EMULSIFIED FUEL COMPOSITIONS PREPARED EMPLOYING EMULSIFIER DERIVED FROM HIGH POLYDISPERSITY OLEFIN POLYMERS

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ABSTRACT

A water blended fuel composition comprising water, a normally liquid fuel and an emulsifying amount of at least one of a hydrocarbyl-substituted acylating agent and the reaction product of said hydrocarbyl-substituted acylating agent and an amine, an alcohol, a metal, reactive metal compound or a mixture of two or more thereof, wherein the hydrocarbyl substituent is a polymerized olefin having a polydispersity M_n/M_w greater than 5. Such polyolefin substituents can be prepared by polymerization of olefins in the presence of a calcined catalyst comprising a partially or fully neutralized ammonium salt of a heteropolyacid.

Related U.S. Application Data

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BACKGROUND OF THE INVENTION

The present invention relates to emulsified water-blended fuel compositions, more particularly to water-blended fuel compositions containing a liquid fuel, water, an emulsifier and optionally, at least one of a cosurfactant, combustion modifier, an organic cetane improver and an antifreeze.

Internal combustion engines, especially diesel engines, using a mixture of water and fuel in the combustion chamber can produce lower nitrogen oxides (NO\textsubscript{x}), hydrocarbon and particulate emissions per unit of power output. Water is inert toward combustion, but acts to lower peak combustion temperatures which results in less NO\textsubscript{x} formation. Exhaust Gas Recirculation (EGR) works on the same principle (i.e., inert materials tend to lower peak combustion temperatures and hence reduce NO\textsubscript{x}). Water can be separately injected into the cylinder, but hardware costs are high. Water can also be added to the fuel as an emulsion. However, emulsion stability has historically been a problem.

It would be advantageous to provide a water-blended fuel composition that has improved emulsion stability. It would also be advantageous to provide water-blended fuel compositions comprising a reduced chlorine content or chlorine-free emulsifier composition. The present invention provides such advantages.

U.S. Pat. No. 5,669,938, Schwab, Sep. 23, 1997, discloses a fuel composition which consists of (i) a water-in-oil emulsion comprising a major proportion of a hydrocarbonaceous middle distillate fuel and about 1 to 40 volume percent water, (ii) a CO emission, and particulate matter emission reducing amount of at least one fuel-soluble organic nitrate ignition improver, and optionally containing (iii) at least one component selected from the group consisting of di-hydrocarboxyl peroxides, surfactants, dispersants, organic peroxy esters, corrosion inhibitors, antioxidants, antirust agents, detergents, lubricity agents, demulsifiers, dyes, inert diluents, and a cyclopentadienyl manganese tricarbonyl compound.

European Patent EP 0 475 620 B1, Sexton et al., Aug. 11, 1995, discloses a diesel fuel composition which comprises: (a) a diesel fuel; (b) 1.0 to 30.0 weight percent of water based upon said diesel fuel; (c) a cetane number improver additive, present in an amount up to, but less than, 20.0 weight percent based upon said water, said additive being selected from an inorganic oxidizer, a polar organic oxidizer and a nitrogen oxide-containing compound; and (d) 0.5 to 15.0 wt. % based on the diesel fuel of a surfactant system comprising (i) one or more first surfactants selected from surfactants capable of forming a lower phase microemulsion at 20° C. when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said surfactant being an ethoxylated C\textsubscript{12-18} alkyl ammonium salt of C\textsubscript{3-22} alkyl carboxylic or alkylaryl sulfonic acid containing 6 or more ethylene oxide groups; and (ii) one or more second surfactants selected from surfactants capable of forming an upper phase microemulsion at 20° C. when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said surfactant being an ethoxylated C\textsubscript{12-18} alkyl ammonium salt of C\textsubscript{3-22} alkyl carboxylic or alkylaryl sulfonic acid containing less than 6 ethylene oxide groups; the said first and second surfactants being present in a weight ratio which forms with components (a), (b) and (c) a single phase translucent microemulsion.

European patent publication EP 0 561 600 A2, Jahnke, Sep. 22, 1993, discloses a water in oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-supplying component (such as ammonium nitrate); a continuous organic phase comprising at least one carbonaceous fuel; and a minor emulsifying amount of at least one emulsifier made by the reaction of:

(A) at least one substituted succinic acylating agent, said substituted acylating agent consisting of substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene, said acylating agents being characterized by the presence within their structure of an average of at least 1.3 succinic groups for each equivalent weight of substituent groups, and

(B) ammonia and/or at least one amine.

U.S. Pat. No. 5,047,175, Forsberg, Sep. 10, 1991, discloses salt compositions which comprise: (A) at least one salt moiety derived from (A)(I) at least one high-molecular weight polycarboxylic acylating agent, said acylating agent (A)(I) having at least one hydrocarboxyl substituent having an average of from about 20 to about 500 carbon atoms, and (A)(II) ammonium, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; (B) at least one salt moiety derived from (B)(I) at least one low-molecular weight polycarboxylic acylating agent, said acylating agent (B)(I) optionally having at least one hydrocarboxyl substituent having an average of up to about 18 carbon atoms, and (B)(II) ammonium, at least one amine, at least one alkali or alkaline earth metal, and/or at least one alkali or alkaline earth metal compound; said components (A) and (B) being coupled together by (C) at least one compound having (i) two or more primary amino groups, (ii) two or more secondary amino groups, (iii) at least one primary amino group and at least one secondary amino group, (iv) at least two hydroxyl groups or (v) at least one primary or secondary amino group and at least one hydroxyl group. These salt compositions are disclosed to be useful as emulsifiers in water-in-oil explosive emulsions, particularly cap-sensitive water-in-oil emulsions.

U.S. Pat. No. 4,708,753, Forsberg, Nov. 24, 1987, discloses a water-in-oil emulsion comprising (A) a continuous oil phase; (B) a discontinuous aqueous phase; (C) a minor emulsifying amount of at least one salt derived from (C)(I) at least one hydrocarboxyl-substituted carboxylic acid or anhydride, or ester or amide derivative of said acid or anhydride, the hydrocarboxyl substituent of (C)(I) having an average of from about 20 to about 500 carbon atoms, and (C)(II) at least one amine; and (D) a functional amount of at least one water-soluble, oil-insoluble functional additive dissolved in said aqueous phase, with the proviso that when component (D) is ammonium nitrate, component (C) is other
than an ester/salt formed by the reaction of polyisobutyl (M<sub>ω</sub>=950) succinic anhydride with diethanolamine in a ratio of one equivalent of anhydride to one equivalent of amine.

[0011] U.S. Pat. No. 3,756,794, Ford, Sep. 4, 1973, discloses an emulsified fuel composition consisting essentially of (1) a major amount of a hydrocarbon fuel boiling in the range of 20-400° C. as the disperse phase, (2) 0.3% to 5% by weight of an emulsifier, (3) 0.75% to 12% by weight water, (4) 0.3% to 0.7% by weight of urea as emulsion stabilizer and (5) 0.3% to 0.7% by weight of ammonium nitrate.

[0012] PCT Patent Publication WO 00/15740 describes an emulsified water-blended fuel composition comprising: (A) a hydrocarbon boiling in the gasoline or diesel range; (B) water; (C) a minor emulsifying amount of at least one fuel-soluble salt made by reacting (C)(I) at least one acylating agent having about 16 to 50 carbon atoms with (C)(II) ammonia and/or at least one amine; and (D) about 0.001 to about 15% by weight of the water-blended fuel composition of a water-soluble, ashless, halogen-, boron-, and phosphorus-free amine salt, distinct from component (C). In one embodiment, the composition further comprises (E) at least one cosurfactant distinct from component (C), in one embodiment, at least one organic cetane improver; and in one embodiment, (G) at least one antifreeze.

[0013] PCT Patent Publication WO 01/00688 describes dispersants for lubricants which are the reaction product of an amine, an alcohol, or a mixture of two or more of two or more thereof, and a hydrocarbyl-substituted acetylating agent, wherein the hydrocarbyl substituent comprises at least one polymerized olefin, the resulting polyolefin having M<sub>n</sub>/M<sub>w</sub> of greater than 4 or 5, preferably 6 or 7.5 to 20. The polyolefin preferably has M<sub>n</sub> of at least 1500, and preferably at least 30% terminal vinylidene (I) groups.

[0014] Polyolefins have been prepared by heteropolyacid catalyzed polymerization of olefinic compounds. U.S. Pat. No. 5,710,225, Johnson et al., Jan. 20, 1998, discloses a method for producing polymers by polymerization of olefins, by contacting a C<sub>2</sub>-C<sub>50</sub> olefin or a derivative thereof with a heteropolyacid. The heteropolyacid catalyst can be partially or fully exchanged with cations from the elements in groups IA, IIA and IIIA of the periodic chart, Group IB-VIIIB elements and Group VIII metals, including manganese, iron, cobalt, nickel, copper, silver, zinc, boron, aluminum, bismuth, or ammonium or hydrocarbyl-substituted ammonium salt. The heteropolyacids can be used in their initial hydrated form or they can be treated (calcined) to remove some or all of the water of hydration. Calcining is preferably conducted in air at a temperature of, for instance, up to 500° C. although temperatures much over 350° C. generally do not provide much advantage. In the resulting polymers, the combined terminal vinylidene and β-isomer content is preferably at least 30%.

[0015] It is often desirable to use highly reactive polyolefins to prepare hydrocarbyl-substituted acetylating agents (e.g., anhydrides) by way of a thermal route rather than a chlorine catalyzed route. The thermal route involves simply conducting the reaction at an elevated temperature without the use of an added catalyst or promoter. The thermal route avoids products containing chlorine. The reactivity of the polyolefin is believed to be related to the end group in the polymer with terminal olefins (terminal vinylidene) and terminal groups capable of being isomerized thereto, β-isomers, being identified as the reactive species.

[0016] The thermal route to substituted succinic anhydrides using highly reactive polyisobutenes (PIBs) has been discussed in detail in U.S. Pat. Nos. 5,071,919, 5,137,978, 5,137,980 and 5,241,003.

[0017] Conventional PIB has terminal vinylidene content of roughly 5%. The terminal isomer groups of conventional PIB and high vinylidene PIB are given in EP 0,355 895 and in the aforementioned PCT Patent Publication WO 01/00688. High vinylidene materials can contain at least 30 percent terminal vinylidene and β-isomer groups. In preferred cases the polyisobutylene can contain at least 50 percent terminal vinylidene groups, and more preferably at least 60 percent terminal vinylidene groups.

**SUMMARY OF THE INVENTION**

[0018] The present invention provides an emulsified water-blended fuel composition comprising:

- [0019] (A) a liquid hydrocarbon based fuel;
- [0020] (B) water; and
- [0021] (C) a minor emulsifying amount of at least one of a fuel-soluble hydrocarbyl-substituted carboxylic acylating agent and a reaction product of said acylating agent and at least one of ammonia, an amine, an alcohol, a reactive metal, a reactive metal compound and a mixture of two or more thereof, wherein the hydrocarbyl substituent comprises at least one polyolefin, said polyolefin having M<sub>n</sub>/M<sub>w</sub> of greater than 5.

[0022] In one embodiment, the composition further comprises (D) at least one cosurfactant distinct from component (C); in one embodiment, (E) at least one organic cetane improver; and in one embodiment, (F) at least one antifreeze. In another embodiment, the composition further comprises (G) a water-soluble, ashless (i.e. metal-free), halogen-, boron-, and phosphorus-free amine salt, distinct from component (C). The invention also relates to a method for operating an internal combustion engine comprising fueling said engine with the composition of the present invention.

**DETAILED DESCRIPTION OF THE INVENTION**

[0023] The Normally Liquid Hydrocarbon Based Fuel (A)

[0024] The fuels of this invention include all normally liquid hydrocarbon based fuels known in the art. By ‘normally liquid’ is meant a fuel which is liquid or liquefiable at normal operating temperatures. For the purposes of this invention, ‘hydrocarbon based’ fuels are fuels containing hydrocarbon moieties. These fuels may be purely hydrocarbon fuels. These fuels may also be hydrocarbon moieties containing fuels further containing moieties other than hydrocarbon moieties. Included are liquid fuels derived from animal, vegetable mineral sources. The fuels also may comprise mixtures of any of these fuels.

[0025] These fuels include gasoline meeting ASTM Specification D-4814 (formerly ASTM Specification D-439, now discontinued), diesel fuel meeting ASTM Specification
D-975, heating oil meeting ASTM Specification D-396, oxygenates, mixtures of predominantly hydrocarbon fuels and oxygenates, biomass fuel, and synthetic fuels.

[0026] Purely hydrocarbon fuels may be any and all hydrocarbonaceous distillate fuels. These include, but are not necessarily limited to heavy hydrocarbon fuels, hydrocarbons boiling in the gasoline range and middle distillate oils, for example, diesel oil and heating oils, kerosene, naphtha, synthetic hydrocarbon fuels such as polyolefins, alkylated aromatic hydrocarbon containing fuels, hydrocarbon fuels obtained by the Fischer-Tropsch process, and others. Fuels derived from mineral sources such as coal and shale are contemplated. Further gas to liquid fuels are included herein.

[0027] Hydrocarbon group containing fuels further containing groups other than hydrocarbon groups include, but not limited to, alcohols such as methanol, ethanol and the like, ethers such as diethyl ether, methyl ethyl ether and the like, organo nitro compounds, esters, such as fatty acid esters, particularly those derived from vegetable sources such as corn and alfalfa, and the like.

[0028] Biomass fuels are derived from organic materials, such as seeds. Processes for obtaining these oils from biomass are described in numerous U.S. patents, many of which are listed in U.S. Pat. No. 6,166,231 which is hereby incorporated herein by reference for relevant disclosures of such oils and methods for obtaining them. Examples of biomass fuels are vegetable oil, for example, sunflower oil and rapeseed oils.

[0029] The diesel fuels that are useful with this invention can be any diesel fuel or fuel oil. They include those that are defined by ASTM Specification D396. In one embodiment the diesel fuel has a sulfur content of up to 0.05% by weight (low-sulfur diesel fuel) as determined by the test method specified in ASTM D2622-87 entitled “Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry.” Any fuel having a boiling range and viscosity suitable for use in a diesel-type engine can be used. These fuels typically have a 90% point distillation temperature in the range of about 300°C to about 390°C, and in one embodiment about 330°C to about 350°C. The viscosity for these fuels typically ranges from about 1.3 to about 24 centistokes at 40°C. These diesel fuels can be classified as any of Grade Nos. 1-D, 2-D or 4-D as specified in ASTM D 975 entitled “Standard Specification for Diesel Fuel Oils”.

[0030] Useful diesel fuels include mineral oil derived fuels and biomass derived fuels, such as vegetable oils. Diesel fuels can contain alcohols and esters.

[0031] Mixtures of hydrocarbon based fuels and oxygenates include mixtures of any of the aforementioned hydrocarbon based fuels with any of alkanols, especially lower alkanols, and ethers, for example, methyl-t-butyl ether, methyl-t-amyl ether, dimethoxymethylene and diethoxymethylene, and particularly, lower alkanols such as ethanol. The well known ‘gasohol’ blend of gasoline and ethanol is one example.

[0032] The normally liquid hydrocarbon based fuel is generally present at a level ranging from about 50% to about 99% by weight of the water blended fuel composition, more often from about 60% to about 90%, often to about 80% by weight.

[0033] Water (B)

[0034] Water is present in amounts ranging from about 1% to about 50% by weight of the water blended fuel composition.

[0035] The Emulsifier (C)

[0036] The emulsifying agents of the present invention comprise an emulsifying amount of at least one of a fuel-soluble hydrocarbyl-substituted carboxylic acylating agent and a reaction product of said acylating agent with at least one of ammonia, an amine, an alcohol, a reactive metal, a reactive metal compound or a mixture of two or more thereof, wherein the hydrocarbyl substituent comprises a group derived from at least one polyolefin, said polyolefin having Mw/Mn greater than 5.

[0037] The hydrocarbyl substituted acylating agents have a hydrocarbyl group substituent that is derived from a polyolefin, with polydispersity and other features as described below. Generally it has a number average molecular weight of at least 600, 700, or 800, to 5000 or more, often up to 1200, 1300, 1600, 2500 or 3000. Typically, less than 5% by weight of the polyolefin molecules have Mn less than 250, more often the polyolefin has Mn of at least 800. The polyolefin preferably contains at least about 30% terminal vinylidene groups, more often at least 60% and more preferably at least 75% or 85% terminal vinylidene groups. The polyolefin has polydispersity, Mn/Mw greater than about 5, more often from about 6 to about 20. The hydrocarbyl group is typically derived from a polyolefin or a polymerizable derivative thereof, including homopolymers and interpolymerizations of olefin monomers having 2 to 30, to 6, or to 4 carbon atoms, and mixtures thereof. In a preferred embodiment the polyolefin is polyisobutene. Such polyolefins are prepared by the methods set forth in greater detail herein.

[0038] The emulsifier, component (C), is present at a level ranging from about 0.005 to about 15% by weight of the water blended fuel composition.

[0039] Suitable olefin polymer hydrocarbyl groups, having suitable polydispersity, can be prepared by heteropoly-acid catalyzed polymerization of olefins under certain conditions. Preparation of polyolefins under such conditions is also described in PCT Publication WO 01/00694.

[0040] Heteropolyacids are well known materials. Such catalysts can exist as the free acid or as a salt of a heteropolyanion. Heteropolyanions are polymeric oxoanions formed by a condensation reaction of two or more different oxoanions, e.g.,

\[ \text{H}_2\text{WO}_6^2- + \text{HPO}_4^{2-} + 2\text{H}^+ \rightarrow (\text{PW}_{12}\text{O}_{40})^{5-} + 12\text{H}_2\text{O} \]

[0041] A variety of structures are known for these materials; they can have, for instance, the so-called Keggin structure, wherein twelve WO_6 octahedral surround a central PO_4 tetrahedron (in the case where phosphorus is employed). Other structures and related formulas are also known, including PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, PW_{18}O_{42}, where P and W are taken as representative elements and the indicated structure is an ion with the appropriate charge. The central atom of the Keggin structure, which is typically phosphorus, can be, as shown, can also be any of the Group IIIA to Group VIIA (ACS numbering) non-transition metals, including P, As, Sb, Ge, B, Al, Sn, and Te. The tungsten (W)
in the above formula fills the role known as the “poly atom,” which can be any of the Group VB or VIB transition metals, including W, V, Cr, Nb, Mo, or Ta. Thus suitable materials include preferably phosphomolybdates, phosphotungstates, silicomolybdates, and silicotungstates. Other combinations selected from among the above elements are also possible, including borotungstates, titanotungstates, stannotungstates, arsenomolybdates, teluromonobdates, aluminomolybdates, and phosphovanadyltungstates, the latter representing a mixed material having a formula (for the anion portion) of P\textsubscript{2}W\textsubscript{6}O\textsubscript{19}. The preferred material is a phosphotungstate, which term generally encompasses both the acid and the various salts, described below.

The heteropoly catalysts are active both as their acid form, in which the anion is associated with the corresponding number of hydrogen ions, in the fully salt form, in which the hydrogen ions have been replaced by other cations such as metal ions, or in the partially exchanged salt form, in which a portion of the hydrogen ions have been thus replaced. For more detailed information on the structures of heteropoly catalysts, attention is directed to Misono, “Heterogeneous Catalysis by Heteropoly Compounds of Molybdenum and Tungsten,” Catal. Rev.—Sci. Eng., 29(2&3), 269-321 (1987), in particular, pages 270-277 and 278-280. In the present invention, the hydrogen ions have been partially or fully replaced by ammonium, that is the catalyst is a partially or fully neutralized ammonium salt of a heteropolyacid. Moreover, the catalyst has been calcined at about 300°C to about 500°C.

Heteropoly acids are commercially available materials, (e.g., Aldrich Chemical Company, #22,420-0). The salts are similarly commercially available, including most notably ammonium and cesium salts. Alternatively, they can be prepared from the acid materials by neutralization with an appropriate amount of base. Heteropoly acids are generally received in a hydrated form. They can be successfully employed in this form (uncalcined) or as in the present invention, they can be treated (calcined) to remove some or all of the water of hydration, that is, to provide a dehydrated or otherwise modified species, which in the context of the present invention exhibits improved reactivity. Calcining can be conducted by simply heating the hydrated material to a suitable temperature to drive off the desired amount of water. The heating can be under ambient pressure or reduced pressure, or it can be under a flow of air or an inert gas such as nitrogen. The use of air ensures that the acid is in a high oxidation state. The flow of air can be across the surface of the catalyst, or for greater efficiency, it can be through the bulk of the catalyst. The length of time required for calcining is related to the equipment and scale, but in one broad embodiment the calcining can be conducted over the course of 5 minutes to 16 hours, more typically 30 minutes to 8 hours, and preferably 1 hour, 2 hours or even 3 hours, up to 4 hours. The upper limits of time are defined largely by the economics of the process; times in excess of about 5 hours do not generally provide much advantage.

The material which is calcined to prepare the catalysts useful for preparing polymers for use in the present invention is preferably an ammonium salt of H\textsubscript{3}P\textsubscript{2}W\textsubscript{12}O\textsubscript{40}. Said heteropolyacid preferably comprises a material represented by the formula (NH\textsubscript{4})\textsubscript{n}H\textsubscript{3-n}P\textsubscript{2}W\textsubscript{12}O\textsubscript{40} wherein, before calcining, n is 2.5 or where n is 3, or mixtures thereof and after calcining, n ranges from about 1.9 to less than 3.

Typical ammonium salts include (NH\textsubscript{4})\textsubscript{5}P\textsubscript{2}W\textsubscript{12}O\textsubscript{40} and (NH\textsubscript{4})\textsubscript{2}H\textsubscript{8}P\textsubscript{2}W\textsubscript{12}O\textsubscript{40}. Each of these materials, as well as mixtures these species, are suitable. While generally the temperature of calcining will be in the range of above 300°C to 500°C and preferably 375 to 475°C, the optimum conditions will depend on some extent on the particular ammonium salt which is selected. When the starting salt is (NH\textsubscript{4})\textsubscript{5}P\textsubscript{2}W\textsubscript{12}O\textsubscript{40}, it has been found that relatively higher temperatures are desirable for obtaining the most active catalyst. Therefore, such material is preferably calcined at 450 to 475°C. When the starting salt is (NH\textsubscript{4})\textsubscript{2}H\textsubscript{8}P\textsubscript{2}W\textsubscript{12}O\textsubscript{40}, desirable calcining temperatures can be somewhat lower, namely, above 300 to 475°C and preferably above 375 to 475°C. When the calcining temperature is too low, the catalysts may be largely or entirely inactive. This phenomenon is not fully understood, but, without intending to limit the generality or scope of the invention, it is believed that the high temperature calcining serves to remove a portion of the ammonia from the catalyst, thereby leading to a more active species. The time and temperature of the calcining are believed to be interrelated to some extent, so that use of temperatures in the lower ranges can be more effective when the calcining is conducted for a longer period of time, and vice versa, as will be apparent to the person skilled in the art.

The catalyst can be employed as particles of the pure salt, or it can be provided on a solid support of an inert material such as alumina, silica/alumina, an aluminoaphosphate, a zeolite, a carbonyl, or, preferably, silica. The source of the solid silica support can be a colloidal silica, which is subsequently precipitated during the catalyst preparation, or a silica which has already been preformed into a solid material. The catalyst can be coated onto the support by well-known catalyst impregnation techniques, e.g., by applying the catalysts as a solution, followed by drying, such as by spray drying or evaporation. If a support such as silica is employed, the ratio of the active catalyst component to the silica support will preferably be in the range of 0.5:99.5 to 50:50 by weight, preferably 3:97 to 40:60 by weight, and more preferably 10:90 to 30:70 by weight.

Temperatures used for the polymerization of olefins suitable for the present invention are preferably below 20°C and more preferably below 10°C. Preferred temperature ranges are −30 to 20°C, more preferably −20 to 10°C, and most preferably about −5°C, which is the approximate reflux temperature of isobutylene. The polymerization can be conducted in a batch apparatus or using continuous apparatus, such as a continuous stirred tank reactor or a tubular reactor, as will be apparent to those skilled in the art. The residence time of the polymerization reaction will vary with conditions including the type of reactor, generally suitable residence times being from 5 or 10 to 60 minutes, preferably 20 to 40 minutes. The polymerization can be conducted neat but is preferably conducted in the presence of a substantially inert hydrocarbon solvent or diluent, such as isobutane, pentane, hexane, octane, decane, kerosene, or Stoddard Solvent, which will normally be removed by conventional means at the conclusion of the reaction. The reaction using the catalysts of the present invention will generally provide at least a 10% conversion under these conditions, and preferably at least 20 or 25% conversion to polymer. More preferably, the batch and continuous process is conducted to about 50-60% conversion of monomer.
As noted hereinafore, the preferred polymers useful in preparing the acylating agents are polyisobutenes having $M_n$ greater than 500. For the $C_4$ isobutylene, this would correspond to an average degree of polymerization (dp) of about 8.8. The preferred $M_n$ of polyisobutylene is at least 500 and preferably at least 1000 or even higher, preferably in the range of 2000 to 5000 or greater. It is also generally preferred that the polymers (whether polyisobutenes or other polyolefins) do not have an extensive low molecular weight fraction. That is, preferably they should comprise less than 10%, 5%, or 3% by weight of a fraction having a number average molecular weight of less than 350, 500, or 800 units.

Such materials are particularly useful when used in reactions to alkylate maleic anhydride. As well as isobutylene, other $C_3$-$C_{10}$ olefins and derivatives thereof may be used in this invention as well as styrene and derivatives thereof, conjugated dienes such as butadiene and isoprene and non-conjugated polyenes. The reaction to produce polymers may be run with mixtures of starting olefins to form copolymers. The mole ratio of olefin substrate to catalyst in this invention ranges from 1,000:1 to 100,000:1.

Useful polymers produced by the process of this invention are derived from $C_2$-$C_{10}$ olefin monomers and mixtures thereof and derivatives thereof. Under this terminology, styrene and derivatives would be a $C_2$-olefin substituted by a phenyl group.

Useful olefin monomers from which the polyolefins used in the present invention can be derived are polymerizable olefin monomers characterized by the presence of one or more unsaturated double bonds (i.e., $>C=CH$), that is, they are monolefinic monomers such as ethylene, propylene, butene-1, isobutylene, and octene-1 or polyolefinic monomers (usually diolefinic monomers) such as butadiene-1,3 and isoprene.

These olefin monomers are preferably polymerizable terminal olefins; that is, olefins characterized by the presence in its structure of the group $R^1-CH=CH_2$, where $R^1$ is a hydrocarbyl group. However, polymerizable internal olefin monomers (sometimes referred to as medial olefins) characterized by the presence within their structure of the group:

\[CH=C(CH_3)\]

can also be used to form the polyolefins. When internal olefin monomers are employed, they will normally be employed with terminal olefins to produce polyolefins which are interpolymers. For purposes of this invention, when a particular polymerized olefin monomer can be classified as both a terminal olefin and an internal olefin, it will be deemed to be a terminal olefin. Thus, for example, pentadiene-1,3 (i.e., piperylene) is deemed to be a terminal olefin for purposes of this invention.

While the polyolefins used in the present invention generally are hydrocarbon polyolefins, they can contain substituted hydrocarbon groups such as lower alkoxy, and carbonyl, provided the non-hydrocarbon moieties do not substantially interfere with the functionalization reactions of this invention. Preferably, such substituted hydrocarbon groups normally will not contribute more than 10% by weight of the total weight of the polyolefins. Since the polyolefin can contain such non-hydrocarbon substituents, it is apparent that the olefin monomers from which the polyolefins are made can also contain such substituents. Normally, however, as a matter of practicality and expense, the olefin monomers and the polyolefins will be free from non-hydrocarbon groups.

Although the polyolefins useful in the invention may include aromatic groups (especially phenyl groups and lower alkyl- and/or lower alkoxy-substituted phenyl groups such as para-(tert-butyl)phenyl) and cycloaliphatic groups such as would be obtained from polymerizable cyclic olefins or cycloaliphatic substituted-polymerizable acrylic olefins, the polyolefins usually will be free from such groups. Again, because aromatic and cycloaliphatic groups can be present, the olefin monomers from which the polyolefins are prepared can contain aromatic and cycloaliphatic groups.

There is a general preference for polyolefins which are derived from the group consisting of homopolymers and interpolymers of terminal hydrogen olefins of 2 to 16 carbon atoms. A more preferably class of polyolefins are those selected from the group consisting of homopolymers and interpolymers of terminal olefins of 2 to 6 carbon atoms, more preferably 2 to 4 carbon atoms, and especially 4 carbon atoms, most preferably, isobutylene.

Specific examples of terminal and internal olefin monomers which can be used to prepare the polyolefins of this invention include propylene; butene-1; butene-2; isobutylene; pentene-1; hexene-1; heptene-1; octene-1; nonene-1; decene-1; pentene-2; propylene-1-trimer; diisobutylene; isobutylene trimer; butadiene-1,2; butadiene-1,3; pentadiene-1,2; pentadiene-1,3; isoprene; hexadiene-1,5; 2-chlorobutadiene-1,2; 2-methylheptene-1; 3-cyclohexylbutene-1; 2-methyl-5-propyl-hexene-1; pentene-3; octene-4; 3,3-dimethyl-pentene-1; styrene; 2,4-dichlorostyrene; divinylbenzene; vinyl acetate; allyl alcohol; 1-methyl-vinyl acetate; ethyl vinyl ether; and methyl vinyl ketone. Of these, the hydrocarbon polymerizable monomers are preferred and of these hydrocarbon monomers, the terminal olefin monomers are particularly preferred.

Useful polymers include alpha-olefin homopolymers and interpolymers, and ethylene-alpha-olefin copolymers and terpolymers. Specific examples of polyalkenes include propylene, polybutene, ethylene-propylene copolymer, ethylene-butene copolymer, propylene-butene copolymer, styrene-isobutylene copolymer, isobutylene-butadiene-1,3 copolymer, propylene-isoprene copolymer, isobutylene chloroprene copolymer, isobutylene-(para-methyl)styrene copolymer, copolymer of hexene-1 with hexadiene-1,3, copolymer of 3,3-dimethyl-pentene-1 with hexene-1, and terpolymer of isobutylene, styrene and piperylene. More specific examples of such interpolymers include copolymer of 95% (by weight) of isobutylene with 5% (by weight) of styrene; terpolymer of 98% of isobutylene with 1% of piperylene and 1% of chloroprene; terpolymer of 95% of isobutylene with 2% of butene-1 and 3% of hexene-1; terpolymer of 60% of isobutylene with 20% of pentene-1; and 20% of octene-1; terpolymer of 90% of
isobutylene with 2% of cyclohexene and 8% of propylene; and copolymer of 80% of ethylene and 20% of propylene. U.S. Pat. No. 5,334,775 describes polyolefin based polymers of many types and their monomer precursors and is herein incorporated by reference for such disclosure.

[0059] Relative amounts of end units in conventional and high vinylidene polyisobutylene can be determined from \(^1\)H NMR spectra made using a Bruker AMX 500 MHz instrument and UXNMRP software to work up the spectra. CDCl\(_3\) is used as the solvent with a sample concentration of approximately 0.10 g of sample dissolved in 1.5 g solvent with tetramethylsilane (1%) added as a reference. Band assignments in the NMR for the various isomers as parts per million (ppm) downfield shift from tetramethylsilane are: terminal vinylidene 4.68 and 4.89, \(\beta\)-isomer 5.18, tri-substituted 5.17 and 5.35, tetra 2.88.

[0060] The molecular weight of the polymers is typically determined by gel permeation chromatography (GPC) (also known as size exclusion chromatography) using a Waters 1500 instrument run with tetrahydrofuran solvent (mobile phase). A series of 13 narrow molecular weight samples of polystyrene (m.w. 162 to 2,180,000) are preferably used as calibration standards, although known polyisobutylene can also be used as a standard. \(M_n\) (number average molecular weight) and \(M_w\) (weight average molecular weight) are determined from comparative elution volume data. Molecular weight values of the polymers produced by the method of this invention will vary according to their degree of polymerization (dp). The dp range for products of this invention typically range from 6 to 350 or even higher.

[0061] The polydispersity of the products useful in this invention as determined by the ratio of \(M_w/M_n\) have a value of at least 5 (polystyrene standard), and may have a value of up to 20, or even greater, preferably up to 20, depending upon reaction conditions. At any given reaction temperature, the \(M_w/M_n\) is controlled by the chemical nature of the catalyst as well as the contact time of the olefin with the catalyst and the concentration of the olefin during the reaction. Use of the calcined ammonium catalysts of the present invention in the polymerization of isobutylene leads to polyisobutylene having a polydispersity typically greater than 5, or 6, often 7.5 to 20, more commonly 8 to 19 or 18. The polymers of suitable polydispersity are preferably prepared directly, from a single polymerization reaction, as opposed to by blending of different batches prepared from separate polymerization reactions. However, it is possible to blend different batches for convenience, each having suitably large polydispersity, to arrive at a composite material having a similarly large polydispersity.

[0062] It is also permitted to prepare polymeric mixtures of high polydispersity by physical admixture of samples of polymers of significantly different molecular weights, each sample individually having a relatively small value for \(M_w/M_n\), that is, 4 or 5 or less. Such blending may produce polymeric mixtures which are polymodal (including bimodal) or otherwise non-uniform in their molecular weight distribution.

[0063] The hydrocarbyl-substituted carboxylic acylating agents of the present invention include carboxylic acids and their reactive equivalents such as acid halides, anhydrides, and esters, including partial esters. These may be mono or polycarboxylic acid materials or reactive equivalents thereof.

[0064] In one embodiment, the hydrocarbyl substituted carboxylic acylating agent comprises at least one hydrocarbyl-substituted succinic acylating agent consisting of at least one hydrocarbyl substituent and at least one succinic group wherein the hydrocarbyl substituent is derived from a polyolefin, preferably, polyisobutylene.

[0065] The hydrocarbyl-substituted succinic acid or succinic anhydride can be represented correspondingly by the formula

\[
\begin{align*}
\text{R} & \quad \text{CH} \quad \text{COOH} \\
\text{or} & \\
\text{CH}_2 & \quad \text{COOH}
\end{align*}
\]

[0066] wherein R is a hydrocarbyl group.

[0067] The hydrocarbyl substituted carboxylic acylating agents are prepared by the reaction of one or more of the above-described polyolefins with one or more unsaturated carboxylic reagents. The unsaturated carboxylic reagents include unsaturated carboxylic acids per se and functional derivatives thereof, such as anhydrides, esters, salts and acyl halides. The unsaturated carboxylic reagents include mono-, di-, tri, or tetracarboxylic acids. Examples of useful unsaturated monobasic acids include acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, and 2-phenylpropenoic acid. Polybasic unsaturated carboxylic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid, and citraconic acid; their anhydrides are preferred and maleic anhydride is particularly preferred. Reactive equivalents of such anhydrides include the above-mentioned derivative, e.g., acids, esters, half esters, salts, and acyl halides, which can also serve as carboxylic reagents. Another suitable acid is glyoxylic acid, which can be reacted with the polymer as described in U.S. Pat. No. 5,912,213. Reactive equivalents of glyoxylic acid, including esters, acetics, hemiacetals, as well as other materials described in the foregoing U.S. patent, can also be used.

[0068] The acylating agents can be prepared by reacting one or more of the polyolefins with, typically, a stoichiometric excess of a carboxylic reagent such as maleic anhydride. Such reaction provides a substituted carboxylic acylating agent having at least one carboxylic group, preferably succinic groups. For each equivalent weight of the hydrocarbyl group, there may be more than one carboxylic group.

[0069] For purposes of this calculation, the number of equivalent weight of substituent groups is deemed to be the number corresponding to the quotient obtained by dividing the \(M_w\) (number average molecular weight) value of the polyalkene from which the substituent is derived into the total weight of the substituent groups present in the substituted acylating agent. Thus, if a substituted succinic acylating agent is characterized by a total weight of substituent group of 40,000 and the \(M_w\) value for the polyalkene from which the substituent groups are derived is 2000, then that substituted succinic acylating agent is characterized by a total of 20 (40,000/2000=20) equivalent weights of substituent groups.
Methods for preparing succinic acylating agents satisfying these parameters, except for the use of the materials of the high polydispersity, are described in U.S. Pat. No. 4,234,435. In particular, this patent discloses (in column 19) a process for preparing such materials by heating at a temperature of about 160° C. to about 220° C. a mixture comprising: Polybutene characterized by a M_w value of about 1700 to about 2400, in which at least 50% of the total units derived from butenes is derived from isobutene; one or more acidic reactants of the formula

\[ \text{R} - \text{C} = \text{H} \text{C} = \text{CH} - \text{C} - \text{R}' \]

wherein R and R' are each —OH or when taken together, R and R' are —O—; and chlorine.

Specific examples of preparation of such acylating agents are set forth in Examples 1 through 9 of U.S. Pat. No. 4,234,435.

Other processes can be used, if desired, which do not employ chlorine, and this is preferred if the presence of chlorine is undesirable for environmental reasons. Bromine can be used in place of chlorine; or the reactants can be heated together at 150 to 200 or 230° C. in the absence of halogen. Moreover, it is generally unnecessary to use chlorine when using high vinylidene polyolefin reactants. Preparation using a so-called “thermal” route is generally described in European Patent 355,895.

In the formation of the hydrocarbyl-substituted acylating agent, the conditions for the reaction of the polyolefin with the carboxylic acid reactant such as maleic anhydride, and the relative concentrations of such components, should preferably be sufficient that a majority of the olefin polymer has reacted with at least one molecule of the acylating reagent. That is, it is preferred, for optimum performance that no more than 30 percent by weight unreacted polymer should remain unreacted in the resulting acylating agent, preferably no more than 25 percent, and more preferably no more than 20 percent, should remain. While reaction of the polyolefin with the carboxylic acid reagent is preferably conducted in the absence of chlorine, it is possible to prepare hydrocarbyl substituted acylating agents by a process involving chlorine. However, it is especially preferred that the preparation of the hydrocarbyl substituted acylating agent be conducted in the absence of chlorine. The polyolefins prepared employing heteropolyacid catalysts facilitate the process. Determination of conditions to assure a sufficient degree of reaction is within the abilities of the person skilled in the art.

In one embodiment, the acylating agent is made by coupling polyisobutene substituted succinic acids or anhydrides, the polyisobutene substituent of the succinic acid or anhydride having at least about 35 carbon atoms, preferably from about 50 to about 200 carbon atoms. The coupled acylating agent may be represented by the formula

\[ \text{R}^1 - \text{O} - \text{C} = \text{H} \text{C} = \text{CH} - \text{C} - \text{R}^2 \]

wherein each of R¹ and R² is a polyisobutene group of at least about 35 carbon atoms and preferably at least about 50 carbon atoms up to about 200 carbon atoms.

In one embodiment, the succinic acids or anhydrides are reacted with ethylene glycol, the ratio of equivalents being 1: about (2.3-2.7), (which also corresponds to the same mole ratio) and in one embodiment about 1:2.5. In another embodiment, the ratio of equivalents is about (1.8-2.2):1, and in one embodiment about 2:1.

The hydrocarbyl substituted carboxylic acylating agents alone may serve as emulsifier component (C). However, more often the acylating agent is reacted with at least one of ammonia, water, an amine, an alcohol, a reactive metal, a reactive metal compound or a mixture of two or more thereof. When the acylating agent is reacted with 2 or more of these reagents, they may be reacted simultaneously, individually, or in any order.

Derivatives of Acylating Agents

In one embodiment, the emulsifier is the reaction product of the hydrocarbyl substituted acylating agent with ammonia or an amine. The amines useful for reacting with the acylating agent include monoamines, polyamines, or mixtures of these.

The monoamines have only one amine functionality whereas the polyamines have two or more. The amines can be primary, secondary or tertiary amines. The primary amines are characterized by the presence of at least one —NH group; the secondary by the presence of at least one H—N< group. The tertiary amines are analogous to the primary and secondary amines with the exception that the hydrogen atoms in the —NH₂ or H—N< groups are replaced by hydrocarbyl groups. Examples of primary and secondary monoamines include ethylamine, diethylamine, N-butylamine, di-n-butylamine, allylamine, isobutylamine, cocaamine, stearlyamine, laurylamine, methylaluminium, oleylamine, N-methylctyloctylamine, and octadecylamine. Suitable examples of tertiary monoamines include trimethylamine, trimethylamine, tripropyl amine, tributylamine, monoethyl dimethylamine, dimethylpropyl amine, dimethylbutyl amine, dimethylpentyl amine, dimethylhexyl amine, dimethylheptyl amine, and dimethyloctyl amine.

In one embodiment, the amines are hydroxyamines. These hydroxyamines can be primary, secondary, or tertiary amines. Typically, the hydroxyamines are primary, secondary or tertiary alkanolamines, or mixture thereof. Such amines can be represented, respectively, by the formulæ:
and mixtures of two or more thereof; wherein in the above formulae each R is independently a hydrocarbyl group of 1 to about 8 carbon atoms, or a hydroxyl-substituted hydrocarbyl group of 2 to about 8 carbon atoms and each R' independently is a hydrocarbylene (i.e., a divalent hydrocarbyl) group of 2 to about 18 carbon atoms. The group —R—OH in such formulae represents the hydroxyl-substituted hydrocarbylene group. R' can be an acyclic, alicyclic, or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group. When two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxy lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R is independently a lower alkyl group of up to seven carbon atoms.

Suitable examples of the above hydroxyamines include mono-, di-, and triethanolamine, dimethylethanolamine (N,N-dimethylethanolamine), diethylethanolamine (N,N-diethylethanolamine), di-(3-hydroxypropyl)amine, N-(3-hydroxybutyl)amine, N-(4-hydroxybutyl)amine and N,N-di-(2-hydroxypropyl) amine.

The reaction product of the hydrocarbyl substituted carboxylic acylating agent and at least one of ammonia or an amine may be a salt, an ester (when the amine is an alkanolamine), an amide, an imide or a combination thereof. The salt may be an internal salt involving residues of a molecule of the acylating agent and the ammonia or amine wherein one carboxyl group of a dicarboxylic acylating agent becomes ionically bound to a nitrogen atom within the same group, or it may be an external salt wherein the ionic salt group is formed with a nitrogen atom is not part of the same molecule. In one embodiment, the hydrocarbyl substituted carboxylic acylating agent is a hydrocarbyl substituted succinic anhydride and the reaction product is a half-ester half salt.

In another embodiment, the hydrocarbyl substituted carboxylic acylating agent is a polysisobutenyl (Mₙ 900 to about 2500) substituted succinic acid. The emulsifier is prepared by reacting this succinic acid with 2 equivalents of alkanolamine.

The reaction between the hydrocarbyl substituted carboxylic acylating agent and ammonia or amine is carried out under conditions that provide for formation of the desired product. The nature of the reaction and products obtained thereby will depend to some extent on the nature of the carboxylic acylating agent. Typically, the hydrocarbyl substituted carboxylic acylating agent and the ammonia or amine are mixed together and heated to a temperature in the range of from less than about 50°C. to about 250°C., and in one embodiment from about 80°C. to about 200°C., optionally in the presence of a normally liquid, substantially inert organic liquid organic solvent/diluent until the desired product has formed. To restrict the reaction to primarily salt formation, it is necessary that the acylating agent is a carboxylic acid. Employing a carboxylic acid, the reaction is conducted at temperatures ranging from less than about 80°C. up to about 130°C., preferably from less than about 50°C. up to about 110°C. Commonly, reactions to form salt can take place at ambient temperature.

Amides, esters and imides from anhydrides can form readily at temperatures in excess of 50°C., usually at a temperature of at least 80°C., and more often at greater than 90°C., with imide formation generally requiring even higher temperatures. Imides, esters and amides from diacids prepared from anhydrides usually require higher temperatures, for example greater than 120°C. for imides and up to about 250°C. for esters. Ester formation occurs when the amine is an alkanol amine.

Among preferred embodiments is the ester-acid salt prepared from a dicarboxylic anhydride such as an alkyl succinic anhydride and a tertiary alkanol amine. The amine and anhydride react readily to form the monoester while the second carboxylic acid group generated by the ring opening reacts with the tertiary amino nitrogen to form salt.

In one embodiment, the hydrocarbyl substituted carboxylic acylating agent and ammonia or amine are reacted in amounts ranging from about 0.3 to about 3 equivalents of hydrocarbyl substituted carboxylic acylating agent per equivalent of ammonia or amine; in one embodiment the ratio is from about 0.5:1 to about 2:1 and in another embodiment, about 1:1.

In one embodiment, the reaction product is made by reacting a polysisobutenate substituted succinic anhydride having an average of from 1 to about 3 succinic groups for each equivalent of polysisobutenate group with diethanolamine, diethylethanolamine or dimethylethanolamine in an equivalent ratio of 1 to about 0.4-1.25, and in one embodiment, about 1:1.

In one embodiment, the reaction product is made by reacting a polysisobutenate substituted succinic anhydride having an average of from 1 to about 3 succinic groups for each equivalent of polysisobutenate group with water in an equivalent ratio of 1 to about 4, and in one embodiment, about 1:1. That reaction product is further reacted with an alkanols amine, preferably diethanolamine in an equivalent ratio of about 1 acid to about 1 amine.

Amines used to prepare the emulsifiers can be polyamines as disclosed in U.S. Pat. No. 4,234,435 at column 21, line 4 to column 27, line 50. They may also be heterocyclic polyamines or alklylenepolyamines. Alkylene-polyamines are represented by the formula H(R')(N-Alkylene-N(R'))ₙR, where each R' is independently hydrogen or an aliphatic group or a hydroxy-substituted aliphatic group; n is 1 to 10, 2 to 7, or 2 to 5, and the “Alkylene” group has 1 to 10, or 2 to 6, or 2 to 4 carbon atoms. Specific examples of such polyamines are the ethylenediamines, perylenehexylexamine and mixtures thereof, including complex commercial mixtures which include cyclic conden-
sation products. Such materials are described in detail under the heading “Ethylene Amines” in Kirk Othmer’s Encyclopedia of Chemical Technology, 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York, 1965. Other amine mixtures include “polyamine bottoms” which is the residue resulting from stripping of the above-described polyamine mixture. In another embodiment, the polyamine can be a condensed polyamine resulting from the condensation reaction of at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. Such condensates are described in U.S. Pat. No. 5,230,714. Similarly, amines can be amino alcohols of any of a variety of well-known types.

[0094] For the purpose of this invention, an equivalent of amine is that amount of amine corresponding to the total weight of amine divided by the total number of nitrogens present. Thus, octyl amine has an equivalent weight equal to one-half its molecular weight, and ethylenediamine has an equivalent weight equal to one-half its molecular weight, and amino-ethylpiperazine has an equivalent weight equal to one-third of its molecular weight.

[0095] The number of equivalents of acylating agent depends on the number of carboxylic functions present in the acylating agent. Conventional techniques are available for determining the number of carboxylic functions (e.g., acid number, saponification number, etc.) and thus, the number of equivalents of acylating agent available to react with amine.

[0096] U.S. Pat. Nos. 3,172,892; 3,219,666; 3,272,746; and 4,234,435 are expressly incorporated herein by reference for their disclosure with respect to the procedures applicable to reacting the carboxylic compositions (acylating reagents) of this invention with the amines as described above. In applying the disclosures of these patents to the carboxylic compositions of the present invention, the latter can be substituted for the high molecular weight carboxylic acid acylating agents disclosed in these patents on an equivalent basis.

[0097] Alcohols can be used in preparation of the emulsifiers of the present invention resulting in ester group containing compounds. Suitable alcohols can be aliphatic, cycloaliphatic, aromatic, or heterocyclic, alcohols and can contain non-hydrocarbon substituents of a type which do not interfere with the reaction of the alcohol with the acylating agent to form the ester. The alcohols can be monohydric alcohols such as methanol, ethanol, isopropanol, dodecanol, and cyclohexanol, although they are preferably polyhydric alcohols, such as alkylene polyols. Preferably, such polyhydric alcohols contain 2 to 4 and more preferably 2 to 20 carbon atoms; and 2 to 10 hydroxy groups, more preferably 2 to 6. Polyhydric alcohols include ethylene glycols such as di-, tri- and tetraethylene glycols; propylene glycols; glycerol; sorbitol; cyclohexane diol; erythritol; and pentaerythritol, including di- and tri-pentaerythritol.

[0098] Alkanolamines can also serve as alcoholic reagents wherein the hydroxyl group of the alkanolamine can react with the acylating agent. As noted hereinabove, a wide variety of products can be obtained, such as pure esters, ester-salts, ester amides, etc., depending on the nature of the alkanolamine, etc.

[0099] Commercially available polyoxyalkylene alcohols can also be employed as the alcohol component. Such materials include the reaction products of various organic amines, carboxylic acid amides, and quaternary ammonium salts with ethylene oxide. Some such materials are available under the names Ethoxhomeen™, an ethylene oxide condensation product of an N-alkyl alkenediamine; Ethomine™, ethylene oxide condensation products of primary fatty amines; Ethomid™, ethylene oxide condensates of fatty acid amides, and Ethoquad™, polyoxyethylated quaternary ammonium salts such as quaternary ammonium chlorides.

[0100] In one embodiment, the above described coupled acylating agent with the ratio of about 1: about (2.3-2.7), the above ratio of about (1.8-2.2):1, is reacted with dimethyllethanolamine in a mole ratio of ethylene glycol to dimethyllethanolamine of about 1: about 1.8-2.2, and in one embodiment about 1:2. Thus the coupled di-ester/di-acid is converted into the di-salt by reaction of each carboxylic acid group from the coupled acylating agent with one equivalent of dimethyllethanolamine.

[0101] The derivatives useful as emulsifiers can also be reaction products of hydrocarbyl substituted carboxylic acylating agents with reactive metals and reactive metal compounds.

[0102] Reactive metals and reactive metal compounds are those which will form carboxylic acid metal salts with the carboxylic acylating agents of this invention and those which will form metal-containing complexes with the carboxylic derivative compositions produced by reacting the acylating reagents with amines and/or alcohols as discussed above. An extensive listing of useful metals and metal compounds appears in U.S. Pat. Nos. 3,163,603 and 3,271,310. Reactive metal compounds for the formation of complexes with the reaction products of the acylating reagents of this invention and amines are disclosed in U.S. Pat. No. 3,306,908. Complex-forming metal reactants are those of the so-called transition or coordination metals, i.e., they are capable of forming complexes by means of their secondary or coordination valence.

[0103] The emulsifiers used in the present invention can be further borated or treated with metallizing agents. Boration can be effected by well-known techniques, in particular, by reaction of the emulsifier with one or more boron compounds. Suitable boron compounds include boric acid, borate esters, and alkali or mixed alkali metal and alkaline earth metal borates. These metal borates are generally a hydrated particulat.e metal borate and they, as well as the other borating agents, are known in the art and are available commercially. Typically the emulsifier is heated with boric acid at 50-100°C or 100-150°C. In a similar way, the emulsifier can be metallized or treated with reactive metal containing compounds, such as zinc compounds.

[0104] The Cosurfactants (D)

[0105] In addition to the presence of component (C) as an emulsifier, the present composition can also contain other emulsifiers, which may be present as cosurfactants. These cosurfactants are present in emulsion enhancing/stabilizing amounts. These cosurfactants are distinct from (C). These emulsifiers/cosurfactants include, among others, ionic or nonionic compounds, having a hydrophilic lipophilic balance (HLB) in the range of about 2 to about 10, and in one embodiment about 4 to about 8. Examples of these emulsifi-
fiers are disclosed in McCutcheon’s Emulsifiers and Detergents, 1993, North American & International Edition. Some generic examples include alkanolamides, amine salts of fatty carboxylic acids, alkylaryl sulfonates, amine oxides, polyoxyalkylene compounds, including block copolymers comprising alkylene oxide repeat units (e.g., Pluronic™), carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, glycerol esters, glycol esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkyl phenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols or ethoxylated alcohols or fatty esters, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids.

[0106] Hydrocarbyl substituted carboxylic acid and reactive sources thereof, wherein the hydrocarbyl group contains from about 6, often from about 8, up to about 24 carbon atoms, frequently up to about 18 carbon atoms, are also useful cosurfactants. These include mono- and polycarboxylic compounds. In one embodiment, they may comprise fatty monoacetylated fatty acids and reactive equivalents thereof containing from about 8 to about 24 carbon atoms. In another embodiment, the cosurfactant may be a hydrocarbyl substituted succinic acid or anhydride containing from about 8 to about 24 carbon atoms in the hydrocarbyl group. In one preferred embodiment, the cosurfactant is a hexadecenyl substituted succinic acid or anhydride.

[0107] Derivatives of the carboxylic acid as for (C) are also useful cosurfactants. Amine salts of these fatty carboxylic acids, particularly alkanol amine salts, are useful cosurfactants. Preferred alkanolamine reactants are those that are water soluble. In one preferred embodiment, a salt is obtained by mixing one mole oleic acid with one mole diethylethanolamine. In another preferred embodiment, the cosurfactant is an ester salt obtained by reaction of hexadecenyl substituted succinic anhydride with a dialkyl alkanolamine, for example, diethyl ethanolamine. In another preferred embodiment, the cosurfactant is a diester obtained by reaction of hexadecenyl substituted succinic acid with two moles of diethyl ethanolamine.

[0108] The Organic Nitrate Cetane Improver (E)

[0109] In one embodiment of the present invention, the present composition further comprises at least one organic cetane improver. The organic nitrate cetane improver includes nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, preferably from 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Specific examples of nitrate compounds suitable for use in the present invention include methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-aminyl nitrate, 3-aminyl nitrate, tert-aminyl nitrate, n-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methyl-cyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also suitable are the nitrate esters of alkoxy substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. While not particularly preferred, the nitrate esters of higher alcohol may also be useful. Such higher alcohols tend to contain more than about 10 carbon atoms. Preferred are the alkyl nitrates having from about 5 to about 10 carbon atoms, most especially mixtures of primary amyl nitrates, mixtures of primary hexyl nitrates, and octyl nitrates such as 2-ethylhexyl nitrate.

[0110] The concentration of the organic nitrate cetane improver in the present composition can be any concentration sufficient to counteract the reduction in cetane number caused by the addition of water in the present water-blended fuel compositions. Generally, addition of water to fuel acts to lower the cetane number of the fuel. As a general rule of thumb, the cetane number of fuel goes down by ¼ unit per each 1% addition of water. Lowering of cetane number results in ignition delay, which can be counteracted by the addition of cetane enhancers/improvers. Generally, the amount of organic nitrate cetane improver ester will fall in the range of about 0.05 to about 10% and in one embodiment about 0.05 to about 1% by weight of the water-blended fuel composition.

[0111] The Antifreeze (F)

[0112] In one embodiment of the present invention, the composition further comprises an antifreeze. The antifreeze is usually an alcohol. Examples of suitable alcohols useful as an antifreeze for the present invention include, but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, and mixtures thereof.

[0113] The antifreeze can be present at any concentration sufficient to keep the present composition from freezing within the operable temperature range. In one embodiment, it is present at a level of about 0.1% to about 10%, and in one embodiment, about 0.1 to 5% by weight of the water-blended fuel composition.

[0114] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, certain ions can migrate to sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing or using the components described above.

[0115] Amine Salt (G)

[0116] Another optional component of the present composition is a water-soluble, ashless (i.e. metal-free), halogen-, boron-, and phosphorus-free amine salt, distinct from component (C). The term “amine” here includes ammonia.
In one embodiment, the amine salt (G) is represented by the formula

$$H_2[NR_3]_3^{	ext{+}}\cdot \text{An}^{	ext{-}}$$

Wherein in the formula, Z is hydrogen, hydroxyl, alkoxy, or an organic neutral radical of 1 to about 8 carbon atoms, and in one embodiment 1 to 2 carbon atoms, having a valence of y; each R independently is hydrogen or a hydrocarbyl group of 1 to about 10 carbon atoms, and in one embodiment 1 to about 5 carbon atoms, and in one embodiment 1 to 2 carbon atoms; X^{	ext{+}} is an anion having a valence of p; and k, y, n and p are independently at least 1, provided that when Z is H, y is 1, and further provided that the sum of the positive charge ky^{	ext{+}} is equal to the sum of the negative charge nx^{	ext{-}}. such that the amine salt (G) is electrically neutral. In one embodiment, G is a hydrocarbyl or hydrocarbylene group of 1 to about 5 carbon atoms, and in one embodiment 1 to 2 carbon atoms. In one embodiment, X^{	ext{-}} is a nitrate ion (y=1); in one embodiment it is an acetate ion (y=1). Suitable examples of the amine salt include ammonium nitrate, ammonium acetate, methylammonium nitrate, methylammonium acetate, ethylene diamine diacetate, urea nitrate, hydroxyammonium nitrate and urea dinitrate.

Doesn’t look like this list included hydroxyammonium nitrate—should it be included?

As an illustration, ethylene diamine diacetate can be written in its ionic form as

$$[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2]^{	ext{+}}\text{2CH}_3\text{CO}_2^-$$

In this case, in formula Z is $-\text{CH}_2\text{CH}_2-;\ R$ is hydrogen, y is 2; n is 2; p is 1; and X^{	ext{-}} is CH$_3$CO$_2$-. This sentence is confusing!

In one embodiment, the amine salt (G) of the present composition functions as an emulsion stabilizer, i.e., it acts to stabilize the present emulsified water-blended fuel composition. Compositions with the amine salt (G) have longer stability as emulsions than the compositions without the amine salt (G).

In one embodiment, the amine salt (G) functions as a combustion improver. A combustion improver is characterized by its ability to increase the mass burning rate of water-blended fuel composition. It is known that the presence of water in fuels reduces the power output of an internal combustion engine. The presence of a combustion improver has the effect of improving the power output of an engine. The improved power output of the engine can often be seen in a plot of mass burning rate versus crank angle (which angle corresponds to the number of degrees of revolution of the crankshaft which is attached to the piston rod, which in turn is connected to pistons). The mass burning rate will be higher for a fuel with a combustion modifier than for a fuel lacking the combustion modifier. This improved power output caused by the presence of a combustion improver is to be distinguished from improvement in ignition delay caused by a cetane improver. Although some cetane improvers may function as combustion improvers, and some combustion improvers as cetane improvers, the actual performance characteristics or effects of combustion improvement are clearly distinct from improvements in ignition delay. Improving ignition delay generally relates to changing the onset of combustion whereas improving the power output relates to improving the peak cylinder pressure, i.e., the amplitude of the peak mass burning rate.

When used, the amine salt (G) is present at a level of about 0.001 to about 15%, and in one embodiment from about 0.001 to about 1%, in one embodiment about 0.05 to about 5%, in one embodiment about 0.5 to about 3%, and in one embodiment about 1 to about 10% by weight of the emulsified water-blended fuel composition.

**EXAMPLES**

The following examples are intended to illustrate several emulsifier compositions of this invention as well as means for preparing same. It is to be understood that these examples are only intended as illustrative of compositions and procedures and are not intended to limit the scope of the invention. Unless indicated otherwise, all parts are by weight, temperatures are in degrees Celsius (° C.), and pressures are atmospheric. When referring to parts by volume, the relationship is as parts by weight in grams to parts by volume in milliliters. Filtrations are conducted using a diatomaceous earth filter aid. All analytical values are by analysis.

Measurements of molecular weight and polydispersity are made as described above using polystyrene standards, unless otherwise noted. In some cases (indicated with the notation “PBU std”), molecular weight is measured using a different model instrument against a standard broad molecular weight distribution polystyrene sample, which in turn is standardized by comparison with a series of narrow molecular weight distribution polystyrene standards. For some specimens for which the polystyrene and PBU standards have been compared, the values for $M_w$ using the PBU standard tend to be roughly 0.7 to 0.8 times those obtained using the polystyrene standard, and the values obtained for $M_w$ tend to be roughly 1.4 to 1.6 times those obtained using the polystyrene standard.

Example 1

In a fume hood, a solution of 3.78 g (0.0394 moles) of (NH$_4$)$_2$CO$_3$ in water (30 mL) is added dropwise to a solution of 100 g (0.0315 moles, containing 9.23% water) of H$_2$PW$_{12}$O$_{40}$ in water (120 mL), resulting in a milky-white slurry. The water is evaporated by heating to isolate the solid (NH$_4$)$_2$H$_3$PW$_{12}$O$_{40}$ catalyst. The catalyst is calcined under air flow in a glass tube mounted in an oven at 450°C for 2 hours.

Example 2

In a fume hood, a 5000 mL bottom drain 4-necked round bottom flask is fitted with a jacketed addition funnel, a cold finger, an N$_2$ inlet, an isobutylene inlet, a solids addition funnel charged with 1.1 g (NH$_4$)$_2$H$_3$PW$_{12}$O$_{40}$ and a thermometer. An N$_2$ atmosphere is established within the vessel whereupon 500 mL isobutylene is added from the jacketed addition funnel. The isobutylene is allowed to reflux until the temperature reaches ~9°C. To the flask is added, in portions over the course of the reaction, 1.1 g of catalyst, prepared as in Example 1. After stirring at ~9°C for 0.3 hour, isobutylene (2500 mL) is added concurrently with catalyst. After a total reaction time of 3.1 hours, the reactor is drained into water to quench the reaction. The liquid is allowed to settle, the organic layer is separated, washed with water, separated again and dried with MgSO$_4$. The solution is gravity filtered then concentrated under
reduced pressure from the liquid portion to provide 287 g of an oil (16% yield) having a \( M_n \) of 1444, and \( M_n/M_w \) 7.7, peak molecular weight 10530 and vinylidene end group content = 73%.

Example 3

The procedure of Example 2 is repeated except catalyst (2.4 g total) is added to the vessel in portions throughout the reaction. After a total reaction time of 2.5 hours the vessel is drained into water, to quench the reaction. The mixture is worked up as in Example 2 to provide an oil [775 g; 46% yield, \( M_n \) 4243, \( M_w/M_n \) 9.06 (or 3147 and 13.9, respectively, PBU std.), vinylidene end group content 80%]. This sample is combined with 4 additional samples prepared by the same procedure, ranging in weight from 542 to 974 g. The total blended sample is 3980 g and has \( M_n \) 3108, \( M_w/M_n \) 12.4 (peak molecular weight 41597), and vinylidene end group content 80%.

Example 4

Following the procedure listed in Example 2, isobutylene (1200 g) is reacted with 4.5 g of the supported catalyst of Example 2 over 1.75 hours before being quenched by a water/hexane mixture. The organic layer is separated, dried over \( \text{MgSO}_4 \), filtered, and concentrated under reduced pressure \([6.66 \text{ kPa} (50 \text{ mm Hg}) \text{ at } 160^\circ \text{ C}]\) to provide 404 g (34% yield) of product having \( M_n \) 9515, \( M_w/M_n \) of 9.52 (or 1367 and 11.70, respectively, PBU std.) and 80% terminal vinylidene content.

Example 6

A mixture of 1464.8 g of polysisobutylene from Example 4 is heated to 165°C and 138.7 g maleic anhydride is added over 0.1 hour. The mixture is heated to 200°C with light subsurface \( N_2 \) purge. Heating with stirring at 200°C is continued for 24 hours. At the end of the reaction time, the temperature is reduced to 170°C. Excess unreacted maleic anhydride is removed under vacuum as the temperature is increased to 190°C, removing a total of 65.4 g distillate. The resulting crude product is cooled and diluted with 1473.4 g mineral oil and filtered. The product contains 0.28 weight percent free maleic anhydride, a Total Acid Number of 24.1 meq/g, and contains 58.45 percent by weight non-polar species, including the diluent oil.

Example 7

A reactor is charged with 20 g (0.0086 mol) of the product of Example 6 and 0.76 g mineral oil. The materials are heated with stirring under slow \( N_2 \) purge to 95°C. Whereupon 0.13 g ethylene glycol is added over 1 minute. The temperature is increased to 102°C over 0.25 hour and is held at temperature for 4.25 hours. To this material is added 0.38 g (0.0043 mole) dimethylaminoethanol over 0.1 hour. The materials are stirred and heated at 102°C for 2 hours, 21.26 g BP Supreme Diesel fuel are added and stirring is continued for 0.2 hour at 75-80°C. The product contains 0.10% \( \text{N} \), and has total acid no. =.93 and total base number 2.72.

Example 8

A reactor is charged with 20 g of the product of Example 6 and 0.79 g mineral oil. The materials are heated with stirring with slow \( N_2 \) purge to 100°C. Whereupon 0.55 g diethylethanolamine is added over 0.1 hour. The materials are stirred and heated at 100°C for 2 hours, 21.34 g BP Supreme Diesel fuel are added and stirring is continued for 0.1 hour at 75°C. The product contains 0.12% \( \text{N} \), and has total acid no. =.44 and total base number 3.56.

Example 9

Several examples of emulsified fuel compositions of this invention are described herein below. All parts are parts by weight and unless expressly stated otherwise, are on an oil/diluent free basis. Unless indicated otherwise, amounts of products of Examples are on an 'as prepared' basis, including solvents/diluents that may be present. The procedure for preparing the emulsions involves blending the aqueous component with the organic component in a high shear mixer.

In the examples in the following table, the aqueous component is a solution of 0.75% by weight ammonium nitrate in water. The organic component is a mixture of fuel, emulsifier, ester-salt cosurfactant obtained by reaction of hexadecene substituted succinic acid with a dialkyl alkanolamine and organic nitrate cetane improver. In each example 20 parts of the aqueous component and 80 parts of the organic component are combined by mixing in a Waring® Blender at low setting [-18,000 revolutions per minute (RPM)] for 5 minutes. The emulsion of each example contains 76.4% of the indicated fuel, 20% of aqueous component, 2.77% of the indicated surfactant, 0.116% cosurfactant, and 0.476% of organic nitrate cetane improver.

<table>
<thead>
<tr>
<th>Example</th>
<th>Emulsifier</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Product of Ex. 7</td>
<td>BP Supreme Diesel</td>
</tr>
<tr>
<td>B</td>
<td>Product of Ex. 8</td>
<td>BP Supreme Diesel</td>
</tr>
<tr>
<td>C</td>
<td>Product of Ex. 7</td>
<td>BP Diesel (50 ppm S)</td>
</tr>
<tr>
<td>D</td>
<td>Product of Ex. 8</td>
<td>BP Diesel (50 ppm S)</td>
</tr>
</tbody>
</table>

Each of these blends was evaluated for emulsion stability at ambient temperature and at 65°C. After one week storage, each emulsion showed excellent stability. At 65°C, no more than 15% of the emulsion separated into an oily or creamy-like phase. At ambient temperature, no more than 10% separation into an oily phase was observed. No water enriched band was visually observed.

Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word “about.” Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, byproducts, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be
What is claimed is:

1. An emulsified water-blended fuel composition comprising:
   (A) a liquid hydrocarbon based fuel;
   (B) water; and
   (C) a minor, emulsifying amount of at least one of a fuel-soluble hydrocarbyl-substituted carboxylic acylating agent and a reactive product of said acylating agent and at least one of ammonia, an amine, an alcohol, a reactive metal, a reactive metal compound and a mixture of two or more thereof, wherein the hydrocarbyl substituent comprises a group derived from at least one polyolefin, said polyolefin having \( M_n / M_w > 5 \)
   resulting in a water in fuel emulsion.

2. The fuel composition of claim 1 wherein the hydrocarbyl fuel (A) is present at a level about 50 to about 99% by weight of the water-blended fuel composition; water (B) is present at a level of about 1 to about 50% by weight of the water-blended fuel composition; and component (C) is present at a level of about 0.005 to about 10% by weight of the water-blended fuel composition.

3. The fuel composition of claim 1 wherein the polyolefin has \( M_n / M_w \) ranges from about 6 to about 20; wherein less than 5 percent by weight of the polyolefin molecules have a number average molecular weight of less than 250; wherein the polyolefin has \( M_n \) of at least about 800; wherein the polyolefin has at least about 50% terminal vinylidene (I) groups.

4. The fuel composition of claim 1 wherein the polyolefin comprises polyisobutylene.

5. The fuel composition of claim 1 wherein the polyolefin is prepared by contacting (a) at least one \( C_2-C_9 \) olefin or polymerizable derivative thereof with (b) a catalyst comprising a partially or fully neutralized salt of a heteropolyacid, wherein said catalyst has been calcined at from about 500° C. for about 1 to about 4 hours; and wherein the heteropolyacid is a phosphotungstic acid, a phosphomolybdic acid, a silicotungstic acid or a siliconmolybdic acid.

6. The fuel composition of claim 5 wherein the salt is selected from the group comprising ammonium salt, cesium salt and combinations thereof.

7. The fuel composition of claim 1 wherein the polyyolefin is prepared by blending at least two polyolefin components having different number average molecular weights, each such component having a \( M_n / M_w \) of less than 5.

8. The fuel composition of claim 1 wherein the hydrocarbyl substituted carboxylic acylating agent is selected from the group comprising at least one monocarboxylic acid or a reactive equivalent thereof; at least one hydrocarbyl-substituted succinic acylating agent consisting of at least one hydrocarbyl substituent and at least one succinic group wherein the hydrocarbyl substituent is derived from a polyolefin; at least one hydrocarbyl-substituted succinic acid or succinic anhydride represented correspondingly by the formula

\[
\begin{align*}
R &-\text{CH-COOH} \\
\text{CH}_2 &-\text{COOH}
\end{align*}
\]

wherein \( R \) is a hydrocarbyl group.

9. The fuel composition of claim 1 wherein the hydrocarbyl substituted carboxylic acylating agent is reacted with an amine selected from the group comprising at least one monoamine; at least one polyamine; at least one hydroxylamine and combinations thereof.

10. The fuel composition of claim 8 wherein the hydroxylamine is selected from the group consisting of primary, secondary and tertiary alkanolamines represented correspondingly by the formula

\[
\begin{align*}
\text{H} &-\text{N-R-OH} \\
\text{H} &-\text{N-R-OH} \\
\text{H} &-\text{N-R-OH}
\end{align*}
\]

and mixtures of two or more thereof; wherein in the above formulae each \( R \) is independently a hydrocarbyl group of one to about 8 carbon atoms, and each \( R' \) is independently a hydrocarbylene group of about 2 to about 18 carbon atoms.

11. The fuel composition of claim 1 wherein the hydrocarbyl substituted carboxylic acylating agent is reacted with an alcohol or water.

12. The fuel composition of claim 1 further comprising (D) an emulsifying amount of at least one cosurfactant distinct from (C).

13. The fuel composition of claim 12 wherein said at least one cosurfactant has a hydrophilic-lipophilic balance (HLB) in the range of about 1 to about 40 and is selected from the group comprising at least one compound selected from the group consisting of (a) Poly(oxyalkylene) compounds; (b) sorbitan esters; and (c) fatty acid diethanolamides and combinations thereof.

14. The fuel composition of claim 12 wherein said at least one cosurfactant comprises a fatty monocarboxylic acid containing from about 8 to about 24 carbon atoms or an amine salt thereof.

15. The fuel composition of claim 12 wherein the at least one cosurfactant comprises a hydrocarbyl substituted succinic acid or anhydride containing from about 8 to about 24 carbon atoms in the hydrocarbyl group.

16. The fuel composition of claim 1 further comprising (E) at least one organic nitrate cetane improver and is present at a level of about 0.05 to about 10% by weight of the water-blended fuel composition.

17. The fuel composition of claim 15 wherein component (E) comprises 2-ethylhexyl nitrate.

18. The fuel composition of claim 1 further comprising (F) at least one antifreeze and is present at a level of about 0.1 to about 10% by weight of the water-blended fuel composition.

19. The fuel composition of claim 1 further comprising (G) at least one water-soluble, ashless, halogen-, boron-, and
phosphorus-free amine salt, distinct from component (C) and is present in amounts ranging from about 0.001 to about 15% by weight of the emulsified water-blended fuel composition.

20. The composition of claim 19 wherein the amine salt (G) is selected from the group consisting of ammonium nitrate, hydroxyammonium nitrate, methy lammonium nitrate, ethylene diamine diacetate, urea dinitrate, and mixtures of at least two thereof.

21. An emulsified water blended fuel composition comprising:

(A) a normally liquid hydrocarbon based fuel boiling in the gasoline or diesel fuel range;

(B) water;

(C) a minor emulsifying amount of the reaction product of a hydrocarbyl substituted carboxylic acylating agent and at least one of ammonia, an amine, an alcohol or a mixture of two or more thereof wherein the hydrocarbon substituent is derived from at least one polymerized olefin which has been prepared by contacting (a) at least one C₁₋₃₀ olefin or polymerizable derivative thereof with (b) a catalyst comprising a partially or fully neutralized salt of a heteropolyacid, wherein said catalyst has been calcined; and

(G) at least one water-soluble, ashless, halogen-, boron-, and phosphorus-free ammonium or amine salt, distinct from component (C).

22. A method for operating an internal combustion engine comprising fueling said engine with the fuel composition of claim 1.

* * * * *