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(54) PROCESS FOR MAKING AQUEOUS HYDROCARBON FUEL COMPOSITIONS AND AQUEOUS HYDROCARBON FUEL COMPOSITIONS

VERFAHREN ZUM HERSTELLEN VON KOHLENWASSERSTOFFBRENNSTOFFZUSAMMENSETZUNGEN UND WÄSSIGRE BRENNSTOFFZUSAMMENSETZUNGEN

PROCEDE POUR PREPARER DES COMPOSITIONS DE COMBUSTIBLE HYDROCARBONE AQUEUSES ET COMPOSITIONS AQUEUSES DE COMBUSTIBLE HYDROCARBONE

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(56) References cited:
WO-A-00/15740 **US-A- 4 708 753**
US-A- 5 873 916 **US-A- 6 068 670**

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Description

Technical Field

5 **[0001]** This invention relates to a process for making aqueous hydrocarbon fuel compositions. The invention also relates to stable aqueous hydrocarbon fuel compositions. The process is suitable for dispensing the fuels to end users in wide distribution network.

Background of the Invention

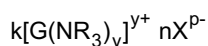
10 **[0002]** Internal combustion engines, especially diesel engines, using water mixed with fuel in the combustion chamber can produce lower NO_x, hydrocarbon and particulate emissions per unit of power output. However, a problem with adding water relates to the fact that emulsions form in the fuel and these emulsions tend to be unstable. This has reduced the utility of these fuels in the marketplace. It would be advantageous to enhance the stability of these fuels sufficiently to make them useful in the marketplace. Another problem relates to the fact that due to the instability associated with these fuels, it is difficult to make them available to end users in a wide distribution network. The fuels tend to break down before they reach the end user. It would be advantageous to provide a process and apparatus that could be used for blending these fuels at the dispensing site for the end user and therefore make the fuels available to end users in wide distribution networks.

20 **[0003]** US-A-4 708 753 describes a water-in-oil emulsion comprising as additive carboxylic acid or its anhydride, a reaction product of a polyisobutenyl succinic anhydride with an alkanol amine and ammonium nitrate.

Summary of the Invention

25 **[0004]** In one aspect, the invention provides a process for making an aqueous hydrocarbon fuel composition, comprising:

(A) mixing a normally liquid hydrocarbon fuel and at least one chemical additive to form a hydrocarbon fuel-additive mixture; the chemical additive comprising an emulsifier composition which comprises: (i) a combination of (i)(a) a first hydrocarbon fuel-soluble product made by reacting a first hydrocarbyl-substituted carboxylic acid acylating agent with alkanol amine, the hydrocarbyl substituent of said first acylating agent having 50 to 500 carbon atoms, and (i)(b) a second hydrocarbon fuel-soluble product made by reacting a second hydrocarbyl-substituted carboxylic acid acylating agent with at least one ethylene polyamine, the hydrocarbyl substituent of said second acylating agent having 50 to 500 carbon atoms; or a mixture of (i) and (ii) an ionic or a nonionic compound having a hydrophilic lipophilic balance of 1 to 10; in combination with (iii) a water-soluble salt distinct from (i) and (ii) represented by the formula



40 wherein: G is hydrogen or an organic group of 1 to 8 carbon atoms having a valence of y; each R Independently is hydrogen or a hydrocarbyl group of 1 to 10 carbon atoms; X^{p-} is an anion having a valence of p; and k, y, n and p are independently integers of at least 1; with the proviso that when G is H, y is 1; and the sum of the positive charge ky* being equal to the sum of the negative charge nX^{p-}; and

45 (B) mixing said hydrocarbon fuel-additive mixture with water under high-shear mixing conditions in a high shear mixer to form said aqueous hydrocarbon fuel composition, said aqueous hydrocarbon fuel composition including a discontinuous aqueous phase, said discontinuous aqueous phase being comprised of aqueous droplets having a mean diameter of 1.0 micron or less.

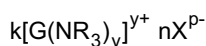
50 **[0005]** A critical feature of this invention relates to the fact that the aqueous phase droplets have a mean diameter of 1.0 micron or less. This feature is directly related to the enhanced stability characteristics of the inventive aqueous hydrocarbon fuel compositions.

55 **[0006]** Apparatus suitable for making the aqueous hydrocarbon fuel composition, comprises: a high shear mixer; a blend tank; a chemical additive storage tank and a pump and conduit for transferring a chemical additive from said chemical additive storage tank to said blend tank; a conduit for transferring a hydrocarbon fuel from a hydrocarbon fuel source to said blend tank; a conduit for transferring a hydrocarbon fuel-additive mixture from said blend tank to said high-shear mixer; a water conduit for transferring water from a water source to said high-shear mixer; a fuel storage tank; a conduit for transferring an aqueous hydrocarbon fuel composition from said high-shear mixer to said fuel storage

tank; a conduit for dispensing said aqueous hydrocarbon fuel composition from said fuel storage tank; and a programmable logic controller for controlling: (i) the transfer of said chemical additive from said chemical additive storage tank to said blend tank; (ii) the transfer of said hydrocarbon fuel from said hydrocarbon fuel source to said blend tank; (iii) the transfer of said hydrocarbon fuel-additive mixture from said blend tank to said high shear mixer; (iv) the transfer of water from said water source to said high shear mixer; (v) the mixing of said hydrocarbon fuel-additive mixture and said water in said high shear mixer; and (vi) the transfer of said aqueous hydrocarbon fuel composition from said high shear mixer to said fuel storage tank. The apparatus may also include a computer for controlling said programmable logic controller.

[0007] The apparatus can be in the form of a containerized equipment package or unit that operates automatically. This unit can be programmed and monitored locally at the site of its installation, or it can be programmed and monitored from a location remote from the site of its installation. The fuel is dispensed to end users at the installation site. This provides a way to make the aqueous hydrocarbon fuels compositions prepared in accordance with the invention available to end users in wide distribution networks.

[0008] In another aspect, the invention provides an aqueous hydrocarbon fuel composition, comprising: a continuous phase of a normally liquid hydrocarbon fuel; a discontinuous aqueous phase, said discontinuous aqueous phase being comprised of aqueous droplets having a mean diameter of 1.0 micron or less; and an emulsifying amount of an emulsifier composition comprising: (i) a combination of (i)(a) a first hydrocarbon fuel-soluble product made by reacting a first hydrocarbyl-substituted carboxylic acid acylating agent with an alkanol amine, the hydrocarbyl substituent of said acylating agent having 50 to 500 carbon atoms, and (i)(b) a second hydrocarbon fuel-soluble product made by reacting a second hydrocarbyl-substituted carboxylic acid acylating agent with at least one ethylene polyamine, the hydrocarbyl substituent of said second acylating agent having 50 to 500 carbon atoms; or a mixture of (i) and (ii) an ionic or a nonionic compound having a hydrophilic lipophilic balance of 1 to 10; in combination with (iii) a water-soluble salt distinct from (i) and (ii) represented by the formula



wherein: G is hydrogen or an organic group of 1 to 8 carbon atoms having a valence of y; each R independently is hydrogen or a hydrocarbyl group of 1 to 10 carbon atoms; X^{p-} is an anion having a valence of p; and k, y, n and p are independently integers of at least 1; with the proviso that when G is H, y is 1; and the sum of the positive charge ky^+ being equal to the sum of the negative charge nX^{p-} .

[0009] Preferably, component (i)(b) is combined with component (i)(a) in an amount from 0.05% to 0.95% based upon the total weight of component (i).

[0010] In the description below, we provide a detailed description of one embodiment of the inventive process and apparatus that can be used for the process. We also describe apparatus that is in the form of a containerized equipment package or unit. Further, the electronic communication between a plurality of programmable logic controllers associated with corresponding apparatus for operating the inventive process is described, the programmable logic controllers being located remotely from a programming computer communicating with such programmable logic controllers and a monitoring computer communicating with such programmable logic controllers.

[0011] One embodiment of the high shear mixer that may be used in accordance with the invention is described, this high shear mixer being a rotor-stator mixer having three rotor-stators arranged in series.

Detailed Description of the Preferred Embodiments

[0012] As used herein, the terms "hydrocarbyl substituent," "hydrocarbyl group," "hydrocarbyl-substituted," "hydrocarbon group," and the like, are used to refer to a group having one or more carbon atoms directly attached to the remainder of a molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include:

(1) purely hydrocarbon groups, that is, aliphatic (e.g., alkyl, alkenyl or alkylene), and alicyclic (e.g., cycloalkyl, cycloalkenyl) groups, aromatic groups, and aromatic-, aliphatic-, and alicyclic-substituted aromatic groups, as well as cyclic groups wherein the ring is completed through another portion of the molecule (e.g., two substituents together forming an alicyclic group);

(2) substituted hydrocarbon groups, that is, hydrocarbon groups containing non-hydrocarbon groups that, in the context of this invention, do not alter the predominantly hydrocarbon nature of the group (e.g., halo, hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

(3) hetero substituted hydrocarbon groups, that is, hydrocarbon groups containing substituents that, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteratoms include sulfur, oxygen, nitrogen. In general, no more than two,

and in one embodiment no more than one, non-hydrocarbon substituent is present for every ten carbon atoms in the hydrocarbon group.

5 [0013] The term "lower" when used in conjunction with terms such as alkyl, alkenyl, and alkoxy, is intended to describe such groups that contain a total of up to 7 carbon atoms.

[0014] The term "water-soluble" refers to materials that are soluble in water to the extent of at least one gram per 100 milliliters of water at 25°C.

10 [0015] The term "fuel-soluble" refers to materials that are soluble in a normally liquid hydrocarbon fuel (e.g. gasoline or diesel fuel) to the extent of at least one gram per 100 milliliters of fuels at 25°C. *[deletion(s)]*

The Process and Apparatus

15 [0016] The inventive process may be conducted on a batch basis or on a continuous basis. The process and apparatus described below relates to a batch process. The apparatus includes high shear mixer, blend tank, hydrocarbon fuel inlet, chemical additive storage tank, water storage tank, antifreeze agent storage tank, aqueous hydrocarbon fuel storage tank, and fuel dispenser.

[0017] Hydrocarbon fuel enters through hydrocarbon fuel inlet and flows to blend tank through conduit. Arranged in series along conduit between inlet and blend tank are isolation valve, pressure gauge, strainer, pump, solenoid valve, flow meter and totalizer, calibration outlet valve, check valve and isolation valve.

20 [0018] Conduit extends from chemical additive storage tank to blend tank and is adapted for transferring the chemical additive from chemical additive storage tank to blend tank. Arranged in series along conduit are isolation valve, quick disconnect, isolation valve, strainer, pump, solenoid valve, flow meter and totalizer, calibration outlet valve, check valve and isolation valve.

25 [0019] Conduit extends from water storage tank to connecting tee where it connects with conduit. Arranged in series along conduit between water storage tank and connecting tee are valves and strainer, pump, solenoid valve, flow meter and totalizer, calibration outlet valve, check valve, and isolation valve. Conduit extends from water inlet to water deionizer. Conduit extends from water deionizer to water storage tank. Conduit extends from antifreeze storage tank to connecting tee. Arranged in series along conduit between antifreeze agent storage tank and connecting tee are valves and strainer, pump, solenoid valve, flow meter and totalizer, check valve and isolation valve.

30 [0020] Conduit extends from connecting tee to connecting tee. Conduit extends from blend tank to connecting tee. Actuated valve is positioned between blend tank and connecting tee in conduit. Conduit extends from connecting tee to the inlet to high shear mixer. Check valve is located in conduit between connecting tee and the inlet to high shear mixer.

35 [0021] Conduit extends from the outlet to high shear mixer to aqueous hydrocarbon fuel storage tank. Arranged in series along conduit are throttling valve, connecting tee and actuated valve. Conduit extends from connector tee to blend tank. Actuated valve is positioned in conduit between connecting tee and blend tank. Conduit is provided for recycling the mixture of hydrocarbon fuel-additive mixture and water (and optionally antifreeze agent) back through blend tank and then again through high shear mixer.

40 [0022] Conduit extends from aqueous hydrocarbon fuel storage tank to connecting tee and is provided for recycling aqueous hydrocarbon fuel composition from tank back through high shear mixer when it is desired to subject the aqueous hydrocarbon fuel composition to additional high shear mixing. Arranged in series along conduit are isolation valve, actuated valve and calibration outlet valve. This recycling can be done to avoid undesired settling in tank after the aqueous hydrocarbon fuel composition has been blended.

45 [0023] Conduit extends from aqueous hydrocarbon fuel storage tank to fuel dispenser. Dispensing pump is connected to conduit and is positioned between aqueous hydrocarbon fuel storage tank and fuel dispenser. Dispensing pump is adapted for pumping the aqueous hydrocarbon fuel composition from aqueous hydrocarbon fuel storage tank to fuel dispenser. Users of the aqueous hydrocarbon fuel composition may obtain the fuel from dispenser.

50 [0024] A programmable logic controller (PLC), is provided for controlling: (i) the transfer of chemical additive from the chemical additive storage tank to blend tank ; (ii) the transfer of hydrocarbon fuel from hydrocarbon fuel inlet to the blend tank; (iii) the transfer of hydrocarbon fuel-additive mixture from the blend tank to high shear mixer; (iv) the transfer of water from the water storage tank to high shear mixer; (v) the mixing in high shear mixer of the hydrocarbon fuel-additive mixture and the water; and (vi) the transfer of the aqueous hydrocarbon fuel composition from the high shear mixer to the aqueous hydrocarbon fuel storage tank. When an antifreeze agent is used, the PLC controls the transfer of the antifreeze agent from the antifreeze agent storage tank to connecting tee where it is mixed with water from conduit. When it is desired to recycle the aqueous hydrocarbon fuel composition through mixer for additional high shear mixing, the PLC also controls such recycling. The PLC stores component percentages input by the operator. The PLC then uses these percentages to define volumes of each component required. A blending sequence is programmed into the PLC. The PLC electrically monitors all level switches, valve positions, and fluid meters.

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[0025] In operation, hydrocarbon fuel enters through inlet and flows through conduit to blend tank. The flow of the hydrocarbon fuel is controlled by the PLC that monitors and controls the flow of the hydrocarbon fuel by monitoring and controlling pump, solenoid valve, and flow meter and totalizer.

5 [0026] The chemical additive is transferred from chemical additive storage tank to blend tank through conduit. The flow of chemical additive through conduit is controlled by pump, solenoid valve, and flow meter and totalizer that are monitored and controlled by the PLC.

[0027] Water is transferred from the water storage tank to connecting tee through conduit. The flow of water from water storage tank to the connecting tee is controlled by pump, solenoid valve, and flow meter and totalizer, that are monitored and controlled by the PLC.

10 [0028] The antifreeze agent is used when the process is conducted in an environment where the water may freeze. When used the antifreeze agent is transferred from antifreeze storage tank to connecting tee through conduit. The flow of the antifreeze agent through conduit is controlled by pump, solenoid valve, and flow meter and totalizer, that are monitored and controlled by the PLC.

15 [0029] The hydrocarbon fuel and the chemical additive are mixed in blend tank. The resulting hydrocarbon fuel-additive mixture is transferred from blend tank to connecting tee through conduit. The flow of hydrocarbon fuel-additive mixture from blend tank is controlled by actuated valve that is controlled by the PLC. Water flows from connecting tee to connecting tee through conduit. The antifreeze agent, when used, mixes with the water in connecting tee and the resulting mixture of antifreeze agent and water flows to connecting. In connecting tee, the hydrocarbon fuel-additive mixture is mixed with the water and, if used, the antifreeze agent. Connecting tee is located at the entrance to high shear mixer. The mixture of hydrocarbon fuel-additive and water, and optionally antifreeze agent, is then transferred to high shear mixer wherein it is subjected to high shear mixing.

20 [0030] In one embodiment, the initial mixing of the hydrocarbon fuel-additive mixture and water (and optionally antifreeze agent) during step (B) of inventive process occurs in the high shear mixer or at the inlet to high shear mixer. In one embodiment, high shear mixing is commenced up to 15 seconds after such initial mixing, and in one embodiment 2 to 15 seconds, and in one embodiment 5 to 10 seconds after such initial mixing. The high shear mixing of the hydrocarbon fuel-additive mixture and water (and optionally antifreeze agent) results in the formation of the desired aqueous hydrocarbon fuel composition. A critical feature of the invention is that the water phase of the aqueous hydrocarbon fuel composition is comprised of droplets having a mean diameter of 1.0 micron or less. Thus, the high shear mixing is conducted under sufficient conditions to provide such a droplet size. In one embodiment, the mean droplet size is less than 0.95 micron, and in one embodiment less than 0.8 micron, and in one embodiment less than 0.7 micron. In a preferred embodiment, the mean droplet size is in the range of 0.01 to 0.95 micron, more preferably 0.01 to 0.8 micron, more preferably 0.01 to 0.7 micron. In an especially preferred embodiment, the droplet size is in the range of 0.1 to 0.7 micron.

25 [0031] The aqueous hydrocarbon fuel composition can be recycled through conduits, and tank in order to obtain the desired droplet size. This recycling is controlled by actuated valves that are controlled by the PLC. In one embodiment, the aqueous hydrocarbon fuel composition is recycled 1 to 35 times, and in one embodiment 1 to 10 times, and in one embodiment 1 to 5 times.

30 [0032] When the desired droplet size is achieved, the aqueous hydrocarbon fuel composition is stored in aqueous hydrocarbon fuel composition storage tank. The aqueous hydrocarbon fuel composition that is stored in storage tank is a stable emulsion that, in one embodiment, can remain stable for at least 90 days at a temperature of 25°C, and in one embodiment at least 60 days, and in one embodiment at least 30 days. The aqueous hydrocarbon fuel composition may be dispensed from storage tank through dispenser. The aqueous hydrocarbon fuel composition flows from storage tank to dispenser through conduit. The flow of the aqueous hydrocarbon fuel composition through conduit is controlled by pump.

35 [0033] The chemical additive storage tank has a low-level alarm switch incorporated into it. When the level in the tank drops below the low-level switch, a low-level alarm is activated. The batch in progress when the low-level alarm condition occurs is permitted to finish. This is possible because sufficient volume exists below the level of the switch to do a complete batch. Further batch blending is prevented until the low level is corrected and the alarm is reset.

40 [0034] When chemical additive is called for in the blending process, pump is started. This pump, that in one embodiment is a centrifugal pump, supplies chemical additive to the blend tank. If the pump fails to start or if its starter overload circuit trips, an alarm signal is sent to the PLC. The PLC shuts down the batch in progress and activates an alarm. Further operation is prevented until the fault is corrected.

45 [0035] In one embodiment, the flow meter of the flow meter and totalizer is an oval gear meter with high resolution. An electronic pulse pickup is utilized to read revolutions of the meter. The meter provides better than one electrical pulse per milliliter. An electronic factoring totalizer accumulates pulses generated by the meter. Calibrated during initial setup, the totalizer resolves the volumetric pulses into hundredths of gallons of chemical additive delivered. With each one hundredth of a gallon of flow, an electrical pulse is transmitted to the PLC. Based upon this flow the totalizer counts up to a target volume of chemical additive and then turns off the chemical additive flow.

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5 [0036] Solenoid valve controls the chemical additive flow. The PLC actuates this valve when additive flow is needed. Strainer in conduit prevents any solid contaminates from damaging the flow meter and totalizer. Valve, that may be a manually operated ball valve, is used to isolate the chemical additive during calibration and to throttle the flow of chemical additive. Valve, which may be a manually operated ball valve, is used to isolate a calibration tap. This tap is utilized to catch a volumetric sample during calibration of the totalizer of the flow meter and totalizer.

10 [0037] The antifreeze agent storage tank has a low-level alarm switch incorporated into it. When the level in the storage tank drops below the low-level switch, a low-level alarm is activated. The batch in progress when the low-level alarm condition occurs is permitted to complete. This is possible because sufficient volume exists below the level of the switch to do a complete batch. Further batch blending is prevented until the low level is corrected and the alarm is reset.

15 [0038] When antifreeze agent is called for in the blending process, pump is started. Pump, that in one embodiment is a centrifugal pump, supplies antifreeze agent to connecting tee where the antifreeze agent mixes with water from conduit. If pump fails to start or if its starter overload circuit trips, an alarm signal is sent to the PLC. The PLC shuts down the batch in progress and activates an alarm. Further batch blending is prevented until the fault is corrected and the alarm is reset.

20 [0039] In one embodiment, the flow meter of flow meter and totalizer is an oval gear meter with high resolution. An electronic pulse pickup is utilized to read revolutions of the meter. The meter provides better than one electrical pulse per milliliter. The totalizer, that is an electronic factoring totalizer, accumulates pulses generated by the meter. Calibrated during initial setup, the totalizer resolves the volumetric pulses into hundredths of gallons of antifreeze agent delivered. With each one hundredth of a gallon of flow, an electrical pulse is transmitted to the PLC. Based upon this flow the totalizer counts up to a target volume of antifreeze agent and turns off the antifreeze agent flow.

25 [0040] Solenoid valve controls the antifreeze agent flow. The PLC actuates this valve when the antifreeze agent flow is needed. Strainer in conduit prevents any solid contaminates from damaging flow meter and totalizer. Valve, that may be a manually operated ball valve, is used to isolate the antifreeze agent during calibration and to throttle flow of the antifreeze agent during normal operation. Valve, that may be a manually operated ball valve, is used to isolate a calibration tap. This tap is utilized to catch a volumetric sample during the calibration of the flow meter and totalizer.

30 [0041] In one embodiment, the water is deionized. For smaller volume demand systems water may be taken from a municipal supply and passed through a deionizing unit and then into storage tank. For high capacity systems, larger deionizing units may be used, or bulk delivery of water may be used. In one embodiment, water storage tank is a 550-gallon (2083.3-liter) maximum fill, stainless steel tote, or a similarly sized polymeric material tank.

35 [0042] The water storage tank has a low-level alarm switch incorporated into it. When the level in the water storage tank drops below the low-level switch, a low-level alarm is activated. The batch in progress when the low-level alarm condition occurs is permitted to complete. This is possible because sufficient volume exists below the level of the switch to do a complete batch. Further batch blending is prevented until the low level is corrected and the alarm is reset.

[0043] The water storage tank also has a high-level float switch in it. This switch is used in conjunction with a solenoid valve in the water supply line tank to automatically control re-filling of the water storage tank.

40 [0044] When water is called for in the blending process, pump is started. Pump, which may be a centrifugal pump, supplies water to connecting tee where the water mixes with the antifreeze agent when an antifreeze agent is used. If the pump fails to start or if its starter overload circuit trips, an alarm signal is sent to the PLC. The PLC shuts down the batch in progress and activates an alarm. Further batch blending is prevented until the fault is corrected and the alarm is reset.

45 [0045] In one embodiment, the flow meter of the flow meter and totalizer is an oval gear meter with moderately high resolution. An electronic pulse pickup is utilized to read revolutions of the meter. The meter can provide approximately 760 pulses per gallon (2878.8 pulses per liter) of water passing through it. The totalizer is an electronic factoring totalizer that accumulates pulses generated by the meter. Calibrated during initial setup, the totalizer resolves the volumetric pulses into tenths of gallons of water delivered. With each one tenth of a gallon of flow, an electrical pulse is transmitted to the PLC. Based upon this flow the PLC counts up to a target volume of water and turns off water flow.

50 [0046] Solenoid valve controls the water flow. The PLC actuates this valve when water is needed. Strainer in conduit prevents any solid contaminates from damaging the flow meter and totalizer. Valve, that may be a manually operated ball valve, is used to isolate the water during calibration and to throttle flow of the water components during normal operation. Valve, that may be a manually operated ball valve, isolates a calibration tap. This tap is utilized to catch a volumetric sample during the calibration of the totalizer of flow meter and totalizer.

55 [0047] When fuel is called for in the blending process, pump is started. This pump, that may be a centrifugal pump, supplies fuel to blend tank through conduit. If the pump fails to start or if its starter overload circuit trips, an alarm signal is sent to the PLC. The PLC shuts down the batch in progress and activates an alarm. Further batch blending is prevented until the fault is corrected and the alarm is reset.

[0048] In one embodiment, the flow meter of the flow meter and totalizer is an oval gear meter with moderately high resolution. An electronic pulse pickup is utilized to read revolutions of the meter. The meter can provide approximately

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135 pulses (511.4 pulses per liter) per gallon of fuel passing through it. The totalizer, that can be an electronic factoring totalizer, accumulates pulses generated by the meter. Calibrated during initial setup, the totalizer resolves the volumetric pulses into tenths of gallons of fuel delivered. With each one-tenth of a gallon of flow, an electrical pulse is transmitted to the PLC. Based upon this flow the controller counts up to a target volume of fuel and turns off fuel flow.

5 **[0049]** Solenoid valve controls fuel flow. The PLC actuates this valve when fuel is needed in the blend. Strainer in conduit prevents any solid contaminates from damaging the flow meter and totalizer. Valve, that may be a manually operated ball valve, is used to isolate the fuel during calibration and to throttle the flow of the fuel during normal operation. Valve, that may be a manually operated ball valve, is used to isolate a calibration tap. This tap is utilized to catch a volumetric sample during the calibration of the totalizer.

10 **[0050]** Blend tank, which in one embodiment may be a vertically oriented cylindrical steel tank, is used as a mixing vessel. In one embodiment, this tank has a capacity of approximately 130 gallons (492.4 liters). This tank may be equipped with two liquid level float switches. The high-level switch is used to warn the PLC if the tank has been overfilled during the blending process. This may occur if a flow meter fails. The low-level switch is used by the PLC to shut off high-shear mixer. Blend tank includes conduit and valve that are used for draining the contents of tank.

15 **[0051]** The high-shear mixer may be a rotor-stator mixer, an ultrasonic mixer or a high-pressure homogenizer. The rotor-stator mixer may be comprised of a first rotor-stator and a second rotor-stator arranged in series. The hydrocarbon fuel-additive mixture and water are mixed in the first rotor-stator and then the second rotor-stator to form the desired aqueous hydrocarbon fuel composition. In one embodiment, a third rotor-stator is arranged in series with the first rotor-stator and said second rotor-stator. The hydrocarbon fuel-additive mixture and water advance through the first rotor-stator, then through the second rotor-stator, and then through the third rotor-stator to form the aqueous hydrocarbon fuel composition.

20 **[0052]** In one embodiment, high-shear mixer is an in-line rotor-stator mixer. This mixer includes rotor-stators arranged in series. Mixer has an inlet, an outlet, a mechanical seal, a heating or cooling jacket, and an inlet to the heating or cooling jacket. Each of the rotor-stators has a rotor mounted coaxially within a stator. The rotors are rotated by a motor. The rotor-stators may have the same design or each may be different. Rotor and stator for rotor-stator have multi-
25 rowed arrays of teeth and arranged in concentric circles projecting from circular disks and, respectively. Rotor has an interior opening. Stator has an interior opening and an annular space defined by circular disk and projecting cylindrical wall. Cylindrical wall does not project as high as teeth. Rotor and stator are dimensioned so that the rotor fits inside the stator with the rotor teeth and the stator teeth being interleaved. The grooves between the teeth may be radial or
30 angled, continuous or interrupted. The teeth may have triangular, square, round, rectangular or other suitable profiles, with square and rectangular being particularly useful. The rotor rotates at a speed of up to 10,000 rpm, and in one embodiment 1000 to 10,000 rpm, and in one embodiment 4000 to 5500 rpm, relative to the stator that is stationary. The tangential velocity or tip speed of rotor ranges from 3000 to 15,000 feet per minute (914.4 to 457.2 meters per second), and in one embodiment 4500 to 5400 feet per minute (1371.6 to 1645.9 meters per second). The rotation of
35 the rotor draws the mixture of hydrocarbon fuel-additive mixture and water (and optionally antifreeze agent) axially through inlet into the center opening of rotor-stator, defined by opening, and disperses the mixture radially through the concentric circles of teeth and then out of rotor-stator. The mixture is then drawn through the center opening of rotor-stator and dispersed radially outwardly through the concentric circles of teeth in rotor-stator and then out of rotor-stator. The mixture is then drawn through the center opening of rotor-stator and dispersed radially outwardly through the
40 concentric circles of teeth in rotor-stator and then out of rotor-stator to outlet. The mixture that is advanced through the rotor-stators is subjected to high-speed mechanical and hydraulic shearing forces resulting in the formation of the desired aqueous hydrocarbon fuel composition. In one embodiment, the mixer is a Dispax-Reactor™ Model DR3 equipped with Ultra-Turrax™ UTL-T./8 rotor-stators supplied by IKA-Maschinenbau.

45 **[0053]** As indicated above, the high-shear mixer can be an ultrasonic mixer. In this mixer a liquid mixture of hydrocarbon fuel-additive mixture and water (and optionally antifreeze agent) is forced under high pressure (e.g., 2000 to 10,000 psig (103,401 to 517,006 mmHg), and in one embodiment 4000 to 6000 psig (206,802 to 310,203 mmHg) through an orifice at a high velocity (e.g., 100 to 400 feet per second (fps) (30.48 to 121.92 meters per second), and in one embodiment 150 to 300 fps (45.72 to 91.44 meters per second)), and directed at the edge of a blade-like obstacle in its path. Between the orifice and blade-like obstacle, the liquid mixture sheds vortices perpendicular to the original
50 flow vector. The shedding pattern alternates such that a steady oscillation, in the sonic range, occurs within the liquid mixture. The stresses set up within the liquid mixture by sonic oscillations cause the liquid mixture to cavitate in the ultrasonic frequency range. Examples of ultrasonic mixers that can be used include Triplex Sonilator Models™ XS-1500 and XS-2100 that are available from Sonic Corporation.

55 **[0054]** The high-shear mixer may be a high-pressure homogenizer. In such a mixer a mixture of the hydrocarbon fuel-additive mixture and water (and optionally antifreeze agent) is forced under high pressure (e.g., 10,000 to 40,000 psig (517,006 to 2,068,027 mmHg)) through a small orifice (e.g., 1/4 inch to 3/4 inch (0.635 to 1.905 cm) in diameter) to provide the desired mixing. An example of a useful homogenizer is available from Microfluidics International Corporation under the tradename Microfluidizer.

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[0055] The aqueous hydrocarbon fuel storage tank, in one embodiment, is a 550-gallon (2083.3-liter) stainless steel tote tank. This tank may have a normal maximum fill of 500 gallons (1893.9 liters), permitting room for thermal expansion of the blend if needed.

5 **[0056]** Three float-type level detection switches may be installed in tank. Switch, that is a high-level alarm switch guarantees that a shutdown and alarm shall occur if the storage tank level becomes abnormally high. Switch, that is a batch initiate level switch, may be positioned, for example, at the 400-gallon (1515.2-liter) level in the tank. When the amount of the aqueous hydrocarbon fuel composition drops to this level in the tank, the controller may be sent a signal that initiates the blending of a 100-gallon (378.8-liter) makeup batch. Finally, switch is a low-level switch located near the bottom of the tank. If the aqueous hydrocarbon fuel composition reaches this level, the pump is prevented from running.

10 **[0057]** The dispenser pump may be located on top of the aqueous hydrocarbon fuel storage tank. This pump, that in one embodiment may be a thirty-gallon-per-minute (113.64 liter per minute) pump, supplies fuel to the dispenser. Pump may be started by a nozzle stow switch located on dispenser. Should a low-level alarm occur in tank, pump is locked off by the PLC.

15 **[0058]** Dispenser may be a high capacity unit specifically designed for fleet fueling applications. The dispenser is placed in a position that facilitates vehicular traffic past it. The dispenser may have a manually resettable totalizer on it for indicating the total fuel dispensed into a vehicle. A one-inch (2.54 cm) hose (e.g., 30 feet (9.14 meters) in length) may be stored on a reel attached to the dispenser and used to dispense the fuel. An automatic shutoff nozzle may be used.

20 **[0059]** In one embodiment, the PLC is an Allen-Bradley™ SLC503 programmable logic controller. A communications adapter can be installed into the unit to allow it to be remotely accessed. The adapter can be an Allen-Bradley model 1747-KE module. To interface the communications adapter to a standard telephone line, an asynchronous personal computer (PC) modem may be used.

25 **[0060]** The process can be programmed and monitored on site or from a remote location using personal desktop computers. In this regard, multiple blending operations or units can be programmed and monitored from a remote location. For example, a PC1 (personal computer No. 1) can monitor the operation of N blending units (Unit 1, Unit 2, Unit N) and PC2 (personal computer No. 2) is used to program the operation of each blending unit. PC1 can be operated using Rockwell Software RSsql. PC2 can be operated using Rockwell Software RSlogix. PC1 and PC2 communicate with the PLC of each blending unit through phone lines using a card/modem. PC1 and PC2 may be run on Windows NT operating systems.

30 **[0061]** During operation, a record can be made for each of the aqueous hydrocarbon fuel compositions that are produced using PC1. This record may include the amount of each blend component used, the date and time the blend was completed, a unique batch identification number, and any alarms that may have occurred during the batch. In addition to the batch records, two running grand totals can be produced. One is the total amount of additive used in the batches and the other is the total aqueous hydrocarbon fuel composition produced. These two numbers can be used to reconcile against the batch totals to verify production.

35 **[0062]** Access of data may be begun automatically with PC1. On a preprogrammed interval, PC1 dials the telephone number of the blending unit. The blending unit modem answers the incoming call and links the PC1 to the blending unit. Data requested by PC1 is automatically transferred from the blending unit to PC1 via the telephone link. PC1 then disconnects the remote link. The data retrieved is transferred into an SQL (structured query language) compliant database in PC1. The data can then be viewed or reports generated using a number of commonly available software programs (e.g., Access or Excel from Microsoft, or SAP R/3 from SAP AG). **[deletion(s)]**

40 **[0063]** The operating parameters of the process (e.g., high-shear mixing time, amount of each component used per batch, etc.) are controlled by the PLC. The PLC can be programmed by PC2. These parameters can be changed using PC2.

45 **[0064]** In one embodiment, the apparatus is in the form of containerized equipment package or unit. The apparatus can be housed within an elongated rectangular housing that has access doors. The housing can be mounted on wheels to provide it with mobility for travel from one user's location to another, or it can be permanently mounted at one user's location. Within the housing, chemical additive storage tank and antifreeze agent storage tank are mounted next to each other adjacent one side wall of housing. Blending tank is mounted next to chemical additive storage tank. Pumps, and high-shear mixer are aligned side-by-side next to tanks. Pump is mounted next to blend tank. Aqueous hydrocarbon fuel composition storage tank is mounted next to high shear mixer and pump. Water storage tank and deionizer are mounted next to each other adjacent the other side wall of housing. Electrical controls for the PLC and a display for the PLC are mounted on housing walls. Dispenser is mounted exterior to the housing. The interconnections of the components of assembly and their operation are as described above.

The Aqueous Hydrocarbon Fuel Compositions

5 [0065] The aqueous hydrocarbon fuel compositions of the invention will now be described. These fuel compositions may be prepared in accordance with the foregoing process using the apparatus described above. The water used in forming these compositions can be from any convenient source. In one embodiment, the water is deionized prior to being mixed with the normally liquid hydrocarbon fuel and chemical additives. In one embodiment, the water is purified using reverse osmosis or distillation.

10 [0066] The water is present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of 5 to 40% by weight, and in one embodiment 10 to 30% by weight, and in one embodiment 15 to 25% by weight.

The Normally Liquid Hydrocarbon Fuel

15 [0067] The normally liquid hydrocarbon fuel may be a hydrocarbonaceous petroleum distillate fuel such as motor gasoline as defined by ASTM Specification D439 or diesel fuel or fuel oil as defined by ASTM Specification D396. Normally liquid hydrocarbon fuels comprising non-hydrocarbonaceous materials such as alcohols, ethers, organo-nitro compounds and the like (e.g., methanol, ethanol, diethyl ether, methyl ethyl ether, nitromethane) are also within the scope of this invention as are liquid fuels derived from vegetable or mineral sources such as corn, alfalfa, shale and coal. Normally liquid hydrocarbon fuels that are mixtures of one or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials are also contemplated. Examples of such mixtures are combinations of gasoline and ethanol and of diesel fuel and ether.

20 [0068] In one embodiment, the normally liquid hydrocarbon fuel is gasoline, that is, a mixture of hydrocarbons having an ASTM distillation range from 60°C. at the 10% distillation point to 205°C. at the 90% distillation point. In one embodiment, the gasoline is a chlorine-free or low-chlorine gasoline characterized by a chlorine content of no more than 10 ppm.

25 [0069] The diesel fuels that are useful with this invention can be any diesel fuel. These diesel fuels typically have a 90% point distillation temperature in the range of 300°C to 390°C, and in one embodiment 330°C to 350°C. The viscosity for these fuels typically ranges from 1.3 to 24 centistokes at 40°C. The diesel fuels can be classified as any of Grade Nos. 1-D, 2-D or 4-D as specified in ASTM D975. These diesel fuels may contain alcohols and esters. 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 specked in ASTM D2622-87. In one embodiment, the diesel fuel is a chlorine-free or low-chlorine diesel fuel characterized by a chlorine content of no more than 10 ppm.

30 [0070] The normally liquid hydrocarbon fuel is present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of 50 to 95% by weight, and in one embodiment 60 to 95% by weight, and in one embodiment 65 to 85% by weight, and in one embodiment 70 to 80% by weight.

The Chemical Additives

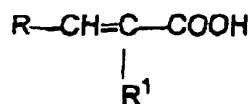
35 [0071] In one embodiment, the chemical additive used in accordance with the invention is an emulsifier composition as defined above. Mixtures of (i), (ii) and (iii) are preferred. This emulsifier composition is present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of 0.05 to 20% by weight, and in one embodiment 0.05 to 10% by weight, and in one embodiment 0.1 to 5% by weight, and in one embodiment 0.1 to 3% by weight, and in one embodiment 0.1 to 2.5% by weight.

The Hydrocarbon Fuel-Soluble Product (I)

40 [0072] The hydrocarbyl-substituted carboxylic acid acylating agent for the hydrocarbon fuel-soluble product (i) may be a carboxylic acid or a reactive equivalent of such acid. The reactive equivalent may be an acid halide, anhydride, or ester. Including partial esters and the like. The hydrocarbyl substituent for the carboxylic acid acylating agent may contain from 50 to 300 carbon atoms, and in one embodiment 60 to 200 carbon atoms. In one embodiment, the hydrocarbyl substituent of the acylating agent has a number average molecular weight of 750 to 3000, and in one embodiment 900 to 2000.

45 [0073] In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent for the hydrocarbon fuel soluble product (i) may be made by reacting one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing 2 to 20 carbon atoms, exclusive of the carboxyl groups, with one or more olefin polymers as described more fully hereinafter.

50 [0074] The alpha-beta olefinically unsaturated carboxylic acid reagents may be either monobasic or polybasic in nature. Exemplary of the monobasic alpha-beta olefinically unsaturated carboxylic acid include the carboxylic acids corresponding to the formula:



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wherein R is hydrogen, or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, preferably hydrogen or a lower alkyl group, and R¹ is hydrogen or a lower alkyl group. The total number of carbon atoms in R and R¹ typically does not exceed 18 carbon atoms. Specific examples of useful monobasic alpha-beta olefinically unsaturated carboxylic acids include acrylic acid; methacrylic acid; cinnamic acid; crotonic acid; 3-phenyl propenoic acid; alpha, and beta-decenoic acid. The polybasic acid reagents are preferably dicarboxylic, although tri- and tetracarboxylic acids can be used. Exemplary polybasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid. Reactive equivalents of the alpha-beta olefinically unsaturated carboxylic acid reagents include the anhydride, ester or amide functional derivatives of the foregoing acids. A preferred reactive equivalent is maleic anhydride.

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[0075] The olefin monomers from that the olefin polymers may be derived are polymerizable olefin monomers characterized by having one or more ethylenic unsaturated groups. They can be monoolefinic monomers such as ethylene, propylene, butene-1, isobutene and octene-1 or polyolefinic monomers (usually di-olefinic monomers such as butadiene-1,3 and isoprene). Usually these monomers are terminal olefins, that is, olefins characterized by the presence of the group >C=CH₂. However, certain internal olefins can also serve as monomers (these are sometimes referred to as medial olefins). When such medial olefin monomers are used, they normally are employed in combination with terminal olefins to produce olefin polymers that are interpolymers. Although, the olefin polymers may also include aromatic groups (especially phenyl groups and lower alkyl and/or lower alkoxy-substituted phenyl groups such as para(tertiary-butyl)-phenyl groups) and alicyclic groups such as would be obtained from polymerizable cyclic olefins or alicyclic-substituted polymerizable cyclic olefins, the olefin polymers are usually free from such groups. Nevertheless, olefin polymers derived from such interpolymers of both 1,3-dienes and styrenes such as butadiene-1,3 and styrene or para-(tertiary butyl) styrene are exceptions to this general rule.

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[0076] Generally the olefin polymers are homo- or interpolymers of terminal hydrocarbyl olefins of 2 to 30 carbon atoms, and in one embodiment 2 to 16 carbon atoms. A more typical class of olefin polymers is selected from that group consisting of homo- and interpolymers of terminal olefins of 2 to 6 carbon atoms, and in one embodiment 2 to 4 carbon atoms.

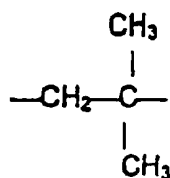
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[0077] Specific examples of terminal and medial olefin monomers that can be used to prepare the olefin polymers include ethylene, propylene, butene-1, butene-2, isobutene, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, pentene-2, propylene tetramer, diisobutylene, isobutylene trimer, butadiene-1,2, butadiene-1,3, pentadiene-1,2, pentadiene-1,3, isoprene, hexadiene-1,5, 2-chlorobutadiene-1,3, 2-methylheptene-1, 3-cyclohexylbutene-1, 3,3-dimethylpentene-1, styrene divinylbenzene, vinyl-acetate allyl alcohol, 1-methylvinylacetate, acrylonitrile, ethyl acrylate, ethylvinylether and methyl-vinylketone. Of these, the purely hydrocarbon monomers are more typical and the terminal olefin monomers are especially useful.

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[0078] In one embodiment, the olefin polymers are polyisobutylenes such as those obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75% by weight and an isobutene content of 30 to 60% by weight in the presence of a Lewis acid catalyst such as aluminum chloride or boron trifluoride. These polyisobutylenes generally contain predominantly (that is, greater than 50 percent of the total repeat units) isobutene repeat units of the configuration:

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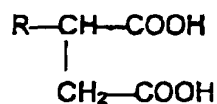
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[0079] In one embodiment, the olefin polymer is a polyisobutene group (or polyisobutylene group) having a number average molecular weight of 750 to 3000, and in one embodiment 900 to 2000.

[0080] In one embodiment, the acylating agent for the hydrocarbon fuel-soluble product (i) is a hydrocarbyl-substituted succinic acid or anhydride represented correspondingly by the formulae

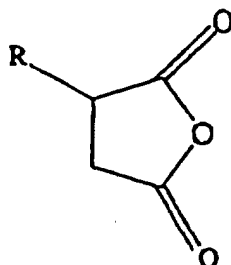
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or

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wherein R is hydrocarbyl group of 50 to 500 carbon atoms, and in one embodiment from 50 to 300, and in one embodiment from 60 to 200 carbon atoms. The production of these hydrocarbyl-substituted succinic acids or anhydrides via alkylation of maleic acid or anhydride or its derivatives with a halohydrocarbon or via reaction of maleic acid or anhydride with an olefin polymer having a terminal double bond is well known to those of skill in the art and need not be discussed in detail herein.

25

[0081] In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent for the product hydrocarbon fuel-soluble product (i) is a hydrocarbyl-substituted succinic acylating agent consisting of hydrocarbyl substituent groups and succinic groups. The hydrocarbyl substituent groups are derived from an olefin polymer as discussed above. The hydrocarbyl-substituted carboxylic acid acylating agent is characterized by the presence within its structure of an average of at least 1.3 succinic groups, and in one embodiment from 1.5 to 2.5, and in one embodiment from 1.7 to 2.1 succinic groups for each equivalent weight of the hydrocarbyl substituent

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[0082] For purposes of this invention, the equivalent weight of the hydrocarbyl substituent group of the hydrocarbyl-substituted succinic acylating agent is deemed to be the number obtained by dividing the number average molecular weight (M_n) of the polyolefin from which the hydrocarbyl substituent is derived into the total weight of all the hydrocarbyl substituent groups present in the hydrocarbyl-substituted succinic acylating agents. Thus, if a hydrocarbyl-substituted acylating agent is characterized by a total weight of all hydrocarbyl substituents of 40,000 and the M_n value for the polyolefin from which the hydrocarbyl 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.

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[0083] The ratio of succinic groups to equivalent of substituent groups present in the hydrocarbyl-substituted succinic acylating agent (also called the "succination ratio") can be determined by one skilled in the art using conventional techniques (such as from saponification or acid numbers). For example, the formula below can be used to calculate the succination ratio where maleic anhydride is used in the acylation process:

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$$\text{SR} = \frac{M_n \times (\text{Sap. No. of acylating agent})}{(56100 \times 2) - (98 \times \text{Sap. No. of acylating agent})}$$

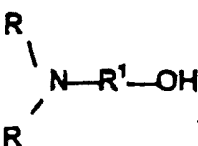
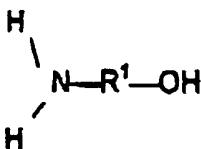
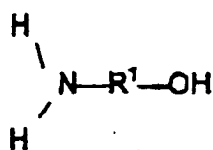
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In this equation, SR is the succination ratio, M_n is the number average molecular weight, and Sap. No. is the saponification number. In the above equation, Sap. No. of acylating agent = measured Sap. No. of the final reaction mixture/ AI wherein AI is the active ingredient content expressed as a number between 0 and 1, but not equal to zero. Thus an active ingredient content of 80% corresponds to an AI value of 0.8. The AI value can be calculated by using techniques such as column chromatography that can be used to determine the amount of unreacted polyalkene in the final reaction mixture. As a rough approximation, the value of AI is determined after subtracting the percentage of unreacted polyalkene from 100.

50

[0084] The hydrocarbon fuel-soluble product (i)(a) may be formed using an alkanol amine, typically primary, secondary or tertiary alkanolamines. The alkanol amines may be represented by the formulae:

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wherein in the above formulae each R is independently a hydrocarbyl group of 1 to 8 carbon atoms, or a hydroxyl-substituted hydrocarbyl group of 2 to 8 carbon atoms and each R¹ independently is a hydrocarbylene (i.e., a divalent hydrocarbon) group of 2 to 18 carbon atoms. The group —R¹—OH in such formulae represents the hydroxyl-substituted hydrocarbylene group. R¹ may be an acyclic, alicyclic, or aromatic group. In one embodiment, R¹ 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 may 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-(hydroxyl 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.

[0085] Suitable examples of the above alkanol amines include mono-, di-, and triethanolamine, dimethylethanolamine, diethylethanolamine, di-(3-hydroxyl propyl) amine, N-(3-hydroxyl butyl) amine, N-(4-hydroxyl butyl) amine, and N,N-di-(2-hydroxyl propyl) amine.

[0086] The hydrocarbon fuel-soluble product (i) may be a salt, an ester, 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 of the carboxyl groups 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 that is not part of the same molecule. In one embodiment, the amine is a hydroxyamine, the hydrocarbyl-substituted carboxylic acid acylating agent is a hydrocarbyl-substituted succinic anhydride, and the resulting hydrocarbon fuel-soluble product (i) is a half ester and half salt, i.e., an ester/salt.

[0087] The reaction between the hydrocarbyl-substituted carboxylic acid acylating agent and the alkanol amine is carried out under conditions that provide for the formation of the desired product. Typically, the hydrocarbyl-substituted carboxylic acid acylating agent and the alkanol amine are mixed together and heated to a temperature in the range of from 50°C to 250°C, and in one embodiment from 80°C to 200°C; optionally in the presence of a normally liquid, substantial inert organic liquid solvent/diluent, until the desired product has formed, in one embodiment, the hydrocarbyl substituted carboxylic acid acylating agent and the alkanol amine are reacted in amounts sufficient to provide from 0.3 to 3 equivalents of hydrocarbyl substituted carboxylic acid acylating agent per equivalent of amine. In one embodiment, this ratio is from 0.5:1 to 2:1, and in one embodiment 1:1.

[0088] In one embodiment, the hydrocarbon fuel-soluble product (i)(a) is made by reacting a polyisobutene-substituted succinic anhydride having an average of 1 to 3 succinic groups for each equivalent of polyisobutene group with diethanolamine or dimethylethanolamine in an equivalent ratio (i.e. carbonyl to amine ratio) of 1 to 0.4-1.25, and in one embodiment 1:1. The polyisobutene group has a number average molecular weight of 750 to 3000, and in one embodiment 900 to 2000.

[0089] Component : (i) is a combination of (i)(a) at least one reaction product of an acylating agent with an alkanol amine and (i)(b) at least one reaction product of an acylating agent with at least one ethylene polyamine.

[0090] More specifically, component (i)(a) is a hydrocarbon fuel-soluble product made by reacting an acylating agent

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with alkanol amine, wherein said alkanol amine is preferably a dimethylethanol amine or a diethylethanolamine. Preferably, component (i)(a) is made from a polyisobutylene group having a number average molecular weight (Mn) range of from 1500 to 3000, and that is maleinated or succinated in the range from 1.3 up to 2.5.

[0091] Component (i)(b) is a hydrocarbon fuel-soluble product made by reacting an acylating agent with at least one ethylene polyamine such as TEPA (tetraethylenepentamine), PEHA (pentaethylenhexaamine), TETA (triethylenetetramine), polyamine bottoms, or at least one heavy polyamine. The ethylene polyamine can be condensed to form a succinimide, as exemplified in Example 3. The equivalent ratio of the reaction for CO:N is from 1:1.5 to 1:0.5, more preferably from 1:1.3 to 1:0.70, and most preferably from 1:1 to 1:0.70, wherein CO:N is the carbonyl to amine nitrogen ratio. Also, component (i)(b) is preferably made from a polyisobutylene group having a number average molecular weight of from 700 to 1300 and that is succinated in the range from 1.0 up to 1.3.

[0092] The polyamines useful in reacting with the acylating agent for component (i)(b) can be aliphatic, cycloaliphatic, heterocyclic or aromatic compounds. Especially useful are the alkylene polyamines represented by the formula:



wherein n is from 1 to 10, preferably from 1 to 7; each R is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted hydrocarbyl, group having up to 700 carbon atoms, and in one embodiment up to 100 carbon atoms, and in one embodiment up to 50 carbon atoms, and in one embodiment up to 30 carbon atoms; and the "Alkylene" group has from 1 to 18 carbon atoms, and in one embodiment from 1 to 6 carbon atoms.

[0093] Heavy polyamines typically result from stripping of polyamine mixtures, to remove lower molecular weight polyamines and volatile components, to leave, as residue, what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below 200°C. In the instance of ethylene polyamine bottoms, which are readily available and found to be quite useful, the bottoms contain less than 2% (by weight) total diethylenetriamine (DETA) or triethylenetetramine (TETA), as set forth in U.S. Patent No. 5,912,213, incorporated herein by reference in its entirety. A typical sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Tex., designated "E-100" has a specific gravity at 15.6°C, of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C. of 121 centistokes. Gas chromatography analysis of such a sample showed it contains 0.93% "Light Ends" (most probably diethylenetriamine), 0.72% triethylene tetramine, 21.74% tetraethylenepentamine and 76.61% pentaethylenhexamine and higher (by weight). Another commercially available sample is from Union Carbide, known as HPA-X®. These alkylene polyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetramine and the like.

[0094] The term "heavy polyamine" can also refer to a polyamine that contains 7 or more nitrogens per molecule, or polyamine oligomers containing 7 or more nitrogens per molecule and with 2 or more primary amines per molecule, for example, as set forth in European Patent No. EP 0770098, incorporated herein by reference in its entirety.

[0095] In another embodiment, both i(a) and i(b) can each made from a higher molecular weight polyisobutylene group (meaning Mn greater than or equal to 1500, preferably from 1500 to 3000). In an alternative embodiment, components i(a) and i(b) can each made from a lower molecular weight polyisobutylene group (meaning Mn less than or equal to 1300, preferably from 700 to 1300).

[0096] In another embodiment, component i(a) is made from a polyisobutylene group having a number average molecular weight range of from 700 to 1300, and component i(b) is made from a polyisobutylene group having a Mn range of from 1500 to 3000.

[0097] Preferably, component (i)(b) is made by reacting (a succinic acylating agent with a polyamine) at a sufficient temperature to remove water and form a succinimide.

[0098] Preferably, component (i)(b) is combined with component (i)(a) in an amount from 0.05% to 0.95% based upon the total weight of component (i).

[0099] The following example illustrates the preparation of the component (i)(b).

Example

[0100] A reaction mixture composing 196 parts by weight of mineral oil, 280 parts by weight of a polyisobutenyl (M. W. 1000) -substituted succinic anhydride (0.5 equivalent) and 15.4 parts of a commercial mixture of ethylene polyamine having an average composition corresponding to that of tetra ethylene pentamine (0.375 equivalent) is mixed over a period of approximately fifteen minutes. The reaction mass is then heated to 150°C over a five-hour period and sub-

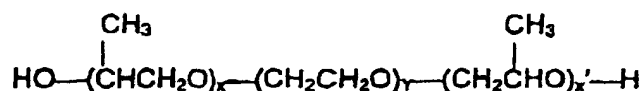
sequently blown with nitrogen at a rate of five parts per hour for five hours while maintaining a temperature of 150°C to 155°C to remove water. The material is then filtered producing 477 parts of product in oil solution.

[0101] The hydrocarbon fuel soluble product (i) may be present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of 0.1 to 15% by weight, and, in one embodiment, 0.1 to 10% by weight, and in one embodiment 0.1 to 5% by weight, and in one embodiment 0.1 to 2% by weight, and in one embodiment 0.1 to 1% by weight, and in one embodiment 0.1 to 0.7% by weight.

The Ionic or Nonionic Compound (ii)

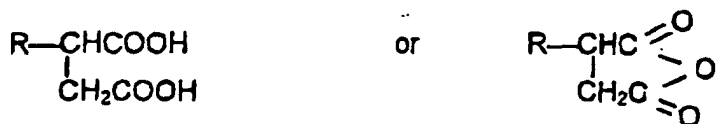
[0102] The ionic or nonionic compound (ii) has a hydrophilic lipophilic balance (HLB) in the range of 1 to 10, and in one embodiment 4 to 8. Examples of these compounds are disclosed in *McCutcheon's Emulsifiers and Detergents*, 1998, North American & International Edition. Pages 1-235 of the North American Edition and pages 1-199 of the International Edition disclose such ionic and nonionic compounds having an HLB in the range of 1 to 10. Useful compounds include alkanolamides, alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including block copolymers comprising alkylene oxide repeat units, carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkyl phenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fatty acid amides, glycerol esters, glycol esters, sorbitan 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, sulfosucanates and derivatives, and tridecyl and dodecyl benzene sulfonic acids.

[0103] In one embodiment, the ionic or nonionic compound (ii) is a poly(oxyalkene) compound. These include copolymers of ethylene oxide and propylene oxide. In one embodiment, the ionic or nonionic compound (ii) is a copolymer represented by the formula



wherein x and x' are the number of repeat units of propylene oxide and y is the number of repeat units of ethylene oxide, as shown in the formula. In one embodiment, x and x' are independently numbers in the range of zero to 20, and y is a number in the range of 4 to 60. In one embodiment, this copolymer has a number average molecular weight of 1800 to 3000, and in one embodiment 2100 to 2700.

[0104] In one embodiment, the ionic or nonionic compound (ii) is a hydrocarbon fuel-soluble product made by reacting an acylating agent having 12 to 30 carbon atoms with ammonia or an amine. The acylating agent may contain 12 to 24 carbon atoms, and in one embodiment 12 to 18 carbon atoms. The acylating agent may be a carboxylic acid or a reactive equivalent thereof. The reactive equivalents include acid halides, anhydrides, esters, and the like. These acylating agents may be monobasic acids or polybasic acids. The polybasic acids are preferably dicarboxylic, although tri- and tetra-carboxylic acids may be used. These acylating agents may be fatty acids. Examples include myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, and the like. These acylating agents may be succinic acids or anhydrides represented, respectively, by the formulae:



wherein each of the foregoing formulae R is a hydrocarbyl group of 10 to 28 carbon atoms, and in one embodiment 12 to 20 carbon atoms. Examples include tetrapropylene-substituted succinic acid or anhydride, hexadecyl succinic acid or anhydride, and the like. The amine may be any of the amines described above as being useful in making the hydrocarbon fuel-soluble product (i). The product of the reaction between the acylating agent and the ammonia or amine may be a salt, an ester, 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 of the carboxyl groups 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 that is not part of the same molecule. The reaction between the acylating agent and the

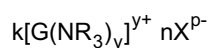
ammonia or amine is carried out under conditions that provide for the formation of the desired product. Typically, the acylating agent and the ammonia or amine are mixed together and heated to a temperature in the range of from 50°C to 250°C, and in one embodiment from 80°C to 200°C; optionally in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, until the desired product has formed. In one embodiment, the acylating agent and the ammonia or amine are reacted in amounts sufficient to provide from 0.3 to 3 equivalents of acylating agent per equivalent of ammonia or amine. In one embodiment, this ratio is from 0.5:1 to 2:1, and in one embodiment 1:1.

[0105] In one embodiment, the ionic or nonionic compound (ii) is an ester/salt made by reacting hexadecyl succinic anhydride with dimethylethanolamine in an equivalent ratio (i.e., carbonyl to amine ratio) of 1:1 to 1:1.5, and in one embodiment 1:1.35.

[0106] The ionic or nonionic compound (ii) may be present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of 0.01 to 15% by weight, and in one embodiment 0.01 to 10% by weight, and one embodiment 0.01 to 5% by weight, and in one embodiment 0.01 to 3% by weight, and in one embodiment 0.1 to 1% by weight.

The Water-Soluble Salt (iii)

[0107] The water-soluble salts (iii) are the amine or ammonium salts represented by the formula



wherein G is hydrogen or an organic group of 1 to 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 10 carbon atoms, and in one embodiment 1 to 5 carbon atoms, and in one embodiment 1 to 2 carbon atoms; X^{p-} is an anion having a valence of p; and k, y, n and p are independently integers of at least 1. When G is H, y is 1. The sum of the positive charge ky⁺ is equal to the sum of the negative charge nX^{p-}. In one embodiment, X is a nitrate ion; and in one embodiment it is an acetate ion. Examples include ammonium nitrate, ammonium acetate, methylammonium nitrate, methylammonium acetate, ethylene diamine diacetate, ureanitrate, and urea dinitrate. Ammonium nitrate is particularly useful.

[0108] In one embodiment, the water-soluble salt (iii) functions as an emulsion stabilizer, i.e., it acts to stabilize the aqueous hydrocarbon fuel compositions.

[0109] In one embodiment, the water-soluble salt (iii) functions as a combustion improver. A combustion improver is characterized by its ability to increase the mass burning rate of the fuel composition. Thus, the presence of such combustion improvers has the effect of improving the power output of an engine.

[0110] The water-soluble salt (iii) may be present in the aqueous hydrocarbon fuel compositions of the invention at a concentration of 0.001 to 1% by weight, and in one embodiment from 0.01 to 1% by weight.

Cetane Improver

[0111] In one embodiment, the aqueous hydrocarbon fuel composition of the invention contains a cetane improver. The cetane improvers that are useful include peroxides, nitrates, nitrites, nitrocarbmates, and the like. Useful cetane improvers include nitropropane, dinitropropane, tetranitromethane, 2-nitro-2-methyl-1-butanol, 2-methyl-2-nitro-1-propanol, and the like. Also included are nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols that may be monohydric or polyhydric. These include substituted and unsubstituted alkyl or cycloalkyl nitrates having up to 10 carbon atoms, and in one embodiment 2 to 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Examples 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-amyl nitrate, 3-amyl nitrate, tert-amyl 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, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also useful are the nitrate esters of alkoxy substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy) ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. A particularly useful cetane improver is 2-ethylhexyl nitrate.

[0112] The concentration of the cetane improver in the aqueous hydrocarbon fuel compositions of the invention can be any concentration sufficient to provide such compositions with the desired cetane number. In one embodiment, the concentration of the cetane improver is at a level of up to 10% by weight, and in one embodiment 0.05 to 10% by weight, and in one embodiment 0.05 to 5% by weight, and in one embodiment 0.05 to 1% by weight.

Additional Additives

[0113] In addition to the foregoing chemical additives, other additives that are well known to those of skill in the art can be used. These include antiknock agents such as tetraalkyl lead compounds, lead scavengers such as haloalkanes (e.g., ethylene dichloride and ethylene dibromide), ashless dispersants, deposit preventers or modifiers such as triaryl phosphates, dyes, cetane improvers, anti-oxidants such as 2,6-di-tertiary-butyl-4-methylphenol, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal deactivators, demulsifiers, upper cylinder lubricants and anti-icing agents. These chemical additives can be used at concentrations of up to 1% by weight based on the total weight of the aqueous hydrocarbon fuel compositions, and in one embodiment 0.01 to 1% by weight.

[0114] The total concentration of chemical additives in the aqueous hydrocarbon fuel compositions of the invention may range from 0.05 to 30% by weight, and in one embodiment 0.1 to 20% by weight, and in one embodiment 0.1 to 15% by weight, and in one embodiment 0.1 to 10% by weight, and in one embodiment 0.1 to 5% by weight.

Organic Solvent

[0115] The chemical additives may be diluted with a substantially inert, normally liquid organic solvent such as naphtha, benzene, toluene, xylene or a normally liquid hydrocarbon fuel as described above, to form an additive concentrate which is then mixed with the normally liquid hydrocarbon fuel pursuant to this invention. These concentrates generally contain from 10% to 90% by weight of the foregoing solvent. The aqueous hydrocarbon fuel compositions may contain up to 60% by weight organic solvent, and in one embodiment 0.01 to 50% by weight, and in one embodiment 0.01 to 20% by weight, and in one embodiment 0.1 to 5% by weight, and in one embodiment 0.1 to 3% by weight.

Antifreeze Agent

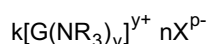
[0116] In one embodiment, the aqueous hydrocarbon fuel compositions of the invention contain an antifreeze agent. The antifreeze agent is typically an alcohol. Examples include ethylene glycol, propylene glycol, methanol, ethanol, and mixtures thereof. Methanol, ethanol and ethylene glycol are particularly useful. The antifreeze agent is typically used at a concentration sufficient to prevent freezing of the water used in the inventive composition. The concentration is therefore dependent upon the temperature at which the process is operated or the temperature at which the fuel is stored or used. In one embodiment, the concentration is at a level of up to 10% by weight, and in one embodiment 0.1 to 10% by weight of the aqueous hydrocarbon fuel composition, and in one embodiment 1 to 5% by weight.

[0117] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A process for making an aqueous hydrocarbon fuel composition, comprising:

(A) mixing a normally liquid hydrocarbon fuel and at least one chemical additive to form a hydrocarbon fuel-additive mixture; the chemical additive comprising an emulsifier composition which comprises: (i) a combination of (i)(a) a first hydrocarbon fuel-soluble product made by reacting a first hydrocarbyl-substituted carboxylic acid acylating agent with alkanol amine, the hydrocarbyl substituent of said first acylating agent having 50 to 500 carbon atoms, and (i)(b) a second hydrocarbon fuel-soluble product made by reacting a second hydrocarbyl-substituted carboxylic acid acylating agent with at least one ethylene polyamine, the hydrocarbyl substituent of said second acylating agent having 50 to 500 carbon atoms; or a mixture of (i) and (ii) an ionic or a nonionic compound having a hydrophilic lipophilic balance of 1 to 10; in combination with (iii) a water-soluble salt distinct from (i) and (ii) represented by the formula



wherein: G is hydrogen or an organic group of 1 to 8 carbon atoms having a valence of y; each R independently is hydrogen or a hydrocarbyl group of 1 to 10 carbon atoms; X^{p-} is an anion having a valence of p; and k, y, n and p are independently integers of at least 1; with the proviso that when G is H, y is 1; and the sum of the positive charge ky⁺ being equal to the sum of the negative charge nX^{p-}, and

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(B) mixing said hydrocarbon fuel-additive mixture with water under high-shear mixing conditions in a high shear mixer to form said aqueous hydrocarbon fuel composition, said aqueous hydrocarbon fuel composition including a discontinuous aqueous phase, said discontinuous aqueous phase being comprised of aqueous droplets having a mean diameter of 1.0 micron or less.

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2. The process of claim 1 wherein an antifreeze agent is added to said water, and then said hydrocarbon fuel-additive mixture is mixed with said water and said antifreeze agent during step (B) to form said aqueous hydrocarbon fuel composition.

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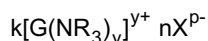
3. The process of claim 1 wherein said high shear mixer is a rotor-stator mixer comprising a first rotor-stator, a second rotor-stator and a third rotor-stator arranged in series, said fuel-additive mixture and said water being mixed in said first rotor-stator, then said second rotor-stator and then said third rotor-stator to form said aqueous hydrocarbon fuel composition.

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4. An aqueous hydrocarbon fuel composition, composing a continuous phase of a normally liquid hydrocarbon fuel; a discontinuous aqueous phase, said discontinuous aqueous phase being comprised of aqueous droplets having a mean diameter of 1.0 micron or less; and an emulsifying amount of an emulsifier composition comprising: (i) a combination of (i)(a) a first hydrocarbon fuel-soluble product made by reacting a first hydrocarbyl-substituted carboxylic acid acylating agent with an alkanol amine, the hydrocarbyl substituent of said acylating agent having 50 to 500 carbon atoms, and (i)(b) a second hydrocarbon fuel-soluble product made by reacting a second hydrocarbyl-substituted carboxylic acid acylating agent with at least one ethylene polyamine, the hydrocarbyl substituent of said second acylating agent having 50 to 500 carbon atoms; or a mixture of (i) and (ii) an ionic or a nonionic compound having a hydrophilic lipophilic balance of 1 to 10; in combination with (iii) a water-soluble salt distinct from (i) and (ii) represented by the formula

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wherein: G is hydrogen or an organic group of 1 to 8 carbon atoms having a valence of y; each R independently is hydrogen or a hydrocarbyl group of 1 to 10 carbon atoms; X^{p-} is an anion having a valence of p; and k, y, n and p are independently integers of at least 1; with the proviso that when G is H, y is 1; and the sum of the positive charge ky^+ being equal to the sum of the negative charge nX^{p-} .

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5. The aqueous hydrocarbon fuel composition of claim 4 wherein said normally liquid hydrocarbon fuel is a diesel fuel.

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6. The aqueous hydrocarbon fuel composition of claim 4 wherein said component (i) is a combination of (i)(a) at least one reaction product of an acylating agent with an alkanol amine selected from the group consisting of a dimethylethanolamine or diethylethanolamine and (i)(b) at least one reaction product of an acylating agent with at least one ethylene polyamine selected from the group consisting of TEPA, PEHA, or TETA.

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7. The aqueous hydrocarbon fuel composition of claim 4 wherein component (i) is a product made by reacting a polyisobutylene-substituted succinic acid or anhydride with a hydroxyamine wherein the polyisobutylene group has a number average molecular weight in the range of 750 to 3000.

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8. The aqueous hydrocarbon fuel composition of claim 4 wherein component (i) is comprised of (I) a first polyisobutene-substituted succinic acid or anhydride, the polyisobutene substituent of said first acid or anhydride having a number average molecular weight of 2000 to 2600, (II) a second polyisobutene-substituted succinic acid or anhydride, the polyisobutene substituent of said second acid or anhydride having a number average molecular weight of 700 to 1300, said polyisobutene-substituted succinic acids or anhydrides (I) and (II) being coupled together by (III) a linking group derived from ethylene glycol, said polyisobutene-substituted succinic acids or anhydrides (I) and (II) forming a salt with ammonia or an amine.

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9. The aqueous hydrocarbon fuel composition of claim 4 wherein component (ii) is a product made by reacting an acylating agent having 12 to 30 carbon atoms with ammonia or an amine.

10. The aqueous hydrocarbon fuel composition of claim 4 wherein component (iii) is ammonium nitrate.

11. The aqueous hydrocarbon fuel composition of claim 4 wherein the chemical additive further comprises a cetane

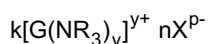
improver, antiknock agent, lead scavenger, ashless dispersant, deposit preventer or modifier, dye, anti-oxidant rust inhibitor, gum inhibitor, metal deactivator, demulsifier, upper cylinder lubricant or anti-icing agent.

12. A process for fueling an internal combustion engine comprising fueling said engine with the fuel composition of claim 4.

Patentansprüche

1. Verfahren zum Herstellen einer wässrigen Kohlenwasserstoffbrennstoffzusammensetzung, umfassend:

(A) Mischen eines normalerweise flüssigen Kohlenwasserstoffbrennstoffs und mindestens eines chemischen Additivs, um ein Kohlenwasserstoffbrennstoff-Additiv-Gemisch zu bilden, wobei das chemische Additiv eine Emulgatorzusammensetzung umfasst, die umfasst: (i) eine Kombination (i)(a) eines ersten Kohlenwasserstoffbrennstoff-löslichen Produkts, das dadurch hergestellt wird, dass ein erstes Hydrocarbyl-substituiertes Carbonsäure-Acylierungsmittel mit Alkanolamin umgesetzt wird, wobei der Hydrocarbylsubstituent des ersten Acylierungsmittels 50 bis 500 Kohlenstoffatome aufweist, und (i)(b) eines zweiten Kohlenwasserstoffbrennstoff-löslichen Produkts, das dadurch hergestellt wird, dass ein zweites Hydrocarbyl-substituiertes Carbonsäure-Acylierungsmittel mit mindestens einem Ethylenpolyamin umgesetzt wird, wobei der Hydrocarbylsubstituent des zweiten Acylierungsmittels 50 bis 500 Kohlenstoffatome aufweist, oder ein Gemisch von (i) und (ii) einer ionischen oder einer nichtionischen Verbindung mit einem Hydrophile-Lipophile-Gleichgewichtswert von 1 bis 10, zusammen mit (iii) einem wasserlöslichen Salz, das von (i) und (ii) verschieden ist und der Formel



entspricht, worin G ein Wasserstoffatom oder eine organische Gruppe mit 1 bis 8 Kohlenstoffatomen und einer Valenz von y ist, jede R-Gruppe unabhängig ein Wasserstoffatom oder eine Hydrocarbylgruppe mit 1 bis 10 Kohlenstoffatomen ist, X^{p-} ein Anion mit einer Valenz von p ist und k, y, n und p unabhängig voneinander ganze Zahlen mit einem Wert von mindestens 1 sind, mit der Maßgabe, dass, wenn G H ist, y den Wert 1 aufweist, und wobei die Summe der positiven Ladung ky^+ gleich zu der Summe der negativen Ladung nX^{p-} ist, und

(B) Mischen des Kohlenwasserstoffbrennstoff-Additiv-Gemischs mit Wasser unter Hochschermischbedingungen in einem Hochschermischer, um die wässrige Kohlenwasserstoffbrennstoffzusammensetzung zu bilden, wobei die wässrige Kohlenwasserstoffbrennstoffzusammensetzung eine diskontinuierliche wässrige Phase beinhaltet, wobei die diskontinuierliche wässrige Phase aus wässrigen Tröpfchen mit einem durchschnittlichen Durchmesser von 1,0 Micron oder weniger besteht.

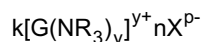
2. Verfahren nach Anspruch 1, wobei ein Antiegefriermittel zu dem Wasser gegeben wird und sodann das Kohlenwasserstoffbrennstoff-Additiv-Gemisch mit dem Wasser und dem Antiegefriermittel während des Schritts (B) gemischt wird, um die wässrige Kohlenwasserstoffbrennstoffzusammensetzung zu bilden.

3. Verfahren nach Anspruch 1, wobei der Hochschermischer ein Rotor-Stator-Mischer ist, umfassend einen ersten Rotor-Stator, einen zweiten Rotor-Stator und einen dritten Rotor-Stator, die in Reihe angeordnet sind, wobei das Brennstoff-Additiv-Gemisch und das Wasser in dem ersten Rotor-Stator, sodann dem zweiten Rotor-Stator und sodann dem dritten Rotor-Stator gemischt werden, um die wässrige Kohlenwasserstoffbrennstoffzusammensetzung zu bilden.

4. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung, umfassend eine kontinuierliche Phase eines normalerweise flüssigen Kohlenwasserstoffbrennstoffs, eine diskontinuierliche wässrige Phase, wobei die diskontinuierliche wässrige Phase aus wässrigen Tröpfchen mit einem durchschnittlichen Durchmesser von 1,0 Micron oder weniger besteht, und eine emulgierende Menge einer Emulgatorzusammensetzung, umfassend: (i) eine Kombination (i)(a) eines ersten Kohlenwasserstoffbrennstoff-löslichen Produkts, das dadurch hergestellt wird, dass ein erstes Hydrocarbyl-substituiertes Carbonsäure-Acylierungsmittel mit einem Alkanolamin umgesetzt wird, wobei der Hydrocarbylsubstituent des Acylierungsmittels 50 bis 500 Kohlenstoffatome aufweist, und (i)(b) eines zweiten Kohlenwasserstoffbrennstoff-löslichen Produkts, das dadurch hergestellt wird, dass ein zweites Hydrocarbyl-substituiertes Carbonsäure-Acylierungsmittel mit mindestens einem Ethylenpolyamin umgesetzt wird, wobei der Hy-

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drocarbylsubstituent des zweiten Acylierungsmittels 50 bis 500 Kohlenstoffatome aufweist, oder ein Gemisch von (i) und (ii) einer ionischen oder einer nichtionischen Verbindung mit einem Hydrophile-Lipophile-Gleichgewichtswert von 1 bis 10, zusammen mit (iii) einem wasserlöslichen Salz, das von (i) und (ii) verschieden ist und der Formel



entspricht, worin G ein Wasserstoffatom oder eine organische Gruppe mit 1 bis 8 Kohlenstoffatomen und einer Valenz von y ist, jede R-Gruppe unabhängig ein Wasserstoffatom oder eine Hydrocarbylgruppe mit 1 bis 10 Kohlenstoffatomen ist, X^{p-} ein Anion mit einer Valenz von p ist, und k, y, n und p unabhängig voneinander ganze Zahlen mit einem Wert von mindestens 1 sind, mit der Maßgabe, dass, wenn G H ist, y den Wert 1 aufweist, und wobei die Summe der positiven Ladung ky^+ gleich zu der Summe der negativen Ladung nX^{p-} ist.

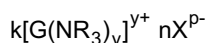
5. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei der normalerweise flüssige Kohlenwasserstoffbrennstoff ein Dieselmotortreibstoff ist.
6. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei die Komponente (i) eine Kombination (i)(a) mindestens eines Reaktionsprodukts eines Acylierungsmittels mit einem Alkanolamin, ausgewählt aus der Gruppe bestehend aus einem Dimethylethanolamin oder Diethylethanolamin, und (i)(b) mindestens eines Reaktionsprodukts eines Acylierungsmittels mit mindestens einem Ethylenpolyamin ist, das aus der Gruppe bestehend aus TEPA, PEHA oder TETA ausgewählt ist.
7. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei die Komponente (i) ein Produkt ist, das dadurch hergestellt wird, dass eine/ein Polyisobutyl-substituierte Bernsteinsäure oder -anhydrid mit einem Hydroxyamin umgesetzt wird, wobei die Polyisobutylengruppe ein Molekulargewicht-Zahlenmittel von 750 bis 3000 aufweist.
8. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei die Komponente (i) aus (I) einer/einem ersten Polyisobuten-substituierten Bernsteinsäure oder -anhydrid, wobei der Polyisobuten-substituent der ersten Säure oder des ersten Anhydrids ein Molekulargewicht-Zahlenmittel von 2000 bis 2600 aufweist, (II) einer/einem zweiten Polyisobuten-substituierten Bernsteinsäure oder -anhydrid, wobei der Polyisobuten-substituent der zweiten Säure oder des zweiten Anhydrids ein Molekulargewicht-Zahlenmittel von 700 bis 1300 aufweist, besteht, wobei die Polyisobuten-substituierten Bernsteinsäuren oder -anhydride (I) und (II) über (III) eine verbindende Gruppe, die von Ethylenglykol abstammt, zusammen verbunden sind, wobei die Polyisobuten-substituierten Bernsteinsäuren oder -anhydride (I) und (II) ein Salz mit Ammoniak oder einem Amin bilden.
9. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei die Komponente (ii) ein Produkt ist, das dadurch hergestellt wird, dass ein Acylierungsmittel mit 12 bis 30 Kohlenstoffatomen mit Ammoniak oder einem Amin umgesetzt wird.
10. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei die Komponente (iii) Ammoniumnitrat ist.
11. Wässrige Kohlenwasserstoffbrennstoffzusammensetzung nach Anspruch 4, wobei das chemische Additiv ferner ein Cetanverbesserungsmittel, ein Antiklopfmittel, einen Bleifänger, ein aschefreies Dispergiermittel, ein Ablagerungsverhinderungsmittel oder -modifizierungsmittel, einen Farbstoff, einen Antioxidierungs-Rostinhibitor, einen Stabilisator, einen Metalldeaktivator, einen Demulgator, ein Schmiermittel des oberen Zylinders oder ein Antiverseisungsmittel umfasst.
12. Verfahren zum Versorgen eines Verbrennungsmotors mit Brennstoff, umfassend ein Versorgen des Motors mit der Brennstoffzusammensetzung nach Anspruch 4.

Revendications

1. Procédé de fabrication d'une composition aqueuse de carburant hydrocarboné comprenant les opérations consistant à :

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(A) mélanger un carburant hydrocarboné normalement liquide et au moins un additif chimique pour former un mélange carburant hydrocarboné-additif ; l'additif chimique comprenant une composition d'émulsifiant qui comprend : (i) une combinaison de (i)(a), un premier produit soluble dans le carburant hydrocarboné fabriqué en mettant à réagir, un premier agent acylant acide carboxylique substitué par un hydrocarbyle avec une alcanolamine, le substituant hydrocarbyle dudit premier agent acylant ayant de 50 à 500 atomes de carbone, et (i)(b) un second produit soluble dans le carburant hydrocarboné fabriqué en mettant à réagir un second agent acylant acide carboxylique substitué par un hydrocarbyle avec au moins une éthylènepolyamine, le substituant hydrocarbyle dudit second agent acylant ayant de 50 à 500 atomes de carbone ; ou un mélange de (i) et (ii), un composé ionique ou non ionique ayant un équilibre hydrophile-lipophile de 1 à 10 ; en combinaison avec (iii), un sel hydrosoluble distinct de (i) et (ii) représenté par la formule



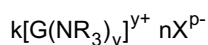
dans laquelle : G est un hydrogène ou un groupe organique de 1 à 8 atomes de carbone ayant une valence de y^- ; chaque R est indépendamment un hydrogène ou un groupe hydrocarbyle de 1 à 10 atomes de carbone ; X^{p-} est un anion ayant une valence de p ; et k, y, n et p sont indépendamment des entiers d'au moins 1 ; avec la condition que lorsque G est H, y soit 1 ; et la somme des charges positives ky^+ étant égale à la somme des charges négatives nX^{p-} , et

(B) mélanger ledit mélange carburant hydrocarboné-additif avec de l'eau dans des conditions de mélange à fort cisaillement dans un mélangeur à fort cisaillement pour former ladite composition aqueuse de carburant hydrocarboné, ladite composition aqueuse de carburant hydrocarboné comprenant une phase aqueuse discontinue, ladite phase aqueuse discontinue étant constituée de gouttelettes aqueuses ayant un diamètre moyen de 1,0 micromètre ou moins.

2. Procédé selon la revendication 1, dans lequel on ajoute un agent antigel à ladite eau, et on mélange ensuite ledit mélange carburant hydrocarboné-additif avec ladite eau et ledit agent antigel pendant l'étape (B) pour former ladite composition aqueuse de carburant hydrocarboné.

3. Procédé selon la revendication 1, dans lequel ledit mélangeur à fort cisaillement est un mélangeur rotor-stator comprenant un premier rotor-stator, un second rotor-stator et un troisième rotor-stator disposés en série, ledit mélange carburant-additif et ladite eau étant mélangés dans ledit premier rotor-stator, ensuite dans ledit second rotor-stator et ensuite dans ledit troisième rotor-stator pour former ladite composition aqueuse de carburant hydrocarboné.

4. Composition aqueuse de carburant hydrocarboné, comprenant : une phase continue d'un carburant hydrocarboné normalement liquide ; une phase aqueuse discontinue, ladite phase aqueuse discontinue étant constituée de gouttelettes aqueuses ayant un diamètre moyen de 1,0 micromètre ou moins ; et une quantité émulsifiante d'une composition d'émulsifiant comprenant : (i) une combinaison de (i)(a), un premier produit soluble dans le carburant hydrocarboné fabriqué en mettant à réagir un premier agent acylant acide carboxylique substitué par un hydrocarbyle avec une alcanolamine, le substituant hydrocarbyle dudit agent acylant ayant de 50 à 500 atomes de carbone, et (i)(b) un second produit soluble dans le carburant hydrocarboné fabriqué en mettant à réagir un second agent acylant acide carboxylique substitué par un hydrocarbyle avec au moins une éthylènepolyamine, le substituant hydrocarbyle dudit second agent acylant ayant de 50 à 500 atomes de carbone ; ou un mélange de (i) et (ii), un composé ionique ou non ionique ayant un équilibre hydrophile-lipophile de 1 à 10 ; en combinaison avec (iii), un sel hydrosoluble distinct de (i) et (ii) représenté par la formule



dans laquelle : G est un hydrogène ou un groupe organique de 1 à 8 atomes de carbone ayant une valence de y^- ; chaque R est indépendamment un hydrogène ou un groupe hydrocarbyle de 1 à 10 atomes de carbone ; X^{p-} est un anion ayant une valence de p ; et k, y, n et p sont indépendamment des entiers d'au moins 1 ; avec la condition que lorsque G est H, y soit 1 ; et la somme des charges positives ky^+ étant égale à la somme des charges négatives nX^{p-} .

5. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle ledit carburant hydrocarboné normalement liquide est un carburant Diesel.

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6. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle ledit composant (i) est une combinaison de (i)(a) au moins un produit de réaction d'un agent acylant avec une alcanolamine choisie dans le groupe constitué d'une diméthyléthanolamine ou diéthyléthanolamine, et (i)(b) au moins un produit de réaction d'un agent acylant avec au moins une éthylènepolyamine choisie dans le groupe constitué de TEPA, PEHA ou TETA.
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7. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle le composant (i) est un produit fabriqué en mettant à réagir un acide ou un anhydride succinique substitué par un polyisobutylène avec une hydroxylamine, le groupe polyisobutylène ayant une masse moléculaire moyenne en nombre dans la plage de 750 à 3000.
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8. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle le composant (i) est constitué de (I) un premier acide ou anhydride succinique substitué par un polyisobutylène, le substituant polyisobutylène dudit premier acide ou anhydride ayant une masse moléculaire moyenne en nombre de 2000 à 2600, (II) un second acide ou anhydride succinique substitué par un polyisobutylène, le substituant polyisobutylène dudit second acide ou anhydride ayant une masse moléculaire moyenne en nombre de 700 à 1300, lesdits acides ou anhydrides succiniques substitués par un polyisobutylène (I) et (II) étant couplés ensemble par (III) un groupe de liaison dérivé d'éthylèneglycol, lesdits acides ou anhydrides succiniques substitués par un polyisobutylène (I) et (II) formant un sel avec l'ammoniac ou une amine.
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9. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle le composant (II) est un produit fabriqué en mettant à réagir un agent acylant ayant de 12 à 30 atomes de carbone avec l'ammoniac ou une amine.
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10. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle le composant (III) est le nitrate d'ammonium.
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11. Composition aqueuse de carburant hydrocarboné selon la revendication 4, dans laquelle l'additif chimique comprend en outre un agent d'amélioration d'indice de cétane, un agent antidétonant, un balayeur de plomb, un dispersant sans cendres, un agent d'élimination ou de modification de dépôt, un colorant, un inhibiteur de rouille antioxydant, un inhibiteur de gommages, un désactivant des métaux, un désémulsifiant, un lubrifiant de cylindre supérieur et un agent dégivreur.
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12. Procédé de ravitaillement en carburant d'un moteur à combustion interne comprenant le ravitaillement dudit moteur avec la composition de carburant selon la revendication 4.

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