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(54) **LUBRICANT COMPOSITION SUITABLE FOR
ENGINES FUELED BY ALTERNATE FUELS**

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(57) **ABSTRACT**

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A lubricant composition suitable for use in engines fueled by gasoline or biorenewable fuels or both, comprising an oil of lubricating viscosity and a dispersant system is disclosed herein. Also disclosed is an emulsion composition comprising a biorenewable fuel, an oil of lubricant viscosity, and a dispersant system. A method of reducing aqueous separation in an emulsion composition is also disclosed.

LUBRICANT COMPOSITION SUITABLE FOR ENGINES FUELED BY ALTERNATE FUELS

FIELD OF THE DISCLOSURE

[0001] The present disclosure relates to lubricant and emulsion compositions, and methods of use thereof.

BACKGROUND OF THE DISCLOSURE

[0002] In recent years, there has been an increased interest in the use of biorenewable fuels, such as alcohol-based fuels, for operating internal combustion engines. Early interest in biorenewable fuel powered internal combustion engines resulted from the shortages or threatened shortages such as that which occurred in the 1970s. When the threat of a shortage diminished, however, the automotive companies reduced their efforts to find alternative fuels, e.g., methanol- and ethanol-based fuels, because such fuels required changes in the design of engines to permit the engines to operate. Yet due to recent increased dependence on imported crude oils and continually rising fuel costs, the government and automotive industry have shown a strong renewed desire to use alternate, biorenewable fuel sources.

[0003] Using biorenewable fuels in internal combustion engines poses unique problems. For example, alcohol-based fuels are much more corrosive than traditional gasoline. In response, the automotive industry has engineered fuel tanks, engine parts, and fuel delivery systems with corrosion-resistant materials, such as stainless steel. Accordingly, the automotive industry has also designed specific requirements for lubricant compositions used therein to reduce harm to these and other parts under certain driving conditions, such as the eponymous "Aunt Minnie" driving cycle (a driving cycle that simulates a vehicle being used infrequently for short-distance trips, without the engine fully warming up to optimal operating temperatures before shutoff in cold climates.) As an example, lubricant compositions for use in biorenewable-fueled engines must form stable emulsions without separation of an aqueous layer. Such aqueous phase separation can result in corrosive wear on engine parts, pre-ignition problems, engine stall, and reduced fuel economy, among other undesirable problems.

[0004] Thus, there is a need to develop lubricant compositions which are useful in internal combustion engines fueled by biorenewable fuels and will prevent or minimize aqueous phase separation when used in such engines. It is also desirable that such lubricant compositions can be used in internal combustion engines which can operate on both gasoline and biorenewable fuels (so-called "flexible-fuel" or "variable-fuel" vehicles) because it may not always be possible, such as during an interim or changeover period, to find service stations selling biorenewable fuels. In such cases, it would be desirable for the vehicle to operate on gasoline instead of biorenewable fuels.

SUMMARY

[0005] In accordance with the disclosure, there is disclosed a lubricant composition suitable for use in engines fueled by gasoline or biorenewable fuels or both, comprising an oil of lubricating viscosity, and a dispersant system comprising at least one dispersant selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substi-

tuted amines, and Mannich base adducts derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine

[0006] There is also disclosed an emulsion composition comprising a biorenewable fuel, an oil of lubricant viscosity, and a dispersant system comprising at least one dispersant selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, or Mannich base adducts derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine.

[0007] In an aspect, there is disclosed a method of reducing aqueous separation in an emulsion composition comprising providing an emulsion composition comprising a biorenewable fuel and an oil of lubricating viscosity; and providing to said emulsion composition a dispersant system comprising at least one dispersant selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, or Mannich base adducts derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine.

[0008] Additional advantages of the disclosure will be set forth in part in the description which follows, and/or can be learned by practice of the disclosure. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DESCRIPTION OF THE EMBODIMENTS

[0009] The present disclosure relates to lubricant and emulsion compositions comprising a dispersant system comprising at least one dispersant selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, Mannich base adducts derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine, and mixtures thereof.

[0010] Emulsion compositions, such as such as alcohol-based fuels comprising hybrid fractions, can be used as biorenewable fuels in internal combustion engines. For example, a biorenewable fuel can comprise a carbon-based fraction (e.g., gasoline or diesel) and an alcohol-based fraction (e.g., methanol or ethanol), wherein the two fractions can be induced to form a fuel emulsion that can then be used to power an internal combustion engine. However, a key problem in providing suitable and stable emulsion compositions arises from the limited miscibility of gasoline and alcohol. Due to such limited miscibility, even a small amount of water (which is highly miscible with alcohol) can destabilize the emulsion composition and induce phase separation.

[0011] Phase separation of emulsion compositions can pose acute problems when such emulsion compositions are used as fuel for internal combustion engines. For example, if an emulsion composition destabilizes and an aqueous phase separates, the aqueous phase can be drawn into the engine by the fuel pump and combust in the engine. This combustion can be damaging to the engine because the aqueous phase creates a leaner combustion mixture (e.g., air to fuel ratio is higher than ideal), which tends to combust at higher temperatures and can damage the engine. Thus, there is a need to prevent or minimize aqueous phase separation in biorenewable fuels.

[0012] As used herein, the term "major amount" is understood to mean an amount greater than or equal to 50 wt. %, for example from about 80 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. % relative to the total weight of the composition.

[0013] As used herein, the terms “hydrocarbon”, “hydrocarbyl” or “hydrocarbon based” are understood to mean that the group being described has predominantly hydrocarbon character within the context of this invention. These include groups that are purely hydrocarbon in nature, that is, they contain only carbon and hydrogen. They may also include groups containing substituents or atoms which do not alter the predominantly hydrocarbon character of the group. Such substituents may include halo, alkoxy, nitro, etc. These groups also may contain hetero atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, sulfur, nitrogen and oxygen. Therefore, while remaining predominantly hydrocarbon in character within the context of this invention, these groups may contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

[0014] As used herein, the term “biorenewable fuel” and its grammatical derivatives are understood to mean fuels which are derived from resources other than petroleum. Such resources include, but are not limited to, corn, maize, soybeans and other crops; grasses, such as switchgrass, miscanthus, and hybrid grasses; vegetable oils; natural fats; and mixtures thereof.

[0015] A dispersant system suitable for use herein can comprise at least one dispersant. Useful dispersants include, but are not limited to, basic nitrogen-containing ashless dispersants, such as hydrocarbyl succinimides; hydrocarbyl succinamides; mixed ester/amides of hydrocarbyl-substituted succinic acids formed by reacting a hydrocarbyl-substituted succinic acylating agent stepwise or with a mixture of alcohols and amines, and/or with amino alcohols; Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines; and amine dispersants formed by reacting high molecular weight aliphatic or alicyclic halides with amines, such as polyalkylene polyamines. Mixtures of such dispersants can also be used.

[0016] Methods of preparing such dispersants are extensively described in patent literature. For example, hydrocarbyl-substituted succinimides and succinamides and methods for their preparation are described in U.S. Pat. Nos. 3,018,247; 3,018,250; 3,018,291; 3,172,892; 3,185,704; 3,219,666; 3,272,746; 3,361,673; and 4,234,435. Mixed ester-amides of hydrocarbyl-substituted succinic acid are described, for example, in U.S. Pat. Nos. 3,576,743; 4,234,435 and 4,873,009. Mannich dispersants, which are condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines are described, for example, in U.S. Pat. Nos. 3,368,972; 3,413,347; 3,539,633; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 3,798,247; 3,803,039; 3,985,802; 4,231,759 and 4,142,980. Amine dispersants and methods for their production from high molecular weight aliphatic or alicyclic halides and amines are described, for example, in U.S. Pat. Nos. 3,275,554; 3,438,757; 3,454,555; and 3,565,804.

[0017] In general, amines containing basic nitrogen or basic nitrogen and additionally one or more hydroxyl groups, including amines of the types described in U.S. Pat. No. 4,235,435 can be used in the formation of dispersants suitable for use herein. The amines can be polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines. Examples of polyalkylene polyamines include diethylene triamine, triethylene tetra-

mine, tetraethylene pentamine, pentaethylene hexamine, and dipropylene triamine. Pure polyethylene polyamines can be used, as well as mixtures of linear, branched and cyclic polyethylene polyamines having an average in the range of about 2.5 to about 7.5 nitrogen atoms per molecule, such as about 3 to about 5 nitrogen atoms per molecule. Examples of hydroxy-substituted amines include, but are not limited to, N-hydroxyalkyl-alkylene polyamines such as N-(2-hydroxyethyl)ethylene diamine, N-(2-hydroxyethyl)piperazine, and N-hydroxyalkylated alkylene diamines of the type described in U.S. Pat. No. 4,873,009. Polyoxyalkylene polyamines typically include polyoxyethylene and polyoxypropylene diamines and triamines having average molecular weights in the range of 200 to 2500.

[0018] In an aspect, the at least one dispersant can contain hydrocarbyl substituents such as olefinic hydrocarbons. A non-limiting example of suitable olefinic hydrocarbons includes isobutene, such as those made by cracking a hydrocarbon stream to produce a hydrocarbon mixture of essentially C₄-hydrocarbons. For example, thermocracking processes (streamcracker) produce C₄ cuts comprising C₄ paraffins and C₄ olefins, with a major component being isobutene. Butadiene and acetylene are substantially removed from the stream by additional selective hydrogenation or extractive distillation techniques. The resulting stream is referred to as “raffinate I” and is suitable for polyisobutylene (PIB) synthesis and has the following typical composition: 44-49% of isobutene, 24-28% of 1-butene, 19-21% of 2-butene, 6-8% of n-butane, 2-3% of isobutane. The components of the raffinate I stream may vary depending on operating conditions. Purification of the raffinate I stream provides an essentially pure isobutene product.

[0019] Relatively low molecular weight PIB for can also be used to produce dispersants suitable for use herein, such as those derived from polymerization of isobutene. The resulting product can have a terminal vinylidene group content ranging from about 50 to about 60 percent by weight of the polymerization product. The terminal vinylidene group content is believed to have an effect on the reactivity of the PIB during an alkylation process for making a succinic acid adduct, an amine adduct, or an alkyl phenol adduct.

[0020] Highly reactive PIB can also be used to produce dispersants suitable for use herein, such as those derived from the polymerization of a mixture of raffinate I and isobutene. A hydrocarbyl substituent produced from the polymerization of a mixture of raffinate I and isobutene can be more reactive than PIB, as evidenced by its terminal vinylidene group content. The terminal vinylidene content of a polymerized mixture of raffinate I and isobutene is typically above about 70% by weight. The polymerization product can have a number average molecular weight ranging from about 500 to about 5,000, such as from about 1,000 to about 2,500, for example from about 1,300 to about 2,200.

[0021] The polymerization reaction used to form the polymerization product is generally carried out in the presence of a conventional Ziegler-Natta or metallocene catalyst system. The polymerization medium can include solution, slurry, or gas phase processes, as known to those skilled in the art. When solution polymerization is employed, the solvent may be any suitable inert hydrocarbon solvent that is liquid under reaction conditions for polymerization of alpha-olefins. Examples of satisfactory hydrocarbon solvents include, but are not limited to, straight chain paraffins comprising from about 5 to about 8 carbon atoms, such as hexane; aromatic

hydrocarbons, for example, aromatic hydrocarbons having a single benzene nucleus, such as benzene and toluene; and saturated cyclic hydrocarbons having boiling point ranges approximating those of the straight chain paraffinic hydrocarbons and aromatic hydrocarbons described above. The solvent selected can be a mixture of one or more of the foregoing hydrocarbons. When slurry polymerization is employed, the liquid phase for polymerization is can be liquid propylene. It is desirable that the polymerization medium be free of substances that will interfere with the catalyst components.

[0022] In an embodiment, the dispersant system described herein can comprise at least first and second dispersants each independently selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, and Mannich base adducts derived from hydrocarbyl-substituted phenols condensed with aldehydes. The first and second dispersants can each independently comprise a hydrocarbyl substituent having a number average molecular weight ranging from about 500 to about 5,000, such as from about 1,000 to about 2,500, for example from about 1,300 to about 2,200, as determined by gel permeation chromatography.

[0023] Hydrocarbyl-substituted succinic acylating agents can be used to make hydrocarbyl-substituted succinimides suitable for use herein. The hydrocarbyl-substituted succinic acylating agents can include, but are not limited to, hydrocarbyl-substituted succinic acids, hydrocarbyl-substituted succinic anhydrides, the hydrocarbyl-substituted succinic acid halides (such as add fluorides and acid chlorides), and the esters of the hydrocarbyl-substituted succinic acids and lower alcohols (e.g., those containing up to 7 carbon atoms), that is, hydrocarbyl-substituted compounds which can function as carboxylic acylating agents. In an aspect, the hydrocarbyl-substituted succinic acylating agents can be hydrocarbyl-substituted succinic acids and the hydrocarbyl-substituted succinic anhydrides and mixtures of such acids and anhydrides.

[0024] Hydrocarbyl-substituted acylating agents can be made by reacting a polyolefin of desirable molecular weight (with or without chlorine) with an appropriate carboxylic reactant, such as succinic acid, succinic anhydride, maleic acid, maleic anhydride, fumaric acid, fumaric anhydride, malic acid, malic anhydride, tartaric acid, tartaric anhydride, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, mesaconic anhydride, ethylmaleic acid, ethylmaleic anhydride, dimethylmaleic acid, dimethylmaleic anhydride, hexamaleic acid, hexamaleic anhydride, and the like, including corresponding acid halides and lower aliphatic esters. In an aspect, the dispersant can be the reaction product of a polyolefin and a succinic acid or anhydride.

[0025] Hydrocarbyl-substituted succinic anhydrides can be prepared by heating a mixture of the desired anhydride and an aliphatic olefin under reaction conditions well known in the art. The molecular weight of the olefin can vary depending upon the intended use of the substituted succinic anhydrides. Typically, the substituted succinic anhydrides can have a hydrocarbyl group of from 8-500 carbon atoms. Dispersants comprising a hydrocarbyl group comprising from about 8 to about 150 carbon atoms are herein referred to as "relatively low molecular weight dispersants," whereas dispersants comprising a hydrocarbyl group comprising more than about 150 carbon atoms up to about 500 carbon atoms are herein referred to as "relatively high molecular weight dispersants."

With high molecular weight substituted succinic anhydrides, it is more accurate to refer to number average molecular weight (M_n) since the olefins used to make these substituted succinic anhydrides can include a mixture of different molecular weight components resulting from the polymerization of low molecular weight olefin monomers such as ethylene, propylene and isobutylene.

[0026] The mole ratio of anhydride to olefin can vary widely. It can vary, for example, from 5:1 to 1:5, such as from about 1:1 to about 1:1.6. With olefins such as ethylene-alpha-olefin copolymers and polyisobutylene having a number average molecular weight of about 500 to about 7000, such as of about 800 to about 3000 or higher, the anhydride is can be used in stoichiometric excess, for example about 1.1 to 3 moles anhydride per mole of olefin. The unreacted anhydride can be vaporized from the resultant reaction mixture.

[0027] Hydrocarbyl-substituted succinic anhydrides can include polyalkyl or polyalkenyl succinic anhydrides prepared by the reaction of the desired anhydride with the desired polyolefin or chlorinated polyolefin, under reaction conditions well known in the art. For example, such succinic anhydrides can be prepared by the thermal reaction of a polyolefin and maleic anhydride, as described in U.S. Pat. Nos. 3,361,673; 3,676,089; and 5,454,964. Alternatively, the substituted succinic anhydrides can be prepared by the reaction of chlorinated polyolefins with maleic anhydride, as described, for example, in U.S. Pat. No. 3,172,892. A further discussion of hydrocarbyl-substituted succinic anhydrides can be found, for example, in U.S. Pat. Nos. 4,234,435; 5,620,486 and 5,393,309. These hydrocarbyl substituents can contain from about 40 to about 500 carbon atoms.

[0028] Polyalkenyl succinic anhydrides can be converted to polyalkyl succinic anhydrides by using conventional reducing conditions such as catalytic hydrogenation. For catalytic hydrogenation, a catalyst can be palladium on carbon. Likewise, polyalkenyl succinimides can be converted to polyalkyl succinimides using similar reducing conditions.

[0029] The polyalkyl or polyalkenyl substituent on the succinic anhydrides employed herein can be derived from polyolefins which are polymers or copolymers of mono-olefins, such as 1-mono-olefins, for example ethylene, propylene and butylene. In an aspect, the mono-olefin can have from about 2 to about 24 carbon atoms, such as about 3 to 12 carbon atoms. Other non-limiting examples of mono-olefins include propylene, butylene, isobutylene, 1-octene, and 1-decene. Polyolefins prepared from such mono-olefins can include polypropylene, polybutene, polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

[0030] Dispersants can be prepared, for example, by reacting the hydrocarbyl-substituted succinic acids or anhydrides with an amine. Non-limiting examples of amines include polyamines and hydroxyamines. Examples of polyamines that may be used include, but are not limited to, aminoguanidine bicarbonate (AGBC), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA) and heavy polyamines. A heavy polyamine is a mixture of polyalkylenepolyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA but primarily oligomers comprising 7 or more nitrogen atoms, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures.

[0031] Non-limiting examples of polyamines that are also suitable for preparing the dispersants described herein

include N-arylphenylenediamines, such as N-phenylphenylenediamines, for example, N-phenyl-1,4-phenylenediamine, N-phenyl-1,3-phenylenediamine, and N-phenyl-1,2-phenylenediamine; aminothiazoles such as aminothiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole; aminocarbazoles; aminoindoles; aminopyrroles; amino-indazolinones; aminomercaptotriazoles; aminoperimidines; aminoalkyl imidazoles, such as 1-(2-aminoethyl)imidazole, 1-(3-aminopropyl)imidazole; and aminoalkyl morpholines, such as 4-(3-aminopropyl)morpholine. These polyamines are described in more detail in U.S. Pat. Nos. 4,863,623; and 5,075,383. Such polyamines can provide additional benefits, such as anti-wear and antioxidant, to the final products.

[0032] Additional polyamines useful in forming the hydrocarbyl-substituted succinimides include polyamines having at least one primary or secondary amino group and at least one tertiary amino group in the molecule as taught in U.S. Pat. Nos. 5,634,951 and 5,725,612. Non-limiting examples of suitable polyamines include N,N,N',N''-tetraalkyldialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N''-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N'',N'''-pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), tris(dialkylaminoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which can contain from about 1 to about 4 carbon atoms each. In an aspect, these alkyl groups can be methyl and/or ethyl groups. In another aspect, polyamine reactants of this type can be dimethylaminopropylamine (DMAPA) and N-methyl piperazine.

[0033] Hydroxyamines suitable for use herein include, but are not limited to, compounds, oligomers or polymers containing at least one primary or secondary amine capable of reacting with the hydrocarbyl-substituted succinic acid or anhydride. Non-limiting examples of suitable hydroxyamines include aminoethylethanolamine (AEEA), aminopropyldiethanolamine (APDEA), ethanolamine, diethanolamine (DEA), partially propoxylated hexamethylene diamine (for example HMDA-2PO or HMDA-3PO), 3-amino-1,2-propanediol, tris(hydroxymethyl)aminomethane, and 2-amino-1,3-propanediol.

[0034] The mole ratio of amine to hydrocarbyl-substituted succinic acid or anhydride can range from about 1:1 to about 2.5:1, such as from about 1.5:1 to about 2:1.

[0035] The foregoing dispersants can also be post treated dispersants made, for example, by treating a dispersant with maleic anhydride or boric acid as described, for example, in U.S. Pat. No. 5,789,353, or by treating the dispersant with nonylphenol, formaldehyde and glycolic acid as described, for example, in U.S. Pat. No. 5,137,980. In an embodiment, at least one of the first and second dispersants is a post treated dispersant.

[0036] Mannich base dispersants can be a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines). Examples of Mannich con-

densation products, and methods for their production are described in U.S. Pat. Nos. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

[0037] Hydrocarbon sources suitable for preparation of the Mannich polyamine dispersants can include those derived from substantially saturated petroleum fractions and olefin polymers, such as polymers of mono-olefins comprising from about 2 to about 6 carbon atoms. The hydrocarbon source can contain at least about 40, such as at least about 50 carbon atoms, to provide substantial oil solubility to the dispersant. The olefin polymers having a GPC number average molecular weight between about 600 and 5,000 can be useful due to their of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Other non-limiting examples of hydrocarbon sources include isobutylene polymers and polymers made from a mixture of isobutene and a raffinate I stream.

[0038] Mannich base dispersants suitable for use herein include those formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to 2.5 about moles of formaldehyde and from about 0.5 to about 2 moles of polyalkylene polyamine.

[0039] Polymeric polyamine dispersants suitable for use herein include polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials are illustrated by interpolymers formed from various monomers, such as decyl methacrylate, vinyl decyl ether, or relatively high molecular weight olefins, with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300. Other non-limiting examples of polymeric polyamines include hydrocarbyl polyamines wherein the hydrocarbyl group is comprises the polymerization product of isobutene and a raffinate I stream as described above. PIB-amine and PIB-polyamines may also be used.

[0040] Mixtures of the first and second dispersants can be made by combining the components in a conventional manner. In an aspect, a higher molecular weight dispersant can be present in the mixture can be in an amount ranging from about 30 to about 70% by weight, such as from about 45 to about 65% by weight of the total weight of the mixed dispersants. Accordingly, a lower molecular weight dispersant can be present in the mixture in an amount ranging from about 70 to about 30% by weight, such as from about 35 to about 45% by weight of the total weight of the mixed dispersants. The ratio of the first to second dispersant can vary widely. It can vary, for example, from about 1:3 to about 3:1, such as from about 1:1 to about 1:3.

[0041] Commercially available dispersants according to the embodiments described above include, but are not limited to:

[0042] HiTEC® 1921 dispersant is a 2100 MW_N PIBSA plus a polyamine post treated with nonylphenol, formaldehyde, and glycolic acid, and has a 1.6 SA/PIB mole ratio.

[0043] HiTEC® 643D dispersant is a 1300 MW_N PIBSA plus a polyamine wherein the dispersant was post treated with maleic anhydride and boric acid.

[0044] HiTEC® 1932 dispersant is a 2100 MW_N PIBSA plus a polyamine, and has a 1.6 SA/PIB ratio.

[0045] HiTEC® 1932X dispersant is a 2100 MW_N PIBSA plus a polyamine, and has a 1.75 SA/PIB ratio.

[0046] HiTEC® 743 dispersant is a 1300 MW_N PIBSA plus a polyamine post treated with boric acid, and has a 1.75 SA/PIB ratio.

[0047] All of the foregoing dispersants are available from Afton Chemical Corp. of Richmond, Va. "PIBSA" is defined as polyisobutylene succinic acid or anhydride. The "SA/PIB" ratio is the number of moles of succinic acid or anhydride relative to the number of moles of PIB in the PIBSA adduct.

[0048] Optionally, other components can be present in the disclosed compositions. Non-limiting examples of other components include antiwear agents, detergent, diluents, defoamers, demulsifiers, anti-foam agents, corrosion inhibitors, extreme pressure agents, seal well agents, antioxidants, pour point depressants, rust inhibitors and friction modifiers.

[0049] Base oils suitable for use in formulating the disclosed compositions can be selected from any of the synthetic or mineral oils or mixtures thereof. Mineral oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as other mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also suitable. Further, oils derived from a gas-to-liquid process are also suitable.

[0050] The base oil can be present in a major amount, wherein "major amount" is understood to mean greater than or equal to 50%, for example from about 80 to about 98 percent by weight of the lubricant composition.

[0051] The base oil typically has a viscosity of, for example, from about 2 to about 150 cSt and, as a further example, from about 5 to about 15 cSt at 100° C. Thus, the base oils can normally have a viscosity in the range of about SAE 15 to about SAE 250, and more usually can range from about SAE 20W to about SAE 50. Suitable automotive oils also include cross-grades such as 15W-40, 20W-50, 75W-140, 80W-90, 85W-140, 85W-90, and the like.

[0052] Non-limiting examples of synthetic oils include hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); polyalphaolefins such as poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, di-nonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0053] Alkylen oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils that can be used. Such oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of

polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃₋₈ fatty acid esters, or the C₁₃ Oxo acid diester of tetraethylene glycol.

[0054] Another class of synthetic oils that can be used includes the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didodecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0055] Esters useful as synthetic oils also include those made from C₅₋₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0056] Hence, the base oil which can be used to make the compositions as described herein can be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

[0057] Group I contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120; Group II contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120; Group III contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120; Group IV are polyalphaolefins (PAO); and Group V include all other base oils not included in Group I, II, III or IV.

[0058] The test methods used in defining the above groups are ASTM D2007 for saturates; ASTM D2270 for viscosity index; and one of ASTM D2622, 4294, 4927 and 3120 for sulfur.

[0059] Group IV base oils, i.e. polyalphaolefins (PAO) include hydrogenated oligomers of an alpha-olefin, the most important methods of oligomerisation being free radical processes, Ziegler catalysis, and cationic, Friedel-Crafts catalysis.

[0060] The polyalphaolefins typically have viscosities in the range of 2 to 100 cSt at 100° C., for example 4 to 8 cSt at 100° C. They can, for example, be oligomers of branched or straight chain alpha-olefins having from about 2 to about 30 carbon atoms, non-limiting examples include polypropylenes, polyisobutenes, poly-1-butenes, poly-1-hexenes, poly-1-octenes and poly-1-decene. Included are homopolymers, interpolymers and mixtures.

[0061] Base oils suitable for use herein can be made using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerisation, esterification, and re-refining.

[0062] The base oil can be an oil derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons can be made from synthesis gas containing H₂ and CO using a Fischer-Tropsch catalyst. Such

hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons can be hydroisomerized using processes disclosed in U.S. Pat. No. 6,103,099 or 6,180,575; hydrocracked and hydroisomerized using processes disclosed in U.S. Pat. No. 4,943,672 or 6,096,940; dewaxed using processes disclosed in U.S. Pat. No. 5,882,505; or hydroisomerized and dewaxed using processes disclosed in U.S. Pat. No. 6,013,171; 6,080,301; or 6,165,949.

[0063] Unrefined, refined and rerefined oils, either mineral or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the base oils. Unrefined oils are those obtained directly from a mineral or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives, contaminants, and oil breakdown products.

[0064] Biorenewable fuels suitable for use in formulating the disclosed lubricant and emulsion compositions can comprise any fuel which is derived from resources other than petroleum. Such resources include, but are not limited to, corn, maize, soybeans and other crops; grasses, such as switchgrass, miscanthus, and hybrid grasses; vegetable oils; natural fats; and mixtures thereof. In an embodiment, the biorenewable fuel can comprise monohydroxy alcohols, such as those comprising from 1 to about 5 carbon atoms. Non-limiting examples of suitable monohydroxy alcohols include methanol, ethanol, propanol, n-butanol, isobutanol, t-butyl alcohol, amyl alcohol, and isoamyl alcohol. In an aspect, the disclosed lubricant composition can comprise at least 10%, such as about 15%, by volume of said biorenewable fuel.

[0065] The compositions disclosed herein can be used to lubricate anything. In an aspect, the lubricating composition can be an engine composition that is used to lubricate an engine. However, one of ordinary skill in the art would understand that the disclosed lubricating compositions can be used to lubricate anything, e.g., any surface, such as those present in an environment where biorenewable fuel is used. Moreover, there is disclosed a method of reducing thin-film friction of a fluid between surfaces comprising providing to the fluid the disclosed composition.

[0066] It is further envisioned that the lubricating compositions can be provided to any machinery wherein aqueous separation in an emulsion is an issue, such as a vehicle powered by biorenewable fuels wherein aqueous separation of an emulsion composition can cause a multitude of undesirable effects. In particular, there is disclosed a method of reducing aqueous separation in an emulsion composition comprising providing the disclosed dispersant system to an emulsion composition comprising a biorenewable fuel and an oil of lubricating viscosity.

[0067] Also disclosed herein is a method of lubricating a machine, such as an engine, transmission, automotive gear, a gear set, and/or an axle with the disclosed emulsion composition. In a further aspect, there is disclosed a method of improving fuel efficiency in a machine, such as an engine, transmission automotive gear, a gear set, and/or an axle comprising placing the disclosed lubricating composition in the machine, such as an engine, transmission, automotive gear, a gear set, and/or an axle.

EXAMPLES

[0068] The following examples are illustrative of this disclosure and its advantageous properties. In these examples, as well as elsewhere in this application, all parts and percentages are by weight of the composition, unless otherwise indicated.

[0069] Lubricant compositions according to the present disclosure were formulated as shown in Tables 1 through 3 below. Each Example was treated at an equal activity level of about 2.3 wt. % solid. Each of Examples A to E contains a single dispersant, e.g., 100% of one dispersant. Each of Examples F to W contains a mixed system of two dispersants in various ratios.

[0070] Dispersant 1 was a 1300 MW_N PIBSA plus a polyamine, wherein the dispersant was post treated with boric acid and maleic anhydride, and is commercially available as HiTEC® 643D. Dispersant 2 was a 2100 MW_N PIBSA plus a polyamine post treated with nonylphenol, formaldehyde, and glycolic acid, wherein the dispersant has a 1.6 SA/PIB mol ratio, and is commercially available as HiTEC® 1921. Dispersant 3 was a 2100 MW_N PIBSA plus a polyamine, wherein the dispersant has a 1.6 SA/PIB mol ratio, and is commercially available as HiTEC® 1932. Dispersant 4 was a 2100 MW_N PIBSA plus a polyamine, wherein the dispersant has a 1.75 SA/PIB mol ratio, and is commercially available as HiTEC® 1932X. Dispersant 5 was a 1300 MW_N PIBSA plus a polyamine post treated with boric acid, wherein the dispersant has a 1.75 SA/PIB mol ratio, and is commercially available as HiTEC® 743.

[0071] Each Example was subjected to the E85 Emulsion Screener Test, in which a mixture of 10% E85 fuel, 10% water, and 80% test oil is blended by a Waring blender or equivalent for 1 minute at room temperature, and the resulting emulsion is placed in a graduated cylinder and evaluated after 24 hours at 25° C. for emulsion retention, oil separation, and aqueous phase separation. The desired result of the emulsion test was no aqueous separation (0%) and at least 85% emulsion remaining.

TABLE 1

Examples	A	B	C	D	E
Dispersant 1	100	—	—	—	—
Dispersant 2	—	100	—	—	—
Dispersant 3	—	—	100	—	—
Dispersant 4	—	—	—	100	—
Dispersant 5	—	—	—	—	100
Emulsion, %	100	0	100	20	4
Oil Separation	No	Yes	No	Yes	Yes
Aqueous Separation	No	Yes	No	Yes	Yes

TABLE 2

Examples	F	G	H	I	J	K	L	M	N
Dispersant 1	75	50	25	75	50	25	75	50	25
Dispersant 2	25	50	75	—	—	—	—	—	—
Dispersant 3	—	—	—	25	50	75	—	—	—
Dispersant 4	—	—	—	—	—	—	25	50	75
Emulsion, %	100	5	5	100	100	100	0	0	0
Oil Separation	No	Yes	Yes	No	No	No	Yes	Yes	Yes
Aqueous Separation	No	Yes	Yes	No	No	No	Yes	Yes	Yes

TABLE 3

Examples	O	P	Q	R	S	T	U	V	W
Dispersant 5	75	50	25	75	50	25	75	50	25
Dispersant 2	25	50	75	—	—	—	—	—	—
Dispersant 3	—	—	—	25	50	75	—	—	—
Dispersant 4	—	—	—	—	—	—	25	50	75
Emulsion, %	10	10	5	92	100	100	70	88	92
Oil Separation	Yes	Yes	Yes	Yes	No	No	Yes	Yes	Yes
Aqueous Separation	Yes	Yes	Yes	No	No	No	Yes	No	No

[0072] As can be seen from the results above, Examples A, C, F, I, J, K, R, S, T, V, and W performed acceptably, whereas Examples B, D, E, G, H, L, M, N, O, P, Q and U performed poorly. For instance, Example F comprising Dispersant 1 and Dispersant 2 in a ratio of 75:25 (or 3:1) formed a stable emulsion with no separation of an oil or aqueous layer. In comparison, Example G comprising a lower level of Dispersant 1 did not form a stable emulsion and resulted in separation of both an oil and aqueous layer.

[0073] Moreover, Examples V and W, which comprised a mixture of Dispersant 5 and Dispersant 4 at ratios of 50:50 (or 1:1) and 25:75 (or 1:3), respectively, resulted in no separation of an aqueous layer with more than 85% emulsion remaining. However, each dispersant individually (Examples E and D, respectively) resulted in separation of both an oil and an aqueous layer. These results clearly demonstrated that proper selection of dispersants is an important factor for maintaining stable emulsions as evaluated by the E85 Emulsion Screener Test.

[0074] At numerous places throughout this specification, reference has been made to a number of U.S. patents, published foreign patent applications and published technical papers. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0075] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0076] It is noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the,” include plural referents unless expressly and unequivocally

limited to one referent. Thus, for example, reference to “an antioxidant” includes two or more different antioxidants. As used herein, the term “include” and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0077] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

1-18. (canceled)

19. A method of reducing aqueous separation in an emulsion composition comprising:

- providing an emulsion composition comprising a fuel composition comprising a biorenewable fuel, water, and an oil of lubricating viscosity; and
- providing to said emulsion composition a dispersant system consisting essentially of a first dispersant comprising at least one relatively low molecular weight hydrocarbyl-substituted succinimide; and a second dispersant comprising at least one relatively high molecular weight dispersant selected from the group consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, or Mannich base adducts derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine,

wherein the hydrocarbyl substituent of each of the first and second dispersants comprises a polyisobutylene group having a number average molecular weight of 800 to 2500.

20. (canceled)

21. The method of claim 19, wherein the ratio of first dispersant to second dispersant ranges from about 1:3 to about 3:1.

22. The method of claim 19, wherein the ratio of first dispersant to second dispersant ranges from about 1:1 to about 1:3.

23-25. (canceled)

26. The method of claim 19, wherein the ratio of hydrocarbyl substituent to succinic acid in the first dispersant ranges from about 1.0:1.0 to about 1.0:1.6.

27. The method of claim 19, wherein at least one of the first and second dispersants is a post treated dispersant.

28. The method of claim 19, wherein the emulsion composition comprises at least one additive selected from the group consisting of antiwear agents, detergent, diluents, defoamers, demulsifiers, anti-foam agents, corrosion inhibitors, extreme pressure agents, seal well agents, antioxidants, pour point depressants, rust inhibitors and friction modifiers.

29. The method of claim 19, wherein the biorenewable fuel comprises an alcohol.

30. A method of lubricating an engine operating a fuel composition containing a biorenewable fuel to prevent aqueous phase separation in an emulsion containing a lubricant, the fuel composition, and water, comprising:

- lubricating the engine with a lubricant composition comprising:
- a dispersant system consisting essentially of a first dispersant comprising at least one relatively low molecular weight hydrocarbyl-substituted succinimide; and a second dispersant comprising at least one relatively high molecular weight dispersant selected from the group

consisting of hydrocarbyl-substituted succinimides, hydrocarbyl-substituted amines, or Mannich base adducts derived from a hydrocarbyl-substituted phenol condensed with an aldehyde and an amine, wherein the hydrocarbyl substituent of each of the first and second dispersants comprises a polyisobutylene group having a number average molecular weight of 800 to 2500; and operating the engine on the fuel composition.

31. The method of claim **30**, wherein the ratio of first dispersant to second dispersant ranges from about 1:3 to about 3:1.

32. The method of claim **30**, wherein the ratio of first dispersant to second dispersant ranges from about 1:1 to about 1:3.

33. The method of claim **30**, wherein the ratio of hydrocarbyl substituent to succinic acid in the first dispersant ranges from about 1.0:1.0 to about 1:0:1.6.

34. The method of claim **30**, wherein at least one of the first and second dispersants is a post treated dispersant.

35. The method of claim **30**, wherein the lubricant composition comprises at least one additive selected from the group consisting of antiwear agents, detergent, diluents, defoamers, demulsifiers, anti-foam agents, corrosion inhibitors, extreme pressure agents, seal well agents, antioxidants, pour point depressants, rust inhibitors and friction modifiers.

36. The method of claim **30**, wherein the biorenewable fuel comprises an alcohol.

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