixtures of the abovementioned mineral carrier oils. Examples of suitable synthetic carrier oils are polyolefins (polyalphaolefins or polyinternalolefins), (poly)esters, (poly)alkoxylates, polyethers, alkylphenol-started polyethers and carboxylic esters of long-chain alkanols.

[0068] In some embodiments, the carrier oil may be present in the fuel additive concentrate in an amount of from about 0.5 wt.% to about 50 wt.% or from about 2 wt.% to about 40 wt.% or from about 3 wt.% to about to 30 wt.%, based on the total weight of the fuel additive concentrate.

[0069] The fuel additive concentrate may also include a solvent. The solvent provides for a homogeneous fuel additive concentrate and for facilitating the transfer and handling of the fuel additive concentrate. In some embodiments, the solvent is an aliphatic hydrocarbon, aromatic hydrocarbon, or a mixture thereof.

[0070] Aliphatic hydrocarbons include various naphtha and kerosene boiling point fractions that have a majority of aliphatic components. Aromatic hydrocarbons include benzene, toluene, xylenes and various naphtha and kerosene boiling point fractions that have a majority of aromatic components. In one embodiment, the solvent can be present in the fuel additive concentrate at about 1 wt.% to about 90 wt.%, in another embodiment at about 25 wt.% to about 85 wt.%, and yet in another embodiment, at about 40 wt.% to about 80 wt.%, based on the total weight of the fuel additive concentrate.

[0071] The composition comprising the naphthyl glycidyl ether-modified polyetheramine alone, or as part of a fuel additive concentrate may be added to the fuel at any convenient place in the supply chain. For example, the composition comprising the naphthyl glycidyl

ether-modified polyetheramine or fuel additive concentrate may be added to the fuel at the refinery, at a distribution terminal or after the fuel has left the distribution terminal. If added to the fuel after it has left the distribution terminal, this is termed an aftermarket application. Aftermarket applications include such circumstances as adding the composition comprising the naphthyl glycidyl ether-modified polyetheramine or fuel additive concentrate to the fuel in a delivery tanker, directly to a customer's bulk storage tank, or directly to an end user's vehicle tank. Aftermarket applications may include supplying the composition comprising the naphthyl glycidyl ether-modified polyetheramine or fuel additive concentrate in small bottles suitable for direct addition to storage tanks or vehicle tanks.

[0072] In another embodiment, the present disclosure provides a method of controlling deposits in an engine comprising adding the composition comprising the naphthyl glycidyl ether-modified polyetheramine and optionally a carrier oil, solvent or performance additive into a fuel to be combusted to form an additized fuel composition and combusting the additized fuel composition in the engine.

[0073] In another embodiment, the present disclosure provides a method of improving the efficiency of an engine comprising adding the composition comprising the naphthyl glycidyl ether-modified polyetheramine and optionally a carrier oil, solvent or performance additive into the fuel to be combusted to form an additized fuel composition and combusting the additized fuel composition in the engine.

[0074] In yet another embodiment, the present disclosure provides a method of improving the performance of an engine comprising adding the composition comprising the naphthyl glycidyl ether-modified polyetheramine and optionally a carrier oil, solvent or performance

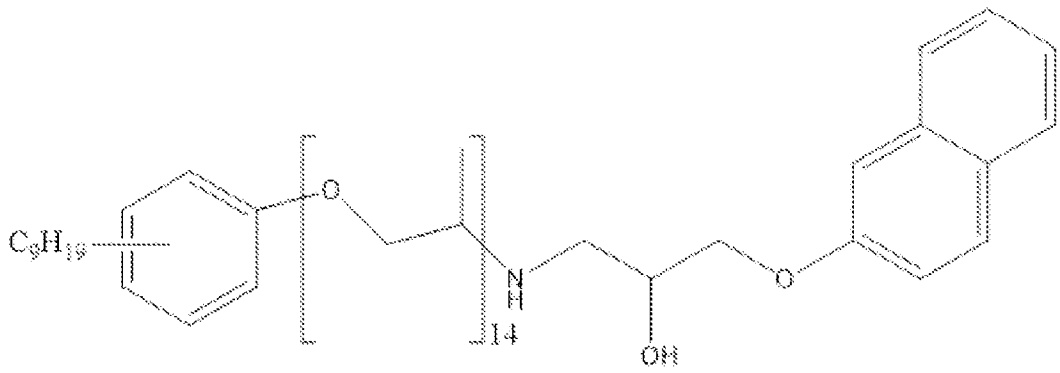
additive into a gasoline to be combusted to form an additized fuel composition and combusting the additized fuel composition in the engine wherein the improved performance is one or more of: improved fuel economy; reduced maintenance; less frequent overhaul or replacement of injectors; improved drivability; improved power; and improved acceleration.

[0075] The present disclosure will now be further described with reference to the following non-limiting examples.

Examples

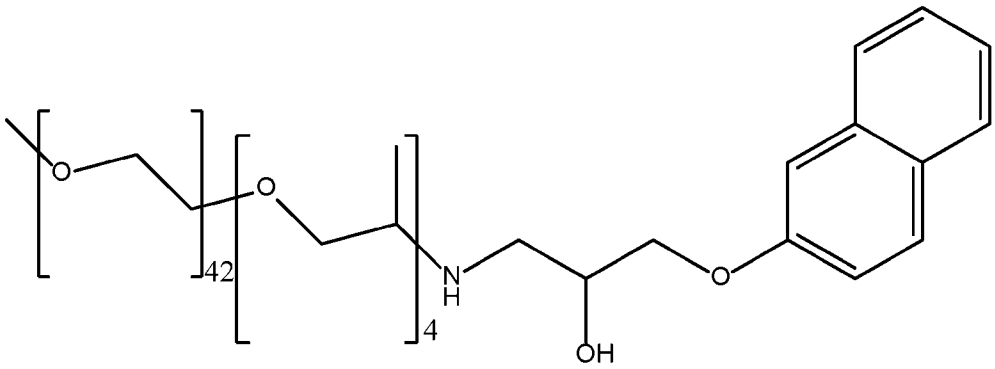
[0076] Example 1-Inventive naphthyl glycidyl ether-modified polyetheramine.

250 g (0.25 moles) Surfonamine® B-100 amine, 3.0 g deionized water and 54.5 grams 2-naphthyl glycidyl ether were charged into a 500 ml 3-neck flask equipped with a mechanical stirrer, thermal couple and condenser. The mixture was heated to 170°C and digested at 170°C for 4 hours. Water was then removed at the conditions of 90°C/20torr/2 hours. The LC-MS analysis of the additive demonstrated that the mono addup product was present in an amount of >90 wt.% with a small amount the di addup product and unconverted Surfonamine® B-100 amine. The mono addup product has a structure according to:



[0077] Example 2-Inventive naphthyl glycidyl ether modified polyetheramine.

212.8 g (0.1 mole) Surfonamine® L-200 amine, 2.4 g deionized water and 21.8 g 2-naphthyl glycidyl ether were charged into a 500 ml 3-neck flask equipped with a mechanical stirrer, thermal couple and condenser. The mixture was heated to 170°C and digested at 170°C for 4 hours. Water was then removed at the conditions of 90°C/20torr/2 hours. The LC-MS analysis of the additive demonstrated that the mono addup product was present in an amount of >90 wt.% with a small amount the di addup product and unconverted Surfonamine® L-200 amine. The mono addup product has a structure according to:



[0078] Example 3 – Dispersion Test Results

[0079] Cabron black is dispersed in paraffin oil using the polyetheramine of Example 1 and Surfonamine® B-100. The dynamic viscosity of the dispersion system at 40 °C was measured using a Brookfield viscometer. The lower the viscosity, the better the dispersion effect of the dispersant. The dispersion system of this Example 3 is provided in Table 1A, below.

[0080]

Table 1A

Material	**Weight (g)**		
	Sample 1	Sample 2	Sample 3
Carbon Black	1.5	1.5	1.5
Surfonamine® B-100	-	1.5	-
Polyetheramine of Example 1	-	-	1.5
Paraffin Oil	48.5	47	47

[0081] Samples 1-3 were fully agitated on a vibrator to obtain good dispersion throughout. The dynamic viscosity of each of Samples 1-3 were measured as indicated above, and the results are shown in Table 1B, below, and the Figure.

Table 1B

Sample	Viscosity at 40 °C (cP)
1	1600.0
2	1600.0
3	1176.0

[0082] As indicated in the Figure, the polyetheramine of Example 1 provides improved dispersion for carbon black.

[0083] Although making and using various embodiments of the present invention have been described in detail above, it should be appreciated that the present invention provides

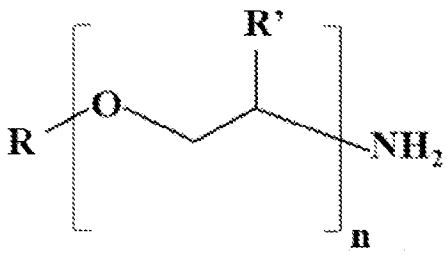
many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and use the invention, and do not delimit the scope of the invention.

CLAIMS

What is claimed is:

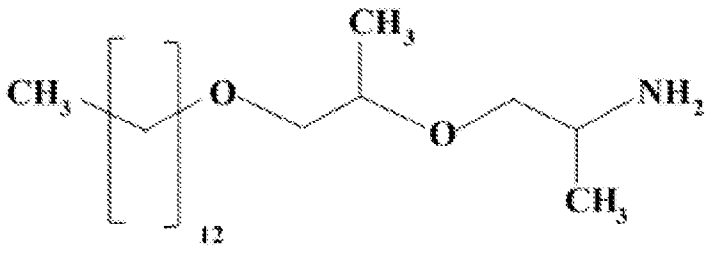
1. A composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of: (a) a polyoxyalkylene monoamine; and (b) naphthyl glycidyl ether.

2. The composition of claim 1, wherein the polyoxyalkylene monoamine is a compound having a general formula:

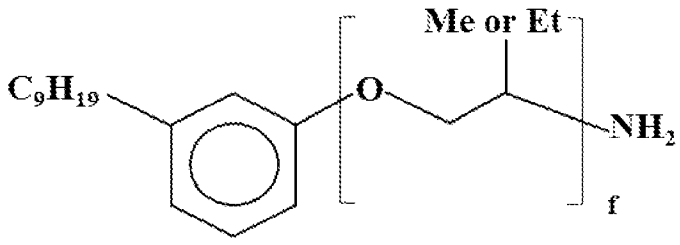


where R is a C_1-C_{40} alkyl group or a C_1-C_{40} alkyl phenol group; each R' is independently hydrogen, methyl or ethyl; and n is an integer from about 1 to about 50.

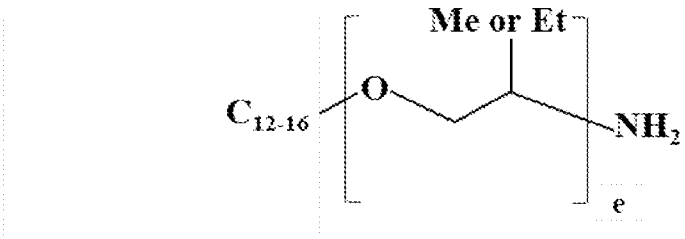
3. The composition of claim 2, wherein the polyoxyalkylene monoamine is a compound having a formula:



; or a formula:



; or a formula:



; or a formula:

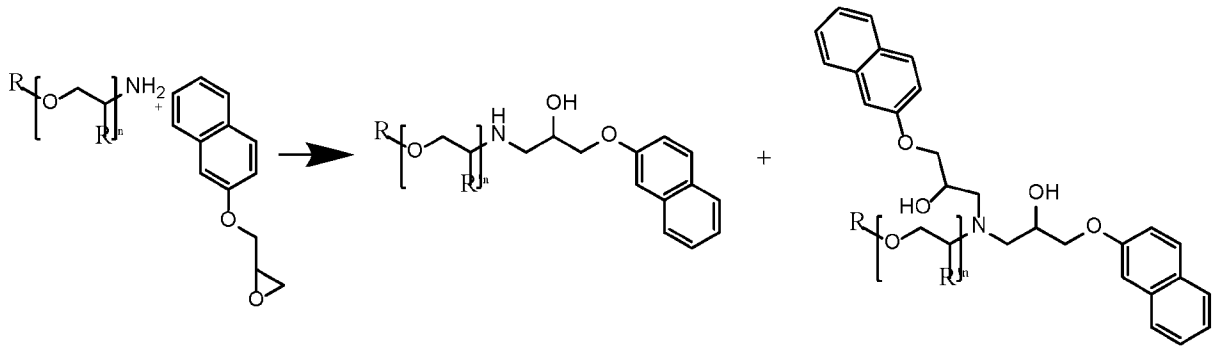
CH_3-[OCH_2CH_2]$_a$-[$OCH_2CH(CH_3)$]$_b$-NH_2

wherein Me is methyl and Et is ethyl; f is an integer from about 13 to about 14; e is an integer from about 2 to about 3; a is an integer from 1 to about 45; and b is an integer from 1 to about 30.

4. The composition of claim 3, wherein a ratio of a/b ranges from about 1/9 to about 41/4.

5. The composition of claim 1, wherein the naphthyl glycidyl ether is 1-napthyl glycidyl, 2-naphthyl glycidyl ether or a mixture thereof.

6. The composition of claim 5, wherein the naphthyl glycidyl ether-modified polyetheramine comprises a mixture of a mono addup compound and a di addup compound as follows:



mono addup di addup

wherein R, R' and n are defined in claim 1.

7. The composition of claim 1, further comprising a water, a solvent, an auxiliary or a mixture thereof.

8. A dispersed composition comprising the composition of claim 1 and at least one of soot, graphene, asphaltene, pigments, and carbon nanotubes.

9. A method of forming the composition of claim 1 comprising reacting (a) the polyoxyalkylene monoamine and (b) naphthyl glycidyl ether at a temperature of between about 150°-200°C.

10. A fuel additive concentrate comprising the composition of claim 1, a carrier oil or a solvent and optionally one or more performance additives.

11. The fuel additive concentrate of claim 10, wherein the carrier oil comprises a mineral carrier oil or a synthetic carrier oil.

12. The fuel additive concentrate of claim 10, wherein the solvent comprises an aliphatic hydrocarbon, aromatic hydrocarbon or a mixture thereof.

13. A fuel composition comprising the composition of claim 1 in a minor amount and a fuel in a major amount.

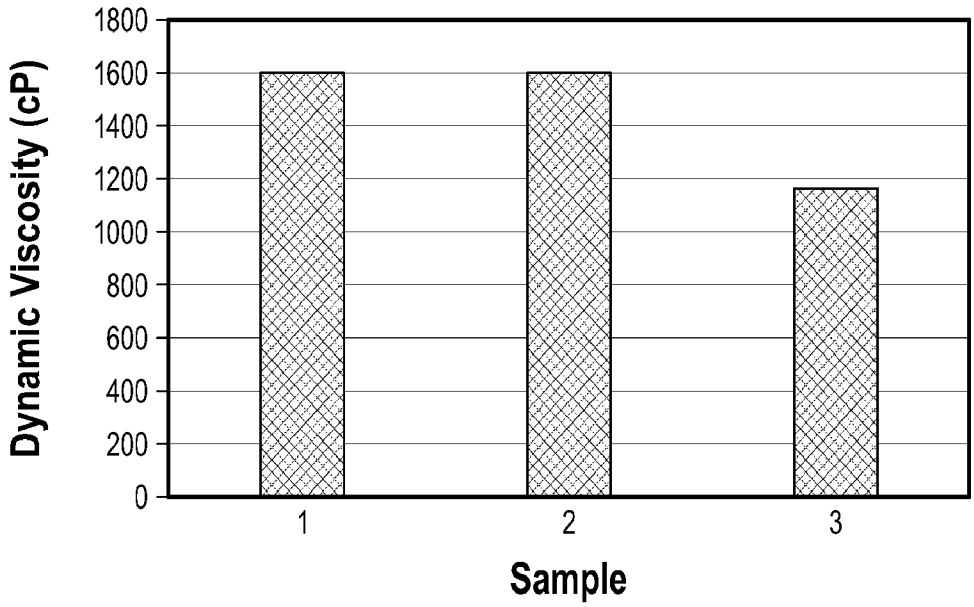
14. The fuel composition of claim 13, wherein the fuel comprises gasoline.

15. The fuel composition of claim 13, wherein the fuel composition is added to the fuel after the fuel has left a distribution terminal.

16. A method of controlling deposits in an engine comprising adding the composition of claim 1 and optionally a carrier oil, a solvent or one or more performance additives into a fuel to be combusted to form an additized fuel composition and combusting the additized fuel composition in the engine.

17. The method of claim 16, wherein the fuel comprises gasoline and the engine is a gasoline direct injection engine.

18. A method of improving the performance of an engine comprising adding the composition of claim 1 and optionally a carrier oil, solvent and one or more performance additives into a gasoline to be combusted to form an additized fuel composition and combusting the additized fuel composition in the engine wherein the improved performance is one or more of: improved fuel economy; reduced maintenance; less frequent overhaul or replacement of injectors; improved drivability; improved power; or improved acceleration.


Dynamic Viscosity (cP)
1800
1600
1400
1200
1000
800
600
400
200
0
1
2
3
Sample

FIGURE

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/032471

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08G 65/26*** (2024.01); ***C10L 1/238*** (2024.01); ***C10L 10/18*** (2024.01)

CPC: ***C08G 65/2624; C10L 1/238; C10L 10/18;*** *C08G 2650/50; C10L 2250/04*

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)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2023/0141337 A1 (BYK-CHEMIE GMBH) 11 May 2023 (11.05.2023) entire document	1-5, 7-18
A	US 2010/0037514 A1 (MALFER et al.) 18 February 2010 (18.02.2010) entire document	1-5, 7-18
A	US 2022/0033579 A1 (HUNTSMAN PETROCHEMICAL LLC) 03 February 2022 (03.02.2022) entire document	1-5, 7-18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent 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	Date of mailing of the international search report
05 August 2024 (05.08.2024)	**26 September 2024 (26.09.2024)**

Name and mailing address of the ISA/US	Authorized officer
Mail Stop PCT, Attn: ISA/US **Commissioner for Patents** **P.O. Box 1450, Alexandria, VA 22313-1450**	**MATOS** **TAINA**
Facsimile No. **571-273-8300**	Telephone No. **571-272-4300**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/032471

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-18 are drawn to compositions, dispersed compositions thereof, methods thereof, and fuel additive concentrates thereof.

The first invention of Group I+ is restricted to a composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of: (a) a polyoxyalkylene monoamine, wherein the polyoxyalkylene monoamine is a compound having the first formula shown in claim 3 of the instant Application PCT/US2024/032471; and (b) naphthyl glycidyl ether, wherein the naphthyl glycidyl ether is 1-napthyl glycidyl; dispersed compositions thereof; methods thereof; and fuel additive concentrates thereof. The first named invention has been selected based on the guidance set forth in section 10.54 of the PCT International Search and Preliminary Examination Guidelines. Specifically, the first named invention was selected based on the first listed element for each of the variables presented in the claims (polyoxyalkylene monoamine – claim 3; naphthyl glycidyl ether – claim 5). It is believed that claims 1-5 and 7-18 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. Each additional elected formula(e) requires the selection of a single definition for each compound variable. An exemplary election would be a composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of: (a) a polyoxyalkylene monoamine, wherein the polyoxyalkylene monoamine is a compound having the first formula shown in claim 3 of the instant Application PCT/US2024/032471; and (b) naphthyl glycidyl ether, wherein the naphthyl glycidyl ether is 2-napthyl glycidyl ether; dispersed compositions thereof; methods thereof; and fuel additive concentrates thereof. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The Groups I+ formulae do not share a significant structural element requiring the selection of alternatives for the polyoxyalkylene monoamine and naphthyl glycidyl ether and accordingly these groups lack unity a priori.

Additionally, even if Groups I+ were considered to share the technical features of a composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of: (a) a polyoxyalkylene monoamine; and (b) naphthyl glycidyl ether; a dispersed composition; a method of forming a composition; a fuel additive concentrate; a method of controlling deposits in an engine; and a method of improving the performance of an engine, these shared technical features do not represent a contribution over the prior art as disclosed by US 2023/0141337 A1 to BYK-Chemie GmbH, and US 2010/0037514 A1 to Malfer et al.

US 2023/0141337 A1 to BYK-Chemie GmbH teaches a composition comprising a naphthyl glycidyl ether-modified polyetheramine obtained by the reaction of: (a) a polyoxyalkylene monoamine; and (b) naphthyl glycidyl ether (Abstract, comb polymer having repeating units of at least one of the structures of formulae (I) to (IV) wherein R1 represents a polyoxyalkylene group and A represents an organic group; Para. [0041], a monoepoxide of the formula (VII) is employed as well … naphthyl glycidyl ether; Para. [0033], Suitable monoamines … include … Jeffamine M-2070); a dispersed composition (Para. [0058], dispersed in a composition); and a method of forming a composition (Para. [0059], process of dispersing solid particles).

US 2010/0037514 A1 to Malfer et al. teaches a fuel additive concentrate (Para. [0004], diesel fuel additive concentrate); a method of controlling deposits in an engine (Para. [0035], methods for reducing the amount

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

of injector deposits of a diesel engine); and a method of improving the performance of an engine (Claim 12, method of improving the injector performance of a fuel injected diesel engine).

The inventions listed in Groups I+ therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-5, 7-18**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.