

DEMULSIFIER FOR RENEWABLE DIESEL

TECHNICAL FIELD

[0001] This disclosure is directed to fuel additive compositions including polymeric blends
5 suitable for demulsification of renewable diesel fuels.

BACKGROUND

[0002] The Renewable Fuel Standard (RFS) under the United States Clean Air Act was
created back in 2005. The RFS program is a policy that relates to the use of alternative or
renewable fuels to replace and/or reduce the quantity of fossil fuels in transportation fuel and
10 other types of fuel. Renewable diesel, which is often referred to as hydrogenated vegetable oil
(HVO), is one such alternative fuel suitable for use in diesel engines and/or in blends with
traditional petroleum-based diesel. HVO and HVO blends are being investigated for further
implementation due to high cetane numbers, lower emissions, and relatively low aromatic
content. HVO is a renewable paraffinic biofuel produced by hydrotreating vegetable oils or
15 animal fats and is distinct from biodiesel (e.g., fatty acid methyl ester or FAME).

[0003] One of the challenges in moving to the use of HVO is poor demulse performance
with the current diesel fuel additive packages, which were designed to work with conventional
petroleum-based diesel fuels. Renewable fuels and fuel blends often contain small amounts of
water, typically from a few ppm up to several percent by weight. Such water may be the result
20 of, for instance, condensation into the fuel while in tanks and/or pipelines during transport and
storage. The amount of water may separate as a layer at the bottom of the storage tank and/or
may be emulsified in the fuel. The presence of water is undesired as it can cause problems
during transport and/or during use in combustion.

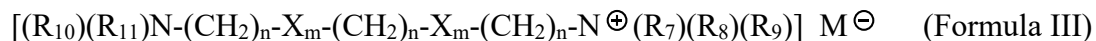
[0004] Water is separated from fuels typically through various agents that demulsify or break
25 the water-fuel emulsion in order to separate the water as a distinct layer in the fuel that can be
removed, as needed, by various applications. However, many common fuel additives tend to
hinder or even limit the functionality of the conventional demulsification agents when used in
HVO fuels or HVO diesel fuel blends. Quaternary ammonium salts, for instance, are one such
additive commonly used in diesel fuels. Quaternary ammonium salts are surface-active, and tend
30 to have a negative effect on fuel demulsibility rendering it more difficult to separate and remove
water from the fuel in tanks and transport lines.

SUMMARY

[0005] In one approach or embodiment, a fuel performance additive composition is described herein including a quaternary ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent and a demulsifier

5 component. In one aspect of this approach, the fuel performance additive includes at least (1) a quaternary ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent; (2) a demulsifying agent including an alkoxylated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxylated alkyl phenol formaldehyde resin includes
10 about 20 to about 45 mol percent of ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived moieties, and about 0.1 to about 15 mole percent of nonyl phenol derived moieties; and (3) an organic carrier solvent.

[0006] In other approaches or embodiments, the fuel performance additive composition of the preceding paragraph may include other features, embodiments, or elements in any
15 combination. These other features, embodiments, or elements include one or more of the following: wherein the alkoxylated alkyl phenol formaldehyde resin has a polydispersity index of about 2.0 to about 4.0; and/or wherein the organic carrier solvent is an aromatic solvent, e.g., xylene, ethyl benzene or a combination thereof; and/or wherein the organic carrier solvent includes about 70 to about 85 weight percent xylene and about 15 to about 30 volume percent
20 ethyl benzene; and/or wherein the alkoxylated alkyl phenol formaldehyde resin has a weight average molecular weight of about 13,000 g/mol to about 30,000 g/mol; and/or wherein the alkoxylated alkyl phenol formaldehyde resin has about 20 to about 30 mol percent of ethylene oxide derived moieties, about 60 to about 70 mol percent of propylene oxide derived moieties, and about 0.1 to about 8 mol percent of nonyl phenol derived moieties; and/or wherein the
25 alkoxylated alkyl phenol formaldehyde resin has a relative solubility number (RSN) of about 10 to about 12; and/or wherein the quaternary ammonium salt has a structure of Formula III



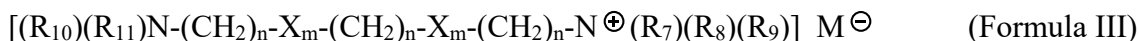
wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R₁₂)-, -C(O)-, -C(O)O-, or -C(O)NR₁₂; each R₇, R₈, and R₉ of Formula III is independently an alkyl group
30 containing 1 to 8 carbon atoms; R₁₀ and R₁₁ of Formula III are independently selected from an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent

of one or both of R₁₀ and R₁₁ has a number average molecular weight of about 700 or greater; R₁₂ of Formula III is independently a hydrogen atom or a group selected from C₁₋₆ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and M[⊖] is a carboxylate; and/or wherein the carboxylate of Formula III is oxalate, salicylate, or combinations thereof; and/or wherein X of Formula III is -O- or -NH-; and/or wherein the quaternary ammonium salt of Formula III is derived from 3-(2-(dimethylamino) ethoxy)propylamine, N,N-dimethyl dipropylenetriamine, or mixtures thereof; and/or wherein R₁₀ and R₁₁ of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide; and/or wherein the hydrocarbyl substituent has a number average molecular weight of about 700 to about 2,500; and/or wherein X is an oxygen atom and wherein R₁₀ and R₁₁ of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide with the hydrocarbyl substituent having a number average molecular weight of about 700 to about 1,500 as measured by GPC using polystyrene as a calibration reference; and/or wherein the fuel performance additive comprises about 10 to about 50 weight percent of the quaternary ammonium salt and about 0.1 to about 1 % by mass of the demulsifying agent; and/or further having a weight ratio of the quaternary ammonium salt to the demulsifying agent of about 2:1 to about 100:1; and/or further comprising a silicone antifoam agent.

[0007] In other approaches or embodiments, a renewable diesel is described herein. In aspects of this approach or embodiment, the renewable diesel includes at least a major amount of a renewable diesel including hydrogenated vegetable oil and a minor amount of a fuel performance additive; and wherein the renewable diesel includes a quaternary ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent; and a demulsifying agent including an alkoxylated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxylated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived moieties, and about 0.1 to about 15 mol percent of the nonyl phenol derived moieties.

[0008] In other approaches or embodiments, the renewable diesel of the previous paragraph may include any embodiment of the fuel additive of this Summary and, in other approaches, may include other features, embodiments, or elements in any combination. The other features,

embodiments, or elements may include one or more of the following: wherein the renewable diesel includes 0 to 80 volume percent petroleum diesel, biodiesel, or combination thereof and 20 to 100 volume percent hydrogenated vegetable oil; and/or wherein the renewable diesel includes about 10 to about 450 ppmw of the quaternary ammonium salt and about 0.1 to about 100 ppmw of the demulsifying agent; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has a polydispersity index of about 2.0 to about 4.0; and/or wherein the demulsifying agent includes the alkoxyated alkyl phenol formaldehyde resin in an organic carrier solvent is xylene, ethyl benzene, aromatic naphtha, or combinations thereof; and/or wherein the organic carrier solvent includes about 70 to about 85 weight percent xylene and about 15 to about 30 weight percent ethyl benzene; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has a weight average molecular weight of about 13,000 g/mol to about 30,000 g/mol; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has about 20 to about 30 mol percent of ethylene oxide derived moieties, about 60 to about 70 mol percent of propylene oxide derived moieties, and about 0.1 to about 8 mol percent of nonyl phenol derived moieties; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has a relative solubility number (RSN) of about 10 to about 12; and/or wherein the quaternary ammonium salt has a structure of Formula I



wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R₁₂)-, -C(O)-, -C(O)O-, or -C(O)NR₁₂; each R₇, R₈, and R₉ of Formula III is independently an alkyl group containing 1 to 8 carbon atoms; R₁₀ and R₁₁ of Formula III are independently selected from an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R₁₀ and R₁₁ has a number average molecular weight of about 700 or greater; R₁₂ of Formula III is independently a hydrogen atom or a group selected from C₁₋₆ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and M[⊖] is a carboxylate; and/or wherein the carboxylate of Formula III is oxalate, salicylate, or combinations thereof; and/or wherein X of Formula III is -O- or -NH-; and/or wherein the quaternary ammonium salt of Formula III is derived from 3-(2-(dimethylamino) ethoxy)propylamine, N,N-dimethyl dipropylenetriamine, or mixtures thereof; and/or wherein R₁₀ and R₁₁ of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide; and/or wherein the hydrocarbyl substituent has a number average molecular weight of about 700 to about 2,500;

and/or wherein X is an oxygen atom and wherein R₁₀ and R₁₁ of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide with the hydrocarbyl substituent having a number average molecular weight of about 700 to about 1,500 as measured by GPC using polystyrene as a calibration reference; and/or wherein the fuel performance additive comprises about 10 to about 50 weight percent of the quaternary ammonium salt and about 0.1 to about 10 percent by mass of the demulsifying agent; and/or further having a weight ratio of the quaternary ammonium salt to the demulsifying agent of about 2:1 to about 100:1; and/or further comprising a silicone antifoam agent.

[0009] In yet other approaches or embodiments, the present disclosure includes a method of improving the demulsibility of an additive-containing renewable diesel. In aspects of this embodiment, the method includes combining a major amount of a renewable diesel including hydrogenated vegetable oil with a fuel performance additive including (i) a quaternary ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent; (ii) a demulsifying agent including an alkoxyated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxyated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived moieties, and about 0.1 to about 15 mol percent of the nonyl phenol derived moieties; and (iii) an organic carrier solvent.

[00010] In other approaches or embodiments, the methods of the previous paragraph include other methods steps, features, or embodiments in any combination. These other steps, features, or embodiments include any embodiment of the fuel additive and/or any embodiment of the renewable diesel of this Summary and/or may also one or more of the following: wherein the renewable diesel includes 0 to 70 volume percent diesel fuel and 30 to 100 volume percent hydrogenated vegetable oil; and/or wherein demulsibility is measured by Turbiscan Stability Analysis and wherein improved demulsibility is a transmission of about 40 to about 50 percent after about 10 minutes and when measured within 0 to 3.5 mm from the bottom of a test vial including the additive containing renewable diesel.

[00011] In yet other approaches or embodiments, the present disclosure includes the use of a demulsifying agent to improving the demulsibility of an additive-containing renewable diesel. In aspects of this embodiment, the use includes a fuel additive including at least (i) a quaternary

ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent; (ii) a demulsifying agent including an alkoxyated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxyated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived moieties, and about 0.1 to about 15 mol percent of the nonyl phenol derived moieties; and (iii) an organic carrier solvent; and wherein the use includes achieving an improved demulsibility as measured by Turbiscan Stability Analysis and wherein demulsibility is a transmission of about 40 to about 50 percent after about 10 minutes and measured within 0 to 3.5 mm from the bottom of a test vial including the additive containing renewable diesel.

DRAWING FIGURES

- [00012] FIG. 1 is a graph of percent transmission along the height of a Turbiscan vial for Inventive System A in R100 renewable diesel.
- [00013] FIG. 2. is a graph of percent transmission along the height of a Turbiscan vial for Comparative System B in R100 renewable diesel.
- [00014] FIG. 3 is a graph of percent transmission along the height of a Turbiscan vial for Comparative System E in R100 renewable diesel.
- [00015] FIG. 4 is a graph of percent mean transmission calculated in the 0 to 3.5 mm height range at the bottom of a vial for Systems A-F in R100 renewable diesel.
- [00016] FIG. 5 is a graph of percent transmission along the height of a Turbiscan vial for Inventive system G in R30 renewable diesel.
- [00017] FIG. 6 is a graph of percent transmission along the height of a Turbiscan vial for Comparative system K in R30 renewable diesel.
- [00018] FIG. 7 is a graph of percent mean transmission calculated in the 0 to 3.5 mm height range at the bottom of a vial for Systems G-L in R30 renewable diesel.

DETAILED DESCRIPTION

- [00019] Described herein are fuel performance additives suitable for renewable diesel, renewable diesel fuel compositions including such fuel performance additives, methods of improving the demulsibility of renewable diesel using the fuel performance additives, and the use of fuel performance additives to improve the demulsibility of renewable diesel. As used

herein, renewable diesel refers to a fuel made from fat or oil and, in one embodiment, includes hydrogenated vegetable oil (HVO), which is a renewable paraffinic biofuel produced from a variety of methods, but generally produced by hydrotreating or hydroprocessing vegetable oil, animal fat, and/or used cooking oil. Those of ordinary skill appreciate that renewable diesel or

5 HVO is distinct from biodiesel or fatty acid methyl ester (FAME) based diesel fuel. HVO-based fuels tend to have poor demulse performance when combined with typical diesel fuel additive packages and especially diesel fuel additive packages including quaternary ammonium salts.

[00020] As used herein, renewable diesel, renewable diesel fuel, or renewable diesel fuel compositions are used interchangeably and include, as a base fuel, up to about 100 volume
10 percent HVO (R100), which is also considered renewable hydrocarbon diesel (RHD), and also blends of HVO and petroleum-based or fossil diesel. Such blended renewable diesel includes at least about 5 volume percent HVO (R5), at least about 10 volume percent (R10), at least about 30 volume percent HVO (R30), at least about 40 volume percent HVO (R40), at least about 50 volume percent (R50), at least about 60 volume percent HVO (R60), at least about 70 volume
15 percent HVO (R70), at least about 80 volume percent (R80), at least about 90 volume percent HVO (R90), or greater levels of HVO blended with petroleum-based diesel. Thus, the base fuel compositions herein may be about 100 weight percent HVO or may be blends of about 5 volume percent to about 90 volume percent (or 5 volume percent to 95 volume percent) HVO with petroleum-based diesel (or any other ranges within such endpoints noted above). All fuel
20 compositions herein also include a fuel performance additive including, in one embodiment, a demulsifying agent as described herein and at least one quaternary ammonium salt additive and, in other embodiments, a demulsifying agent as described herein, at least one quaternary ammonium salt additive, and an antifoam additive (e.g., silicone antifoam additive). The fuel performance additive may also include, in other embodiments, additional conventional diesel
25 fuel additives as needed for a particular application.

[00021] In one aspect, the fuel performance additives herein include at least (i) a quaternary ammonium salt and (ii) a unique demulsifying agent in the form of an alkoxylated alkyl phenol formaldehyde resin that has a relatively high weight average molecular weight, and a selected resin composition including ethylene oxide derived moieties, propylene oxide derived moieties,
30 and only limited amounts of nonyl phenol derived moieties. In other embodiments, the demulsifying agent includes the alkoxylated alkyl phenol formaldehyde resin in an organic

carrier solvent. The novel fuel performance additives herein unexpectedly achieve superior demulsification of water from the renewable diesel that also includes the quaternary ammonium salt known to be detrimental to demulsification in renewable diesel-based fuels.

[00022] As shown by the Examples, demulsibility is evaluated by Turbiscan Stability

5 Analysis (TSA) via a Turbiscan Lab Stability Analyzer (Microtrac Formulation, France), which evaluates emulsion stability and/or demulsibility of the fuel using static multiple light scattering (SMLS) at room temperature (e.g., 20 to 25°C), and scans the height of a vial including the renewable diesel and pH7 buffer using laser light at an incident wavelength of about 880 nm, with detectors for transmitted and backscattered light from the sample. Acceptable demulsibility
10 as used herein is a transmission of about 40 to about 50 percent after about 10 minutes when measured from 0 to 3.5 mm at the bottom of a vial of the renewable diesel including the fuel performance additive. Further details of the test procedures are provided in the Examples below.

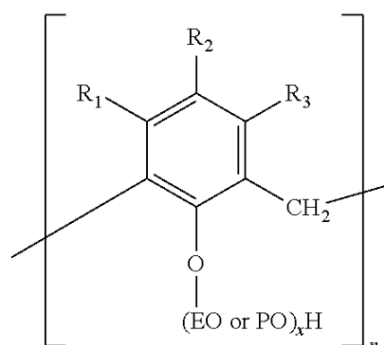
[00023] Alkoxyated Alkyl Phenol Formaldehyde Resin

15 **[00024]** In one approach, the demulsifier agent of the fuel performance additives herein includes a select alkoxyated alkyl phenol formaldehyde resin. Suitable alkoxyated alkyl phenol formaldehyde resins may be obtained from a variety of sources and, while not wishing to be limited by theory, are believed to include alkyl phenol formaldehyde alkoxyates as described below and include ethylene oxide and/or propylene oxide derived alkoxylation and, in
20 embodiments, have a high weight average molecular weight of at least about 13,000 g/mol (in other embodiments, about 13,000 g/mol to about 30,000 g/mol, about 15,000 g/mol to about 25,000 g/mol, or about 18,000 g/mol to about 22,000 g/mol, or about 22,000 g/mol to about 30,000 g/mol) and a specific phenol-formaldehyde resin composition including selected amounts of ethylene oxide derived moieties, propylene oxide derived moieties, and only limited amounts
25 of nonylphenol derived moieties. In addition to the high molecular weight, embodiments of the select alkoxyated alkyl phenol formaldehyde resins suitable for the renewable diesel herein may also have a polydispersity index (PDI) of greater than 2.0 (preferably, greater than 2.1, greater than 2.2, or greater than 2.3 and, in other approaches, about 2.0 to about 4.0, about 2.1 to about 3.5, about 2.2 to about 3.2, about 2.3 to about 3.0, about 2.1 to about 2.5, or about 2.2 to about
30 2.4 or any other ranges between such endpoints). As understood by those of skill, PDI is a ratio of the weight average molecular weight to the number average molecular weight.

[00025] The resins generally are butyl, amyl, nonyl and/or di-nonyl phenol formaldehyde resins with varying amounts of ethylene and/or propylene oxide. Such alkoxyated alkyl phenol formaldehyde resins can be made by conventional methods well known in the art. For example, alkyl phenol and aldehyde are polymerized by condensation reaction to form alkyl phenol formaldehyde resin (also called “resol phenolic resin”), and the resulting resin is subsequently alkylated with a mixture of ethylene oxide and propylene oxide. See, for example, US 4,442,014; US 4,337,828; and US 2023/0256359, which are incorporated herein by reference. Specific examples are nonyl phenol formaldehyde resin with ethylene and propylene oxide with a molar ratio of about 0.1 to about 15 mole ratio of resin to mixed oxide.

[00026] In yet other approaches or embodiments, the alkoxyated alkyl phenol formaldehyde resin may be dissolved in or provided within an organic carrier solvent. Examples of suitable carrier solvent include, but are not limited to, xylene, ethyl benzene, aromatic naphtha, or combinations thereof. In embodiments, the organic carrier solvent is about 70 to about 85 weight percent xylene and about 15 to about 30 weight percent ethyl benzene. In other embodiments, the alkoxyated alkyl phenol formaldehyde resin demulsifier herein may be an additive including about 80 to about 90 weight percent of the resin and about 10 to about 20 weight percent of the carrier solvent (preferably, about 80 to about 90 weight percent of resin, about 5 to about 15 weight percent xylene, and about 1 to about 5 weight percent ethyl benzene).

[00027] In other approaches or embodiments, the alkoxyated alkyl phenol formaldehyde resin of the fuel performance additives herein may include a moiety having a general structure of Formula I:



Formula 1

wherein each R_1 , R_2 , R_3 of Formula I is, independently, a linear or branched C1 to C10 alkyl or alkoxy group (preferably, a linear or branched C3 to C9 alkyl group, more preferably a linear or

branched C6 to C9 alkyl group). In Formula I, x and n are integers sufficient to achieve the desired molecular weights. In some approaches, R₁, R₂ and R₃ may be a branched alkyl group such as a secondary alkyl group selected from iso-propyl (prop-2-yl), sec-butyl (but-2-yl), isobutyl (2-methyl-prop1-yl) and/or tert-butyl group, or a 2-ethyl hexyl group, and the like, and combinations thereof.

[00028] In yet another approach, the alkoxyated alkyl phenol formaldehyde resin has a select molar composition of ethylene oxide derived moieties, propylene oxide derived moieties, and nonyl phenol derived moieties to achieve performance when combined with the high molecular weight. In some instances, the alkoxyated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of ethylene oxide derived moieties (in other approaches, about 20 to about 30 mol percent or about 25 to about 30 mol percent), about 55 to about 80 mole percent of propylene oxide derived moieties (in other approaches, about 60 to about 70 mol percent or about 65 to about 70 mol percent), and limited amounts of nonyl phenol derived moieties, but no more than about 15 mol percent of the nonyl phenol derived moieties (in other approaches, no more than about 10 mol percent or no more than about 8 mol percent, e.g. about 0.1 to about 15 mol percent, about 0.1 to about 10 mol percent, or about 0.1 to about 8 mol percent). As appreciated by those of skill, the sum of the three selected monomer components of the alkoxyated alkyl phenol formaldehyde resin (e.g., the ethylene oxide derived moieties, the propylene oxide derived moieties, and the nonyl phenol derived moieties) is 100 mol percent.

[00029] The alkoxylation and alkylation of such resin polymers is selected to achieve relative solubility numbers of each polymer suitable to achieve the demulsification in the context of quaternary ammonium salt containing renewable diesel fuels. Relative solubility number is known to those of skill as a measure of the solubility of a polymer in water, which is an indication of its hydrophilic or lipophilic tendency. The relative solubility number may be determined by a titration against water of the polymer in a solvent system including, for instance, xylene, diethylene glycol monobutyl ether, toluene, ethylene glycol methyl ether, and/or dimethyl isosorbide. In general, a relative solubility number less than about 13 generally indicates the polymer is more oil soluble whereas a number greater than about 18 generally indicates the polymer is more water soluble with values in between suggesting the polymer is dispersible. Further information on determining the relative solubility number may be obtained in Wu et al, Colloids and surfaces: Physicochemical and engineering aspects; 2004; Vol. 232(2-

3); pages 229-237, which is incorporated herein by reference.

[00030] As used herein, relative solubility number is determined by titration against water of 1 gram of a polymer in 30 grams of solvent (e.g., about 2.6 volume percent toluene and about 97.4 volume percent of ethylene glycol methyl ether). The end point of the titration is when a persistent turbidity holds for at least one minute and the volume of water in milliliters used in the titration is the relative solubility number. In one approach, the alkoxyated alkyl phenol formaldehyde resins herein may have a relative solubility number (RSN) of about 10 or greater, and in other approaches, about 10 to about 12.

[00031] The alkoxyated alkyl phenol formaldehyde resin may be added to a fuel performance additive in amounts suitable to provide demulsification in the presence of quaternary ammonium salts when added to renewable diesel. In some approaches, the demulsifier may be about 0.1 to about 2 weight percent of the fuel performance additive (in other approaches, about 0.5 to about 1.5 weight percent or about 0.7 to about 1.2 weight percent of the fuel performance additive) and, when added to the renewable diesel, may provide, in some embodiments, about 0.1 to about 100 ppmw of the demulsifier to the renewable diesel (in other approaches, about 0.25 to about 75 ppmw, about 1 to about 50 ppmw, about 1 to about 20 ppmw, about 5 to about 18 ppmw, about 5 to about 15 ppmw, or about 5 to about 12 ppm in the renewable diesel).

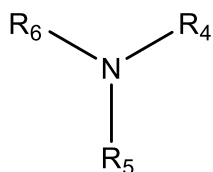
[00032] Quaternary Ammonium Salt

[00033] In another aspect of this disclosure, the fuel performance additives herein also include at least one quaternary ammonium salt, which is known to have a detrimental effect on demulsification of the renewable diesel or HVO-based fuels. Such salts may be formed through a reaction of a nitrogen containing compound having at least a one tertiary amino group and a suitable quaternizing agent.

[00034] The quaternary ammonium salt additives suitable for the fuel performance additives herein may be made by reacting a wide variety of amine, polyamine, or derivatives thereof having a tertiary amino group with a suitable quaternizing agent. For example, the quaternary ammonium salt additives herein may be (i) a reaction product of a hydrocarbyl-substituted acylating agent and a compound having at least one oxygen or nitrogen atom capable of condensing with said acylating agent and further having a tertiary amino group and reacted with (ii) a quaternizing agent. In one approach, the amine with a tertiary amino group may be a wide

variety of amine and polyamines having a tertiary amino group and capable of being quaternized so long as the resultant quaternary ammonium salts have the hydrocarbyl substituents and other characteristics as further described herein.

[00035] In one approach, the general amine or poly amine suitable for the quaternary ammonium salt herein may be a tertiary amine of the general Formula II



(Formula II)

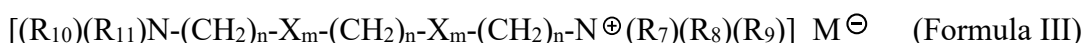
wherein each of R₄, R₅, and R₆ of Formula II is selected from hydrocarbyl groups containing from 1 to 200 carbon atoms may be used. Each hydrocarbyl group R₄ to R₆ of Formula II may independently be linear, branched, substituted, cyclic, saturated, unsaturated, or contain one or more hetero atoms. Suitable hydrocarbyl groups may include, but are not limited to alkyl groups, aryl groups, alkylaryl groups, arylalkyl groups, alkoxy groups, aryloxy groups, amido groups, ester groups, imido groups, and the like. Any of the foregoing hydrocarbyl groups may also contain hetero atoms, such as oxygen or nitrogen atoms. Particularly suitable hydrocarbyl groups may be linear or branched alkyl groups. Some representative examples of amine reactants which can be reacted to yield compounds of this invention are: trimethyl amine, triethyl amine, tri-n-propyl amine, dimethylethyl amine, dimethyl lauryl amine, dimethyl oleyl amine, dimethyl stearyl amine, dimethyl eicosyl amine, dimethyl octadecyl amine, N-methyl piperidine, N,N'-dimethyl piperazine, N-methyl-N-ethyl piperazine, N-methyl morpholine, N-ethyl morpholine, N-hydroxyethyl morpholine, pyridine, triethanol amine, triisopropanol amine, methyl diethanol amine, dimethyl ethanol amine, lauryl diisopropanol amine, stearyl diethanol amine, dioleyl ethanol amine, dimethyl isobutanol amine, methyl diisooctanol amine, dimethyl propenyl amine, dimethyl butenyl amine, dimethyl octenyl amine, ethyl didodecenyl amine, dibutyl eicosenyl amine, triethylene diamine, hexamethylene tetramine, N,N,N',N'-tetramethyl ethylenediamine, N,N,N',N'-tetramethylpropylenediamine, N,N,N',N'-tetraethyl-1,3-propane diamine, methyl-di-cyclohexyl amine, 2,6-dimethylpyridine, dimethylcyclohexylamine, C₁₀-C₃₀-alkyl or alkenyl-substituted amidopropyldimethylamine, C₁₂-C₂₀₀-alkyl or alkenyl-substituted succinic-carbonyldimethylamine, succinimide derivatives thereof, and the like.

[00036] In other approaches, if the amine contains solely primary or secondary amino groups,

it is necessary to alkylate at least one of the primary or secondary amino groups to a tertiary amino group prior to the reaction with the suitable quaternizing agent. In one embodiment, alkylation of primary amines and secondary amines or mixtures with tertiary amines may be exhaustively or partially alkylated to a tertiary amine. It may be necessary to properly account for the hydrogen on the nitrogen and provide base or acid as required (e.g., alkylation up to the tertiary amine requires removal (neutralization) of the hydrogen (proton) from the product of the alkylation). If alkylating agents, such as, alkyl halides or dialkyl sulfates are used, the product of alkylation of a primary or secondary amine is a protonated salt and needs a source of base to free the amine for further reaction.

[00037] In embodiments, general quaternizing agents for the additives herein, in general, may also be a wide variety of compounds suitable for alkylating a tertiary amine. As discussed further below, suitable examples of quaternizing agents include, but are not limited to, dialkyl sulphates, esters of a carboxylic acids, alkyl halides, benzyl halides, hydrocarbyl substituted carbonates, hydrocarbyl epoxides in combination with an acid, or mixtures thereof. Other examples may include halides, hydroxides, sulphonates, bisulphites, alkyl sulphates, sulphones, phosphates, alkylphosphates, borates, alkylborates, nitrites, nitrates, carbonates, bicarbonates, alkanoates, alkyldithiophosphates, and the like quaternizing agent, and/or mixtures thereof.

[00038] In yet another approach or embodiment, the quaternary ammonium salt is a cationic salt having the structure of Formula III



wherein each X of Formula III is a bivalent moiety selected from the group consisting of -O-, -N(R₁₂)-, -C(O)-, -C(O)O-, or -C(O)NR₁₂; each R₇, R₈, and R₉ of Formula III are independently alkyl groups containing 1 to 8 carbon atoms; R₁₀ and R₁₁ of Formula III are independently selected from an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group and, optionally, R₁₀ and R₁₁ together with the N atom to which they are attached, combine to form a ring moiety (such as a succinimide), the hydrocarbyl substituent of one or both of R₁₀ and R₁₁ having a number average molecular weight of about 700 or greater (as described herein); R₁₂ of Formula III is independently a hydrogen or a group selected from C₁₋₆ aliphatic, phenyl, or alkylphenyl; each m of Formula III is independently an integer of 0 or 1 with at least one m being 1; each n of Formula III is independently an integer of 1 to 10; and M[⊖] of Formula III is a

carboxylate. A suitable quaternary ammonium salt is also described in US 10,308,888, which is incorporated herein by reference in its entirety.

[00039] In one approach of this aspect, the amine used to form the quaternary ammonium salt additive may have the structure of Formula IV

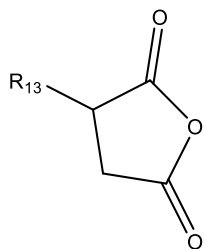


with X, R₇, R₈ and integers n and m as defined above with response to Formula III. In a preferred approach, the X moiety of Formula III or Formula IV is an oxygen atom or nitrogen atom, and more preferably, an oxygen atom. In a preferred approach, the amine is 3-(2-(dimethyl amino)ethoxy)propylamine; N,N-dimethyldipropylenetriamine, or mixtures thereof.

10 **[00040]** Any of the foregoing described tertiary amines may be reacted with a hydrocarbyl substituted acylating agent having to form the quaternary ammonium salt additive. In approaches, the hydrocarbyl substituted acylating agent may be selected from a hydrocarbyl substituted mono-, di-, or polycarboxylic acid or a reactive equivalent thereof to form an amide or imide compound. A particularly suitable acylating agent is a hydrocarbyl substituted succinic
15 acid, ester, anhydride, mono-acid/mono-ester, or diacid. In some approaches, the hydrocarbyl substituted acylating agent is a hydrocarbyl substituted dicarboxylic acid or anhydride derivative thereof, a fatty acid, or mixtures thereof. The hydrocarbyl substituent may have a molecular weight of 700 or more as discussed above.

[00041] In other approaches, the hydrocarbyl substituted acylating agent may be carboxylic
20 acid or anhydride reactant. In one approach, the hydrocarbyl substituted acylating agent may be selected from stearic acid, oleic acid, linoleic acid, linolenic acid, palmitic acid, palmitoleic acid, lauric acid, myristic acid, myristoleic acid, capric acid, caprylic acid, arachidic acid, behenic acid, erucic acid, anhydride derivatives thereof, or a combination thereof.

[00042] In one approach, the hydrocarbyl substituted acylating agent suitable for the
25 quaternary ammonium salt additive is a hydrocarbyl substituted dicarboxylic anhydride of Formula V



(Formula V)

wherein R_{13} of Formula V is a hydrocarbyl or alkenyl group having a high molecular weight as discussed above. In some aspects, R_{13} of Formula V is a hydrocarbyl group having a number average molecular weight from about 500 to about 5,000, about 700 to about 2,500, or about 700 to about 1,500. In other approaches, the number average molecular weight of R_{13} of Formula V may range from about 700 to about 1300, as measured by GPC using polystyrene as a calibration reference. A particularly useful R_{13} of Formula V has a number average molecular weight of about 1000 Daltons and comprises polyisobutylene.

[00043] In some approaches, the R_{13} of Formula V is a hydrocarbyl moiety that may comprise one or more polymer units chosen from linear or branched alkenyl units. In some aspects, the alkenyl units may have from about 2 to about 10 carbon atoms. For example, the polyalkenyl radical may comprise one or more linear or branched polymer units formed from ethylene radicals, propylene radicals, butylene radicals, pentene radicals, hexene radicals, octene radicals and decene radicals. In some aspects, the R_{13} of Formula V polyalkenyl radical may be in the form of, for example, a homopolymer, copolymer or terpolymer. In other aspects, the polyalkenyl radical is polyisobutylene. For example, the polyalkenyl radical may be a homopolymer of polyisobutylene comprising from about 5 to about 60 isobutylene groups, such as from about 15 to about 30 isobutylene groups. The polyalkenyl compounds used to form the R_{13} polyalkenyl radicals may be formed by any suitable methods, such as by conventional catalytic oligomerization of alkenes.

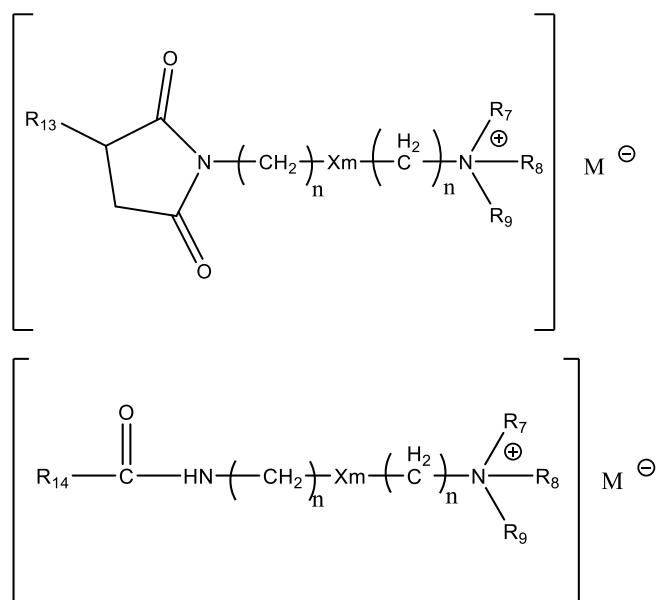
[00044] In some aspects, high reactivity polyisobutylenes having relatively high proportions of polymer molecules with a terminal vinylidene group may be used to form the R_{13} group. In one example, at least about 60%, such as about 70% to about 90%, of the polyisobutylenes comprise terminal olefinic double bonds. In some aspects, approximately one mole of maleic anhydride may be reacted per mole of polyalkylene, such that the resulting polyalkenyl succinic anhydride has about 0.8 to about 1.5 succinic anhydride group per polyalkylene substituent. In other aspects, the molar ratio of succinic anhydride groups to polyalkylene groups may range

from about 0.5 to about 3.5, such as from about 1 to about 1.3.

[00045] A suitable alkylating or quaternizing agent for the quaternary ammonium salt additive is a hydrocarbyl-substituted carboxylate, such as an alkyl carboxylate or dialkyl carboxylate. In some approaches or embodiments, the quaternizing agent is an alkyl carboxylate selected from alkyl oxalate, dialkyl oxalate, alkyl salicylate, and combinations thereof. In other approaches or embodiments, the alkyl group of the alkyl carboxylate includes 1 to 6 carbon atoms, and is preferably methyl groups. Suitable alkylating or quaternizing agents for the second quaternary ammonium salt additive herein may be dimethyl oxalate or methyl salicylate.

[00046] For alkylation with an alkyl carboxylate, it may be desirable in some approaches that the corresponding acid of the carboxylate have a pKa of less than 4.2. For example, the corresponding acid of the carboxylate may have a pKa of less than 3.8, such as less than 3.5, with a pKa of less than 3.1 being particularly desirable. Examples of suitable carboxylates may include, but not limited to, maleate, citrate, fumarate, phthalate, 1,2,4-benzenetricarboxylate, 1,2,4,5-benzenetetracarboxylate, nitrobenzoate, nicotinate, oxalate, aminoacetate, and salicylate. As noted above, preferred carboxylates include oxalate, salicylate, and combinations thereof.

[00047] In some embodiments, suitable examples of the quaternary ammonium salt from the above described reactions include, but are not limited to, compounds of the following exemplary structures:



wherein X, R₇, R₈, R₉, R₁₃ and M as well as integers n and m are as described above with respect to Formula III, IV, or V. R₁₄ above is a C1 to C30 hydrocarbyl group. Due to the length of the

hydrocarbyl chain and the presence of the bivalent moiety therein having, in some approaches, an internal oxygen or nitrogen atoms (*i.e.*, the X moiety), it is believed the quaternary ammonium salts as described herein include a relatively sterically available quaternary nitrogen that is more available for detergent activity than prior quaternary ammonium compounds.

5 **[00048]** In approaches, fuel performance additives herein may include, on an active ingredient basis, about 10 to about 50 weight percent of the quaternary ammonium salt (in other approaches about 10 to about 45 weight percent or about 15 to about 45 weight percent) and, when added to renewable diesel, the fuel performance additive provides, on an active ingredient basis, about 1 to about 450 ppmw of the quaternary ammonium salt to the renewable diesel (in
10 other approaches, about 5 to about 450 ppmw, about 10 to about 450 ppmw, about 5 to about 200 ppmw, about 10 to about 200 ppmw, about 10 to about 100 ppmw, about 5 to about 50 ppmw or about 10 to about 25 ppmw of the quaternary ammonium salt to the renewable diesel. Such amounts refer to the active ingredient basis in the fuel performance additive and/or renewable diesel and excludes the weight of (i) unreacted components associated with and remaining in the
15 product as produced and used, and (ii) solvent(s), if any, used in the manufacture of the product either during or after its formation.

[00049] In some embodiments, the fuels and fuel performance additives herein may have a weight ratio of the quaternary ammonium salt to the demulsifying agent of about 2:1 to about 100:1 (in other embodiments, about 4:1 to about 40:1)

20 **[00050]** Optional Components of the Fuel Performance Additive

[00051] The fuel performance additives and renewable diesel including such additives may also include one or more optional components as needed for a particular application. For example, the additives and/or renewable diesel herein may contain conventional quantities of
25 antifoam (e.g., silicone-based antifoam additives such as about 0.5 to about 3.0 weight percent, about 0.8 to about 2 weight percent), octane improvers, corrosion inhibitors or cold flow improvers (CFPP additive), pour point depressants, solvents, demulsifiers, lubricity additives, friction modifiers, amine stabilizers, combustion improvers, detergents, dispersants, antioxidants, heat stabilizers, conductivity improvers, metal deactivators, marker dyes, organic nitrate ignition
30 accelerators, cycloaromatic manganese tricarbonyl compounds, carrier fluids, and the like. In some aspects, the compositions described herein may contain, unless otherwise specified, about

10 weight percent or less, or in other aspects, about 5 weight percent or less, or about 2 weight percent or less based on the total weight of the additive concentrate, of one or more of the above optional additives. In some aspects, the compositions described herein may further contains cetane improvers at up to 85 weigh percent based on the total weight of the additive concentrate.

5 Similarly, the renewable diesel, biodiesel, or petroleum diesel may contain, if needed, suitable amounts of conventional fuel blending components as needed for a particular application.

[00052] In some aspects of the disclosed embodiments, organic nitrate ignition accelerators that include aliphatic or cycloaliphatic nitrates in which the aliphatic or cycloaliphatic group is saturated, and that contain up to about 12 carbons may be used. Examples of organic nitrate
10 ignition accelerators that may be used are methyl nitrate, ethyl nitrate, propyl nitrate, isopropyl nitrate, allyl nitrate, butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, hexyl nitrate, heptyl nitrate, 2-heptyl nitrate, octyl nitrate, isooctyl nitrate, 2-ethylhexyl nitrate, nonyl nitrate, decyl nitrate, undecyl nitrate, dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate,
15 cyclododecyl nitrate, 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, tetrahydrofuranyl nitrate, and the like. Mixtures of such materials may also be used.

[00053] Examples of suitable optional metal deactivators useful in the compositions of the present application are disclosed in US 4,482,357, the disclosure of which is herein incorporated by reference in its entirety. Such metal deactivators include, for example, salicylidene-o-
20 aminophenol, disalicylidene ethylenediamine, disalicylidene propylenediamine, and N,N'-disalicylidene-1,2-diaminopropane.

[00054] Other commercially available detergents and/or additives may be used in combination with the reaction products described herein. Such detergents include but are not limited to succinimides, Mannich base detergents, quaternary ammonium compounds, bis-aminotriazole
25 detergents as generally described in U.S. patent application Ser. No. 13/450,638, and a reaction product of a hydrocarbyl substituted dicarboxylic acid, or anhydride and an aminoguanidine, wherein the reaction product has less than one equivalent of amino triazole group per molecule as generally described in U.S. patent application Ser. Nos. 13/240,233 and 13/454,697.

[00055] The additives of the present application, including the demulsifier as described above,
30 and any optional additives used in formulating the additives and/or fuels of this disclosure may be blended into a base renewable diesel individually or in various sub-combinations. In some

embodiments, the additive components of the present application may be blended into the renewable diesel concurrently using an additive concentrate, as this takes advantage of the mutual compatibility and convenience afforded by the combination of ingredients when in the form of an additive concentrate. Also, use of a concentrate may reduce blending time and lessen the possibility of blending errors.

[00056] Renewable Diesel, Petroleum Diesel, and Biodiesel

[00057] The fuel performance additives of the present application are suitable for renewable diesel. As noted above, renewable diesel is an alternative fuel that is typically produced from animal fats, cooking oils, and/or vegetable oils, such as but not limited to, soybean oil and/or canola oil, and is often referred to as or includes amounts of hydrogenated vegetable oil (HVO). The renewable diesel, as a base fuel, may be up to about 100 volume percent HVO (R100), which is also considered renewable hydrocarbon diesel (RHD), and also includes blends of HVO and petroleum-based or fossil diesel. Such blended renewable diesel includes at least about 5 volume percent HVO (R5), at least about 10 volume percent (R10), at least about 30 volume percent HVO (R30), or greater levels of HVO blended with petroleum-based diesel as discussed above. Thus, the base fuel compositions herein may be about 100 volume percent HVO or may be blends of about 5 volume percent to about 95 volume percent HVO with petroleum-based diesel.

[00058] Renewable diesel is commonly prepared by hydrotreating, hydroprocessing and/or hydrothermal processing vegetable oils, animal fats, or waste and by-products from oils and fats processing, like used cooking oils, fatty acid distillates, acid oil, etc., which consist mainly of fatty acids and/or triglycerides. Hydrotreating or hydroprocessing is most commonly used and generally involves reacting animal fats and/or vegetable oils with hydrogen under elevated temperatures and pressures in the presence of a catalyst. For example, hydrotreated vegetable oil (HVO) can be prepared from glyceride through hydrogenation through a conceivably simple mechanism. Glyceride is an ester composed of fatty acid, that is, an organic acid with a long paraffinic backbone (R), and glycerol. R is a straight chain hydrocarbon typically in the C₁₅ to C₁₈ carbon range that, depending on the feedstock, is partly unsaturated. During hydrogenation, the bonds between the ester groups and the C₃ central backbone of triglyceride is broken. The resulting paraffin is a good fuel but needs to be isomerized for optimal properties, particularly reduction of freezing point. Hydrogenation may require a catalyst, high pressure (e.g., about 30

to about 70 bar), and high temperature (e.g., about 300 to about 350°C), all of which have been well known in the industry. Transesterification takes place at much milder conditions; at ambient pressure, and about 50 to about 80°C and in a basic solution. Examples of sources of renewable fuels include but are not limited to canola oil, soybean oil, rapeseed oil, palm oil, animal fat, fish oil, and used frying oil or certain industrial oils. Details about renewable diesel and hydrotreated vegetable oil (HVO) can be found in “Hydrogen, Biomass and Bioenergy - Integration Pathways for Renewable Energy Applications” edited by Jacob J. Lamb and Bruno G. Pollet, Academic Press, 2020, Chapter Six, pages 87-119, “Thermochemical Production of Fuels” by Erling Rytter, et al, which is incorporated herein by reference. Renewable diesel meets the ASTM D975 specification and/or the EN 15940 specification for fuel, relevant portions thereof are incorporated herein by reference.

[00059] Petroleum diesel (or petroleum-based diesel), also known as fossil diesel, refers to conventional distillate fuel for use in motor vehicles that use compression ignition engine. Petroleum diesel is produced at petroleum refineries from crude oil, which is formed naturally in the Earth’s crust from the buried remains of prehistoric organisms (animals, plants, or planktons), a process that occurs within geological formations. Typical process for making petroleum diesel is called fractional distillation, in which diesel is collected between about 200 and about 350°C at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 9 and 25 carbon atoms per molecule. Standards for petroleum diesel include EN 950, ASTM D975, NATO F 54, and DIN 51601.

[00060] Biodiesel is also obtained from vegetable oil or animal fats (biolipids) which are mainly fatty acid methyl esters (FAME), and transesterified with methanol. It can be produced from many types of oils, the most common being rapeseed oil (rapeseed methyl ester, RME) in Europe and soybean oil (soy methyl ester, SME) in the US. Methanol can also be replaced with ethanol for the transesterification process, which results in the production of ethyl esters. The transesterification processes use catalysts, such as sodium or potassium hydroxide, to convert vegetable oil and methanol into biodiesel and the undesirable byproducts glycerine and water, which will need to be removed from the fuel along with methanol traces. Biodiesel can be used pure (B100) in engines where the manufacturer approves such use, but it is more often used as a mix with diesel.

[00061] FAME used as fuel is specified in DIN EN 14214 and ASTM D6751 standards. The

fuel performance additives of the present application are suitable for renewable diesel. The renewable diesel, as a base fuel, may be up to about 100 volume percent HVO (R100), which is also considered renewable hydrocarbon diesel (RHD), and also includes blends of HVO and petroleum diesel and/or biodiesel fuel. Such blended renewable diesel includes at least about 5 volume percent HVO (R5), at least about 10 volume percent (R10), at least about 30 volume percent HVO (R30), at least about 50 volume percent HVO (R70), at least about 70 volume percent HVO (R70), or greater levels of HVO blended with petroleum-based diesel. Thus, the base fuel compositions herein may be about 100 volume percent HVO or may be blends of about 5 volume percent to about 95 volume percent HVO with petroleum-based diesel or biodiesel (e.g., FAME) or a combination thereof.

[00062] The renewable diesel and fuel performance additives herein are suitable for use in various internal combustion systems or engines. The systems or engines may include both stationary engines (e.g., engines used in electrical power generation installations, in pumping stations, etc.) and ambulatory engines (e.g., engines used as prime movers in automobiles, trucks, road-grading equipment, military vehicles, etc.). By combustion system or engine herein is meant, internal combustion engines, for example and not by limitation, Atkinson cycle engines, rotary engines, spray guided, wall guided, combined wall/spray guided direct injection engines, and/or compression-ignition engines (e.g., diesel-fueled engines).

[00063] As used herein, the term "hydrocarbyl group" or "hydrocarbyl" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of a molecule and having a predominantly hydrocarbon character. Examples of hydrocarbyl groups include: (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical); (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of the description herein, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, amino, alkylamino, and sulfoxy); (3) hetero-substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this description, contain other than carbon in a ring or chain otherwise

composed of carbon atoms. Hetero-atoms include sulfur, oxygen, nitrogen, and encompass substituents such as pyridyl, furyl, thienyl, and imidazolyl. In general, no more than two, or as a further example, no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; in some embodiments, there will be no non-hydrocarbon substituent in the hydrocarbyl group.

[00064] The term "alkyl" as employed herein refers to straight, branched, cyclic, and/or substituted saturated chain moieties of from about 1 to about 100 carbon atoms. The term "alkenyl" as employed herein refers to straight, branched, cyclic, and/or substituted unsaturated chain moieties of from about 3 to about 10 carbon atoms. The term "aryl" as employed herein refers to single and multi-ring aromatic compounds that may include alkyl, alkenyl, alkylaryl, amino, hydroxyl, alkoxy, halo substituents, and/or heteroatoms including, but not limited to, nitrogen, oxygen, and sulfur.

[00065] As used herein and throughout this disclosure, the term "major amount" is understood to mean an amount greater than or equal to 50 weight percent, for example from about 80 to about 98 weight percent 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 weight percent relative to the total weight of the composition.

[00066] As used herein, the term "percent by weight" or "weight percent," unless expressly stated otherwise, means the percentage the recited component represents to the weight of the entire composition. The term "percent by volume" or "volume percent", unless expressly stated otherwise, means the percentage the recited component represents to the volume of the entire composition.

[00067] As used herein, the term "ppm" or "ppmw," unless expressly stated otherwise, refers to parts per million based on weight.

[00068] The molecular weight (MW) for any embodiment herein may be determined with a gel permeation chromatography (GPC) instrument obtained from Waters or the like instrument and the data was processed with Waters Empower Software or the like software. The GPC instrument may be equipped with a Waters Separations Module and Waters Refractive Index detector (or the like optional equipment). The GPC operating conditions may include a guard column, 4 Agilent PLgel columns (length of 300×7.5 mm; particle size of 5 μ, and pore size

ranging from 100-10000 Å) with the column temperature at about 40 °C. Unstabilized HPLC grade tetrahydrofuran (THF) may be used as solvent, at a flow rate of 1.0 mL/min. The GPC instrument may be calibrated with commercially available polystyrene (PS) standards having a narrow molecular weight distribution ranging from 500 – 380,000 g/mol. The calibration curve can be extrapolated for samples having a mass less than 500 g/mol. Samples and PS standards can be dissolved in THF and prepared at concentration of 0.1-0.5 wt. % and used without filtration. GPC measurements are also described in US 5,266,223, which is incorporated herein by reference. The GPC method additionally provides molecular weight distribution information; *see, for example*, W. W. Yau, J. J. Kirkland and D. D. Bly, “Modern Size Exclusion Liquid Chromatography”, John Wiley and Sons, New York, 1979, also incorporated herein by reference.

[00069] The polydispersity index (PDI) of the copolymer is a measure of the variation in size of the individual chains of the copolymer. The polydispersity index is determined by dividing the weight average molecular weight of the copolymer by the number average molecular weight of the copolymer. The term number average molecular weight (determined by, e.g., ¹H-NMR or GPC) is given its ordinary meaning in the art and is defined as the sum of the products of the weight of each polymer chain and the number of polymer chains having that weight, divided by the total number of polymer chains. The weight average molecular weight of the copolymer is given its ordinary meaning in the art and is defined as the sum of the products of the weight squared of each polymer chain and the total number of polymer chains having that weight, divided by the sum of the products of the weight of each polymer chain and the number of polymer chains having that weight.

EXAMPLES

[00070] A better understanding of the present disclosure and its many advantages may be clarified with the following example. The following examples are illustrative and not limiting thereof in either scope or spirit. Those skilled in the art will readily understand that variations of the components, methods, steps, and devices described in these examples can be used. Unless noted otherwise or apparent from the context of discussion in the Examples below and throughout this disclosure, all percentages, ratios, and parts noted in this disclosure are by weight. Any standardized test method noted in the Examples, disclosure, or claims, unless apparent from the context of its use, refers to the version of the test method publicly available at

the time of the filing of the present disclosure.

[00071] EXAMPLE 1

[00072] Demulsibility tests were conducted on comparative and inventive samples to
5 determine how readily the additive composition provided separation between water and
renewable diesel fuel. In this example, the renewable diesel fuel was either 100 volume percent
HVO or a blend of 30 volume percent HVO and 70 volume percent of petroleum-based diesel.
The fuel performance additive included a quaternary ammonium salt (prepared as described in
US 10,308,888, which is incorporated herein by reference) at different concentrations from 10%
10 by weight to 50% by weight on an active ingredient basis and then about 1% by weight of the
demulsifier additive noted in Table 1. The fuel performance additive was then top treated into
the HVO fuel composition or the 30 percent HVO blended fuel composition at a treat rate of
about 200 μ L in about 200 mL of either fuel. The demulsifier of this invention is commercially
available and can also be readily prepared according to the method described herein. It is nonyl
15 phenol formaldehyde resin alkoxylated with ethylene oxide and propylene oxide.

[00073] Table 1: Demulsifiers

Demulsifier	Demulsifier Type	Molecular Weight M _w (Da)	PDI	EO:PO:NP molar ratio from NMR	Polymer Concentration (w/w)
1	Alkoxylated alkyl phenol formaldehyde resin	20,110	2.31	20-30 : 60-70 : <8	80 - 90%
2	EO/PO block copolymer	3,800	NA	7 : 56	100%
3	Resin oxyalkylate	5,671	1.48	88: 0 : 12	70-90%
4	Resin oxyalkylate	8,587	1.88	0: 82 : 18	70-90%
5	Alkoxylated alkyl phenol formaldehyde resin, EO/PO block copolymer	10,895	1.45	28 : 69 : 3	14%
6	Alkoxylated alkyl phenol formaldehyde resin	6,170	1.6	26 : 64 : 10	75-95%

[00074] A Turbiscan Lab Stability Analyzer (manufactured by Microtrac Inc., formerly
Formulation Inc.) was used for emulsion stability analysis for this Example. This instrument
20 used static multiple light scattering (SMLS) at room temperature (e.g. about 20 to about 25°C),
and scans the height of the vial using laser light at an incident wavelength of about 880 nm, with
detectors for transmitted and backscattered light from the sample. For each evaluation, about 2
mL of pH 7 buffer (Fisher) and about 20 mL of either the 100 percent HVO or the 30 volume
percent HVO blend with fuel performance additive were added to a Turbiscan vial. Emulsions

were prepared by shaking for 5 minutes on high setting in a shaker (e.g., Eberbach, Model 6010 or equivalent), and then the vials were immediately transferred to the Turbiscan sample chamber. Turbiscan data was collected for 30 minutes, with one scan collected every 30 seconds. The Turbiscan software, Turbisoft Lab 3.0.2.0, was used for data analysis. Each system for the evaluations of this Example is provided in Table 2 below.

[00075] Table 2: Fuel Systems Evaluated

System	Demulsifer	Aqueous phase (2mL)	Fuel phase (20 mL)
A	1	pH7 Buffer	100% HVO
B	2	pH7 Buffer	100% HVO
C	3	pH7 Buffer	100% HVO
D	4	pH7 Buffer	100% HVO
E	5	pH7 Buffer	100% HVO
F	6	pH7 Buffer	100% HVO
G	1	pH7 Buffer	30% HVO
H	2	pH7 Buffer	30% HVO
I	3	pH7 Buffer	30% HVO
J	4	pH7 Buffer	30% HVO
K	5	pH7 Buffer	30% HVO
L	6	pH7 Buffer	30% HVO

[00076] After the fuel blend and aqueous buffer was shaken for 5 minutes in the Turbiscan vial, they form a water-in-fuel emulsion. The emulsion was stabilized by the quaternary ammonium salt in the fuel performance additive. Initially, larger water drops in the vial settled to the bottom due to gravity, leading to clearing of the fuel phase near the top of the vial indicated by an increase in transmitted light. As droplets settle and after they reach the bottom of the vial, they coalesce to form larger drops. While not wishing to be limited by theory, an oil film between droplets is believed to drain upwards, causing the larger coalesced water drops to phase separate at the bottom of the vial. This phase separation leads to an increase in transmitted light in the water phase. It is believed that the demulsifier of this invention aids in the phase separation of water at the bottom of the vial. Demulsifier molecules adsorb competitively to the water-fuel interface, displacing the surfactant molecules, and helping to lower the interfacial tension. This aids phase separation by lowering the interfacial energy of the fuel-water interface and driving oil film drainage, resulting in coalescence of water droplets in fuel. For example,

transmission data obtained from the Turbiscan for System A (Demulsifier 1 of the invention with 100% HVO) is shown in FIG. 1.

[00077] As indicated in FIG. 1, for System A containing Demulsifier 1 of the invention in 100% HVO, the water droplets which settled to the bottom of the vial phase (e.g., 0 to 3.5 mm) separate out rather rapidly (indicated by the significant increase in transmission with the first few minutes). This indicated that Demulsifier 1 of the invention was very effective in coalescing water droplets. In the upper fuel phase (greater than 3.5 mm), Demulsifier 1 of the invention showed a slight increase in transmission in the 30-minute period, indicating that while larger droplets settled, sub-micron sized droplets or water sequestered in micelles remain suspended in the fuel phase. As the goal was separation of water, the focus was the rapid increase in transmission at the bottom of the vial as shown in FIG. 1 between 0 and 3.5 mm.

[00078] The Comparative demulsifiers 2-6 did not achieve such phase separation or did not achieve rapid phase separation. For example, FIG. 2 shows the percent transmitted light for System B (e.g., Comparative demulsifier 2, 100% HVO) and FIG. 3 System E (e.g., Comparative demulsifier 5, 100% HVO). Comparative System B shows almost no transmission at the bottom of the vial, indicating that Comparative demulsifier 2 did not coalesce any of the water drops which settle to the bottom over the 30-minute period of the measurement. The settling did however result in an increase in transmission in the fuel phase. Comparative System E, which contained Comparative demulsifier 5, exhibited a gradual increase in transmission at the bottom of the vial indicating slow drainage of the fuel film between droplets, resulting in slow coalescence over the 30-minute period. However, at the end of 30 minutes, Comparative System E exhibited significant increase in transmission in the fuel phase, indicating that not many small droplets remain suspended in the fuel phase. The other Comparative demulsifier and fuel blends failed for similar reasons.

[00079] Figure 4 shows the mean percent transmission calculated over the bottom of the vial (e.g., 0 to 3.5 mm height range) as a function of time for Systems A-F (demulsifiers 1-6 in 100% HVO fuel). As shown in FIG. 4, it is evident that fuel performance additive including Demulsifier 1 of the invention drove rapid coalescence within about 5 minutes or less (or at least about 10 minutes or less) as indicated by the rapid increase in mean transmission at the bottom of the vial. Systems containing Comparative demulsifiers 2, 3, or 4 exhibited almost zero transmission in this height range over the entire 30-min period as shown in FIG. 4. Comparative

demulsifier 5 provided slow coalescence, resulting in significant increase in the clarity of the water phase at the end of 30 minutes. Comparative demulsifier 6 also provided slow coalescence. Only system A with Demulsifier 1 of the invention provided rapid coalescence (e.g., transmission of about 40 to about 50 percent in the bottom 3.5 mm of the vial in 10 minutes or less or about 5 minutes or less.)

[00080] Likewise, with 30 percent HVO as the fuel phase (R30), System G containing Demulsifier 1 of the invention demonstrated a similar rapid increase in transmission in the water phase as shown in Figure 5. This indicates that even at lower HVO volume fractions, Demulsifier 1 of the invention can rapidly coalesce the settled water droplets. Similar to the 100% HVO system, Demulsifier 1 of the invention leaves more droplets suspended in the fuel phase, resulting in lower transmission levels in the 4-42 mm height range at the top of the vial.

[00081] Figure 6 provides the percent transmission data for Comparative system K (e.g., Comparative demulsifier 5 in 30% HVO). Unlike the 100% HVO system, Comparative demulsifier 5 did not cause a large increase in transmission at the bottom of the vial, which means that it was not able to drain the 30% HVO fuel as effectively. While not wishing to be limited by theory, this may be attributed to the interaction of the solvent with the demulsifier molecules because 30% HVO contains more polar moieties than 100% HVO, which may potentially result in greater solubilization of the demulsifier molecules and degrade their ability to form a film or to adsorb at the fuel-water interface. As shown in Figure 7, with 30% HVO as the fuel phase, with the exception of Demulsifier 1 of the invention (e.g., System G), all other Comparative demulsifier systems H-L showed low mean transmission and poor coalescence ability in the desired 0 to 3.5 mm height range in the vial. Thus, the other Comparative demulsifier systems failed in the R30 blend for similar reasons.

[00082] This Example demonstrates that Demulsifier 1 of the invention drives coalescence of emulsified water droplets in both 100% HVO and 30% HVO blend fuels much faster than the other comparative demulsifiers tested using the 30-minute Turbiscan emulsion stability test. Demulsifier 1 of the invention is unique in that it has a high molecular weight and higher PDI as compared to other demulsifiers in this study combined with a selected composition of ethylene oxide moieties, propylene oxide moieties, and nonyl phenol moieties. While Comparative demulsifier 6 had a similar EO:PO:NP ratio as Demulsifier 1 of the invention, its molecular weight was much lower and therefore it performed poorly in the emulsion stability test.

Comparative demulsifiers 3 and 4 also performed extremely poorly in separating the water phase, even though they had a similar phenol backbone as demulsifier 1 of the invention also likely due to their low molecular weight. Comparative demulsifier 2 is neither a resin type demulsifier nor does it have a high molecular weight, and therefore also showed poor demulse
5 behavior. Comparative demulsifier 5 was an alkoxylated phenol formaldehyde resin having a EO:PO:NP ratio similar to that of the demulsifier 1 of the invention, but with a far lower molecular weight. Additionally, demulsifier 5 is believed to be a mixture of demulsifiers, and contains an EO:PO block copolymer in addition to other lower molecular weight components. Demulsifier 5 provided only slow demulsification in 100% HVO, but failed to coalesce water
10 droplets in 30% HVO. Therefore, only Demulsifier 1 of the invention, when used in R30 to R100 HVO fuels, was effective for rapid demulsification, which his believed to be attributed to one or more of a high molecular weight, an alkoxylated phenol formaldehyde resin-type demulsifier, a select EO:PO:NP ratio, and/or higher polydispersity index.

[00083] It is noted that, as used in this specification and the appended claims, the singular
15 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.

[00084] For the purposes of this specification and appended claims, unless otherwise
20 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
25 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.

[00085] It is to be understood that each component, compound, substituent or parameter
30 disclosed herein is to be interpreted as being disclosed for use alone or in combination with one or more of each and every other component, compound, substituent or parameter disclosed

herein.

[00086] It is further understood that each range disclosed herein is to be interpreted as a disclosure of each specific value within the disclosed range that has the same number of significant digits. Thus, for example, a range from 1 to 4 is to be interpreted as an express disclosure of the values 1, 2, 3 and 4 as well as any range of such values.

[00087] It is further understood that each lower limit of each range disclosed herein is to be interpreted as disclosed in combination with each upper limit of each range and each specific value within each range disclosed herein for the same component, compounds, substituent or parameter. Thus, this disclosure is to be interpreted as a disclosure of all ranges derived by combining each lower limit of each range with each upper limit of each range or with each specific value within each range, or by combining each upper limit of each range with each specific value within each range. That is, it is also further understood that any range between the endpoint values within the broad range is also disclosed herein. Thus, a range from 1 to 4 also means a range from 1 to 3, 1 to 2, 2 to 4, 2 to 3, and so forth.

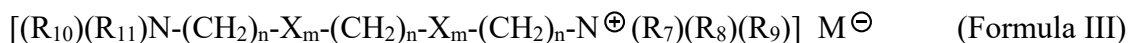
[00088] Furthermore, specific amounts/values of a component, compound, substituent or parameter disclosed in the description or an example is to be interpreted as a disclosure of either a lower or an upper limit of a range and thus can be combined with any other lower or upper limit of a range or specific amount/value for the same component, compound, substituent or parameter disclosed elsewhere in the application to form a range for that component, compound, substituent or parameter.

[00089] 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.

CLAIMS

What is claimed is:

1. A fuel performance additive composition for fuels including hydrogenated vegetable oil, the fuel performance additive comprising:
- a quaternary ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent;
- a demulsifying agent including an alkoxyated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxyated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived moieties, and about 0.1 to about 15 mole percent of nonyl phenol derived moieties; and
- an organic carrier solvent.
2. The fuel performance additive composition of claim 1, wherein the alkoxyated alkyl phenol formaldehyde resin has a polydispersity index of about 2.0 to about 4.0; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has a weight average molecular weight of about 13,000 g/mol to about 30,000 g/mol; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has about 20 to about 30 mol percent of ethylene oxide derived moieties, about 60 to about 70 mol percent of propylene oxide derived moieties, and about 0.1 to about 8 mol percent of nonyl phenol derived moieties; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has a relative solubility number (RSN) of about 10 to about 12.
3. The fuel performance additive composition of claim 1, wherein the organic carrier solvent includes xylene, ethyl benzene, or a combination thereof.
4. The fuel performance additive composition of claim 1, wherein the quaternary ammonium salt has a structure of Formula III



wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R₁₂)-, -C(O)-, -C(O)O-, or -C(O)NR₁₂; each R₇, R₈, and R₉ is independently an alkyl group containing 1 to 8 carbon atoms; R₁₀ and R₁₁ are independently selected from an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R₁₀ and R₁₁ has a number average molecular weight of about 700 or greater; R₁₂ is independently a hydrogen atom or a group selected from C₁₋₆ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and M[⊖] is a carboxylate.

5. The fuel performance additive composition of claim 4, wherein the carboxylate of Formula III is oxalate, salicylate, or combinations thereof, and X of Formula III is -O- or -NH-; and or wherein the quaternary ammonium salt of Formula III is derived from 3-(2-(dimethylamino)ethoxy)propylamine, N,N-dimethyl dipropylenetriamine, or mixtures thereof; and or wherein R₁₀ and R₁₁ of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide; and or wherein X is an oxygen atom and wherein R₁₀ and R₁₁ of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide with the hydrocarbyl substituent having a number average molecular weight of about 700 to about 1,500 as measured by GPC using polystyrene as a calibration reference.

6. The fuel performance additive composition of claim 1, wherein the fuel performance additive comprises about 10 to about 50 weight percent of the quaternary ammonium salt and about 0.1 to about 1 % by mass of the demulsifying agent.

7. The fuel performance additive composition of claim 6, further having a weight ratio of the quaternary ammonium salt to the demulsifying agent of about 2:1 to about 100:1.

8. A renewable diesel comprising:
a major amount of a renewable diesel including hydrogenated vegetable oil and a minor amount of a fuel performance additive;

a quaternary ammonium salt obtained from the reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent;

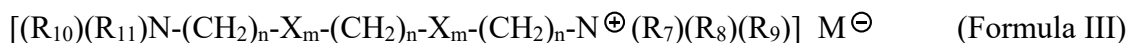
a demulsifying agent including an alkoxyated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxyated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived moieties, and about 0.1 to about 15 mol percent of the nonyl phenol derived moieties.

9. The renewable diesel of claim 8, wherein the renewable diesel includes 0 to 80 volume percent petroleum diesel, biodiesel, or combination thereof and 20 to 100 volume percent hydrogenated vegetable oil.

10. The renewable diesel of claim 8, wherein the renewable diesel includes about 10 to about 450 ppmw of the quaternary ammonium salt and about 0.1 to about 100 ppmw of the demulsifying agent.

11. The renewable diesel of claim 8, wherein the alkoxyated alkyl phenol formaldehyde resin has a polydispersity index of about 2.0 to about 4.0; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has a weight average molecular weight of about 13,000 g/mol to about 30,000 g/mol; and/or wherein the alkoxyated alkyl phenol formaldehyde resin has about 20 to about 30 mol percent of ethylene oxide derived moieties, about 60 to about 70 mol percent of propylene oxide derived moieties, and about 0.1 to about 8 mol percent of nonyl phenol derived moieties.

12. The renewable diesel of claim 8, wherein the quaternary ammonium salt has a structure of Formula I



wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R₁₂)-, -C(O)-, -C(O)O-, or -C(O)NR₁₂; each R₇, R₈, and R₉ is independently an alkyl group containing 1 to 8 carbon atoms; R₁₀ and R₁₁ are independently selected from an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R₁₀ and R₁₁ has

a number average molecular weight of about 700 or greater; R_{12} is independently a hydrogen atom or a group selected from C_{1-6} aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate.

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13. The renewable diesel of claim 12, wherein the carboxylate of Formula III is oxalate, salicylate, or combinations thereof, and X of Formula III is $-O-$ or $-NH-$; and/or wherein the quaternary ammonium salt of Formula III is derived from 3-(2-(dimethylamino)ethoxy) propylamine, N,N -dimethyl dipropylenetriamine, or mixtures thereof; and/or wherein R_{10} and
10 R_{11} of Formula III, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide.

14. The renewable diesel of claim 8, further having a weight ratio of the quaternary ammonium salt to the demulsifying agent of about 2:1 to about 100:1.

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15. A method of improving the demulsibility of an additive-containing renewable diesel, the method comprising:
combining a major amount of a renewable diesel including hydrogenated vegetable oil with a fuel performance additive including (i) a quaternary ammonium salt obtained from the
20 reaction of a nitrogen containing compound having at least a tertiary amino group and a quaternizing agent; (ii) a demulsifying agent including an alkoxyated alkyl phenol formaldehyde resin having a weight average molecular weight of at least about 13,000 g/mol, wherein the alkoxyated alkyl phenol formaldehyde resin includes about 20 to about 45 mol percent of
ethylene oxide derived moieties, about 55 to about 80 mol percent of propylene oxide derived
25 moieties, and about 0.1 to about 15 mol percent of the nonyl phenol derived moieties; and (iii) an organic carrier solvent.