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(72) Inventors:
• **Oro-Urrea, Leire**
69006 Lyon (FR)
• **Magnin, César**
69700 Montigny (FR)

(71) Applicant: **Total France**
92800 Puteaux (FR)

(74) Representative: **Hirsch & Associés**
58, avenue Marceau
75008 Paris (FR)

(54) **Process and apparatus for making aqueous hydrocarbon fuel compositions**

(57) The invention relates to an apparatus for making an aqueous hydrocarbon fuel composition, comprising:
- a blend tank and a high shear mixer, for mixing a hydrocarbon fuel with an emulsifier and optionally a chemical additive to form a hydrocarbon fuel- emulsifier- optionally chemical additive mixture, and for mixing said hydrocarbon fuel-emulsifier- optionally chemical additive mixture with water to form said aqueous hydrocarbon fuel composition;
- an emulsifier storage tank and optionally a chemical additive storage tank and at least one pump and conduits for transferring said emulsifier from said emulsifier storage tank to said high shear mixer and optionally said chemical additive from said chemical additive storage

tank to said high shear mixer;
- a conduit for transferring said hydrocarbon fuel from a hydrocarbon fuel source to said blend tank;
- conduits and actuated valves for circulating said hydrocarbon fuel, said hydrocarbon fuel-emulsifier- optionally chemical additive mixture, and said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank;
- a water conduit for transferring said water from a water storage tank into said blend tank;
- an aqueous hydrocarbon fuel composition storage tank for storing said aqueous hydrocarbon fuel composition;
- a conduit for transferring said aqueous hydrocarbon fuel composition from said blend tank to said aqueous hydrocarbon fuel composition storage tank.

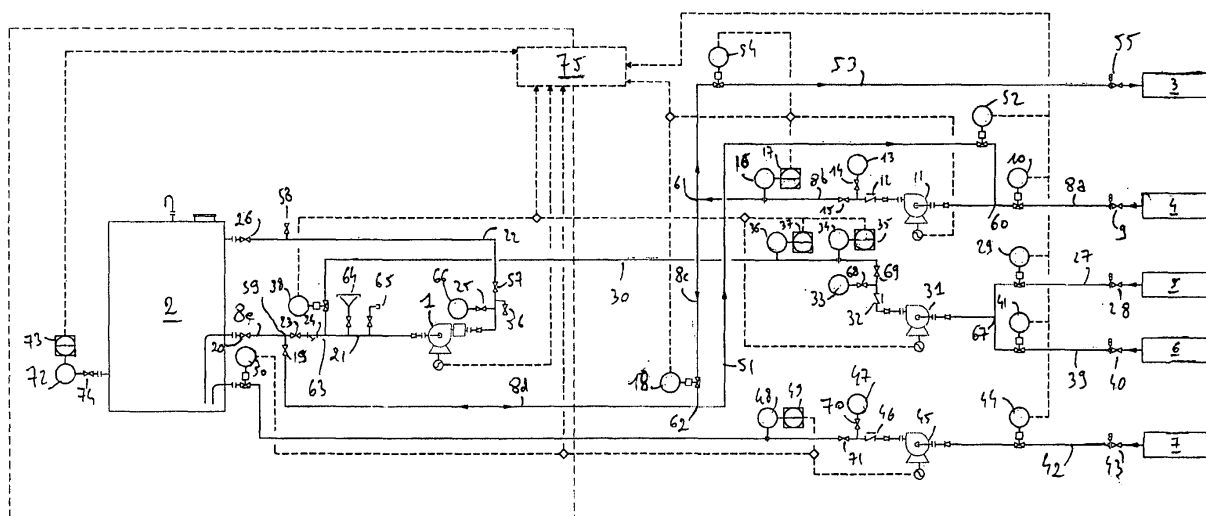


Figure 1

DescriptionTECHNICAL FIELD

5 **[0001]** This invention relates to a process and apparatus for making aqueous hydrocarbon fuel compositions. The process and apparatus are suitable for dispensing the fuels to end users in wide distribution networks, including captive fleets and rail off road applications.

TECHNICAL BACKGROUND

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. Another problem relates to the fact that due to the instability associated with
15 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.

[0003] US Patent No. 6,368,366 discloses a process and apparatus for producing fuel/water emulsions with increased stability. It would be advantageous to enhance even more the stability of these fuels to make them useful in the marketplace and to make the fuels available to end users in wide distribution networks.

SUMMARY OF THE INVENTION

[0004] The invention thus provides the following items.

- 25 **1.** An apparatus for making an aqueous hydrocarbon fuel composition, comprising:
- a blend tank and a high shear mixer, for mixing a hydrocarbon fuel with an emulsifier and optionally a chemical additive to form a hydrocarbon fuel-emulsifier-optionally chemical additive mixture, and for mixing said hydrocarbon fuel-emulsifier-optionally chemical additive mixture with water to form said aqueous hydrocarbon fuel composition;
 - 30 - an emulsifier storage tank and optionally a chemical additive storage tank and at least one pump and conduits for transferring said emulsifier from said emulsifier storage tank to said high shear mixer and optionally said chemical additive from said chemical additive storage tank to said high shear mixer;
 - a conduit for transferring said hydrocarbon fuel from a hydrocarbon fuel source to said blend tank;
 - 35 - conduits and actuated valves for circulating said hydrocarbon fuel, said hydrocarbon fuel-emulsifier-optionally chemical additive mixture, and said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank;
 - a water conduit for transferring said water from a water storage tank into said blend tank;
 - an aqueous hydrocarbon fuel composition storage tank for storing said aqueous hydrocarbon fuel composition;
 - 40 - a conduit for transferring said aqueous hydrocarbon fuel composition from said blend tank to said aqueous hydrocarbon fuel composition storage tank.
- 2.** The apparatus of item 1 wherein said water conduit is arranged to provide for the initial mixing of the hydrocarbon fuel-emulsifier-chemical additive mixture and water in the blend tank.
- 45 **3.** The apparatus of item 1 or 2, wherein the inflow extremity of said water conduit in said blend tank is situated below the inflow extremity of said conduit for transferring said hydrocarbon fuel in said blend tank.
- 4.** The apparatus of any one of items 1 to 3, wherein the inflow extremity of said water conduit in said blend tank is off-centered relative to the inflow extremity of said conduit for transferring said hydrocarbon fuel in said blend tank.
- 5.** The apparatus of any one of items 1 to 4, further comprising:
- 50
- a programmable logic controller for controlling: (i) the transfer of said hydrocarbon fuel from said hydrocarbon fuel source to said blend tank; (ii) the transfer of said emulsifier and optionally chemical additive from said emulsifier storage tank and optionally said chemical additive storage tank to said high shear mixer; (iii) the circulation of said hydrocarbon fuel and said emulsifier and optionally said chemical additive to said high shear mixer and back to said blend tank; (iv) the transfer of water from said water storage tank to said blend tank; (v) the circulation of said hydrocarbon fuel-emulsifier-optionally chemical additive mixture and water from said blend tank to said high shear mixer and back to said blend tank and the mixing in said high shear mixer of said hydrocarbon fuel-emulsifier-optionally chemical additive mixture and said water; and (vi) the transfer of said
- 55

aqueous hydrocarbon fuel composition from said high shear mixer to said aqueous hydrocarbon fuel composition storage tank.

6. The apparatus of item 5 wherein said apparatus further comprises a programming computer communicating with said programmable logic controller.

7. The apparatus of item 5 or 6 wherein said apparatus further comprises a monitoring computer communicating with said programmable logic controller.

8. The apparatus of any one of items 1 to 7, wherein said high shear mixer is a rotor-stator mixer.

9. The apparatus of any one of items 1 to 8, further comprising an antifreeze agent storage tank and a pump and conduit for transferring an antifreeze agent from said antifreeze agent storage tank to a mixing location wherein said antifreeze agent is mixed with water upstream said water storage tank.

10. The apparatus of item 9, wherein the transfer of said antifreeze agent from said antifreeze agent storage tank to said mixing location is controlled by a programmable logic controller.

11. The apparatus of any one of items 1 to 9, wherein the emulsifier is selected from the group consisting of at least one fuel-soluble product (i) made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl-substituted acylating agent having about 50 to about 500 carbon atoms, this fuel-soluble product, (ii) at least one of an ionic or non-ionic compound (ii) having a hydrophilic-lipophilic balance of about 1 to about 40, or (iii) a mixture of the above fuel soluble product (i) and of the above ionic or non ionic compound (ii).

12. A containerized equipment package, comprising: a housing and contained within said housing an apparatus according to any one of items 1 to 11 or a part thereof.

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

(A) flowing a stream of hydrocarbon fuel to a blend tank;

(B) circulating the hydrocarbon fuel from said blend tank to a high shear mixer and back to said blend tank, flowing a stream of emulsifier and optionally chemical additive to said high shear mixer, and mixing said emulsifier and optionally chemical additive with said hydrocarbon fuel, to form a hydrocarbon fuel-emulsifier-optional chemical additive mixture;

(C) flowing a stream of water to said blend tank and mixing it with said hydrocarbon fuel-emulsifier-chemical additive mixture to form said aqueous hydrocarbon fuel composition;

(D) circulating said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank, and mixing it in said high shear mixer, until a desired stability is obtained;

(E) transferring said aqueous hydrocarbon fuel composition from said blend tank to an aqueous hydrocarbon fuel composition storage tank;

wherein said process is carried out in an apparatus of any one of claims 1 to 10.

14. The process of item 12, wherein the flowing of said stream of water of step (C) is conducted while said hydrocarbon fuel-emulsifier-chemical additive mixture remains in said blend tank.

15. The process of item 12, wherein the flowing of said stream of water of step (C) comprises successively:

(C1) flowing a first portion of said stream of water while said hydrocarbon fuel-emulsifier-optional chemical additive mixture remains in said blend tank;

(C2) flowing a second portion of said stream of water while said hydrocarbon fuel-emulsifier-optional chemical additive mixture is circulated from said blend tank to said high shear mixer and back to said blend tank.

16. The process of item 14, wherein the weight amount of water in the blend tank at the end of step (C1) is comprised between 0.5 and 8 %, more preferably between 1 and 4 % and is most preferably of about 1% to about 2 %.

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

(A) flowing a stream of hydrocarbon fuel to a blend tank;

(B) circulating the hydrocarbon fuel from said blend tank to a high shear mixer and back to said blend tank, flowing a stream of emulsifier and optionally chemical additive to said high shear mixer, and mixing said emulsifier and optionally chemical additive with said hydrocarbon fuel, to form a hydrocarbon fuel-emulsifier-optional chemical additive mixture;

(C) flowing a stream of water to said blend tank and mixing it with said hydrocarbon fuel-emulsifier-chemical additive mixture to form said aqueous hydrocarbon fuel composition;

(D) circulating said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank, and mixing it in said high shear mixer, until a desired stability is obtained;

(E) transferring said aqueous hydrocarbon fuel composition from said blend tank to an aqueous hydrocarbon fuel composition storage tank;

wherein the flowing of said stream of water of step (C) comprises successively:

(C1) flowing a first portion of said stream of water while said hydrocarbon fuel-emulsifier-optional chemical additive mixture remains in said blend tank;

(C2) flowing a second portion of said stream of water while said hydrocarbon fuel-emulsifier-optional chemical additive mixture is circulated from said blend tank to said high shear mixer and back to said blend tank.

18. The process of item 16, wherein the weight amount of water in the blend tank at the end of step (C1) is comprised between 0.5 and 8 %, more preferably between 1 and 4 % and is most preferably of about 1% to about 2 %.

19. The process of any one of items 12 to 17, wherein said water is premixed with an antifreeze agent.

20. The process of any of items 12 to 18, wherein the emulsifier is:

- at least one fuel-soluble product (i) made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl-substituted acylating agent having about 50 to about 500 carbon atoms; or
- at least one of an ionic or non-ionic compound (ii) having a hydrophilic-lipophilic balance of about 1 to about 40; or
- a mixture (iii) of the fuel soluble product (i) and of the ionic or non ionic compound (ii) ; or
- a water-soluble compound (iv) selected from the group consisting of amine salts, ammonium, azide compounds, nitro compounds, nitrate esters, nitramine, alkali metal salts, alkaline earth metal salts and mixtures thereof in combination with (i), (ii) or (iii).

21. The process of any of items 12 to 18, wherein the emulsifier is a dehydrated product made by: (I) reacting (A) a hydrocarbyl substituted succinic acid or anhydride with (B) a polyol, a polyamine, a hydroxyamine, or a mixture of two or more thereof, to form a mixture of reaction water and a first intermediate product comprising: an ester, partial ester or a mixture thereof when (B) is a polyol; an amide, imide, salt, amide/salt, partial amide or mixture two or more thereof when (B) is a polyamine; or an ester, partial ester, amide, partial amide, amide/salt, imide, ester/salt, salt or a mixture of two or more thereof when (B) is a hydroxyamine, a mixture of a polyol and a polyamine, a mixture of polyol and a hydroxyamine, a mixture of a polyamine and a hydroxyamine, or a mixture of a polyol, a polyamine and a hydroxyamine; the hydrocarbyl substituent of said acid or anhydride having an average of about 8 to about 200 carbon atoms; and (II) heating said mixture at an effective temperature to separate substantially all of said water from said mixture and to form said dehydrated product, said dehydrated product having a water content of less than about 1 wt%, preferably less than 0.5 wt% and advantageously less than 0.25 wt%, most preferably less than 0.15 wt% and a total acid number of less than about 2, preferably less than about 0.25 mg of KOH/g.

22. The process of any one of items 13 to 21, wherein the emulsifier is selected from the group consisting of at least one fuel-soluble product (i) made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl-substituted acylating agent having about 50 to about 500 carbon atoms, this fuel-soluble product, (ii) at least one of an ionic or non-ionic compound (ii) having a hydrophilic-lipophilic balance of about 1 to about 40, or (iii) a mixture of the above fuel soluble product (i) and of the above ionic or non ionic compound (ii).

[0005] The invention is also directed to the emulsifier as recited in item 21 and to the associated process for manufacturing it.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] In **Figure 1** is shown a diagram of the apparatus for making an aqueous hydrocarbon fuel composition according to the invention.

[0007] In **Figure 2a** (front elevation), **Figure 2b** (top view) and **Figure 2c** (side elevation) is shown a blend tank used in the apparatus according to the invention.

[0008] The invention is also directed to the emulsifier as recited in item 21 and to the associated process for manufacturing it.

DESCRIPTION OF EMBODIMENTS

[0009] The invention will now be described in more detail without limitation in the following description.

[0010] Referring initially to **Fig. 1**, the apparatus includes high shear mixer **1**, blend tank **2**, hydrocarbon fuel storage tank **4** (which can be replaced by a hydrocarbon fuel dispenser or a hydrocarbon fuel source), emulsifier storage tank

5, water storage tank 7, chemical additive storage tank 6 and aqueous hydrocarbon fuel composition storage tank 3.

[0011] Hydrocarbon fuel storage tank 4 is connected to blend tank 2 via a conduit (adapted for transferring hydrocarbon fuel from hydrocarbon fuel storage tank 4 to blend tank 2) successively comprising first conduit section 8a, second conduit section 8b, third conduit section 8c, fourth conduit section 8d and fifth conduit section 8e. Arranged in series along this conduit between hydrocarbon fuel storage tank 4 and blend tank 2 are: on first conduit section 8a, isolation valve 9 and shut-off valve 10; on second conduit section 8b, pump 11, check valve 12, pressure gauge 13 (isolated from second conduit section 8b by valve 14), isolation valve 15, flow transmitter 16 and flow indicator 17; on third section 8c, shut-off valve 18; on fourth conduit section 8d, isolation valve 19; and on fifth conduit section 8e, isolation valve 20.

[0012] First conduit section 8a and second conduit section 8b are connected via connecting tee 60; second conduit section 8b and third conduit section 8c are connected via connecting tee 61; third conduit section 8c and fourth conduit section 8d are connected via connecting tee 62; fourth conduit section 8d and fifth conduit section 8e are connected via connecting tee 59.

[0013] Circulation circuit from blend tank 2 to high shear mixer 1 and back to blend tank 2 comprises: from blend tank 2 to high shear mixer 1, abovementioned fifth conduit section 8e (from blend tank 2 to connecting tee 59) and conduit 21 (from connecting tee 59 to high shear mixer 1); and from high shear mixer 1 to blend tank 2, conduit 22. Arranged in series along conduit 21 from connecting tee 59 to high shear mixer 1 are isolation valve 23, strainer 24, connecting tee 63, spare inlets 64 and 65. Arranged in series along conduit 22 from high shear mixer 1 to blend tank 2 are pressure gauge 66 (isolated from conduit 22 by valve 25), calibration outlet valve 56, isolation valve 57, sampling device valve 58 and isolation valve 26.

[0014] Emulsifier storage tank 5 is connected to conduit 21 via conduit 27 and conduit 30. Conduit 27 extends from emulsifier storage tank 5 to connection tee 67, while conduit 30 extends from connecting tee 67 to connecting tee 63.

[0015] Chemical additive storage tank 6 is connected to conduit 21 via conduit 39 and conduit 30. Conduit 39 extends from chemical additive storage tank 6 to connecting tee 67. The presence of at least one chemical additive being optional, chemical additive storage tank 6 and conduit 39 may be omitted from the apparatus. When present, the at least one chemical additive may comprise a cetane improver.

[0016] Arranged in series along conduit 27 from emulsifier storage tank 5 to connection tee 67 are isolation valve 28 and shut-off valve 29. Arranged in series along conduit 27 from chemical additive storage tank 6 to connecting tee 67 are isolation valve 40 and shut-off valve 41. Arranged in series along conduit 30 from connecting tee 67 to connecting tee 63 are pump 31, check valve 32, pressure gauge 33 (isolated from conduit 30 by valve 68), isolation valve 69, flow transmitter 34 and flow indicator 35, temperature transmitter 36 and temperature indicator 37, and shut-off valve 38.

[0017] Water storage tank 7 is connected to blend tank 2 via conduit 42. Arranged in series along conduit 42 from water storage tank 7 to blend tank 2 are isolation valve 43, shut-off valve 44, pump 45, check valve 46, pressure gauge 47 (isolated from conduit 42 by valve 70), isolation valve 71, flow transmitter 48 and flow indicator 49, and shut-off valve 50.

[0018] Blend tank 2 is connected to aqueous hydrocarbon fuel composition storage tank 3 successively via fifth conduit section 8e (from blend tank 2 to connecting tee 59), fourth conduit section 8d (from connecting tee 59 to connecting tee 62), conduit 51 (from connecting tee 62 to connecting tee 60), second conduit section 8b (from connecting tee 60 to connecting tee 61) and conduit 53 (from connecting tee 61 to aqueous hydrocarbon fuel composition storage tank 3).

[0019] Arranged along conduit 51 from connecting tee 62 to connecting tee 60 is shut-off valve 52. Arranged in series along conduit 53 from connecting tee 61 to aqueous hydrocarbon fuel composition storage tank 3 are shut-off valve 54 and isolation valve 55.

[0020] On blend tank 2 are arranged level transmitter 72 and level indicator 73 (isolated from blend tank 2 by valve 74).

[0021] A programmable logic controller (PLC) 75 is provided for controlling: (i) the transfer of hydrocarbon fuel from hydrocarbon fuel storage tank 4 to blend tank 2; (ii) the transfer of emulsifier from emulsifier storage tank 5 to conduit 21 while mixing with hydrocarbon fuel owing to high shear mixer 1; (iii) before, after or simultaneously with step (ii), the transfer of chemical additive (when used) from chemical additive storage tank 6 to conduit 21 while mixing with hydrocarbon fuel owing to high shear mixer 1; (iv) the transfer of water from water storage tank 7 to blend tank 2; (v) the transfer of hydrocarbon fuel-emulsifier-additive-water mixture from blend tank 2 to high shear mixer 1 and the mixing in high shear mixer 1 of the hydrocarbon fuel-emulsifier-additive-water mixture; (vi) the recycling of the aqueous hydrocarbon fuel composition from high shear mixer 1 to blend tank 2; and (vii) the transfer of the aqueous hydrocarbon fuel composition from blend tank 2 to aqueous hydrocarbon fuel composition storage tank 3.

[0022] An antifreeze agent may be used in association with water. If so, the PLC 75 may control the pre-mixing of the antifreeze agent with water. The PLC 75 stores component percentages input by the operator. The PLC 75 then uses these percentages to define volumes of each component required. A blending sequence is programmed into the PLC 75. The PLC 75 may electrically monitor all level switches, valve positions, and fluid meters.

[0023] In operation, hydrocarbon fuel flows from hydrocarbon fuel storage tank 4 and flows through conduit sections 8a, 8b, 8c, 8d and 8e to blend tank 2. The flow of the hydrocarbon fuel is controlled by the PLC 75 which monitors and controls the flow of the hydrocarbon fuel by monitoring and controlling shut-off valve 10 (open), shut-off valve 52 (closed), pump 11, flow transmitter 16 and flow indicator 17, shut-off valve 54 (closed), shut-off valve 18 (open), level transmitter

72 and level indicator **73**. Besides, during the flowing of hydrocarbon fuel from hydrocarbon fuel storage tank **4** to blend tank **2**, isolation valves **9**, **15**, **19** and **20** are open and isolation valve **23** is closed.

[0024] Then, hydrocarbon fuel is circulated from blend tank **2** to high shear mixer **1** via fifth conduit section **8e** and conduit **21** and back to blend tank **2** via conduit **22**. This circulation is controlled by high shear mixer **1** (turned on), level transmitter **72** and level indicator **73** which are monitored and controlled by PLC **75**. During this operation, isolation valves **20**, **23**, **57** and **26** are open, while isolation valve **19** is closed.

[0025] During this circulation, the emulsifier is transferred from emulsifier storage tank **5** to conduit **21** through conduits **27** and **30**. The flow of emulsifier is controlled by pump **31**, shut-off valve **29** (open), shut-off valve **41** (closed), flow transmitter **34** and flow indicator **35**, temperature transmitter **36** and temperature indicator **37**, as well as shut-off valve **38** (open), which are monitored and controlled by PLC **75**. As a result, the hydrocarbon fuel is mixed with the emulsifier in high shear mixer **1** and circulated back to blend tank **2**.

[0026] Either before or during or after said transfer of the emulsifier and said mixing of the emulsifier with the hydrocarbon fuel, the at least one chemical additive (when used) is transferred from chemical additive storage tank **6** to conduit **21** through conduits **39** and **30**. The flow of chemical additive is controlled by pump **31**, shut-off valve **29** (closed), shut-off valve **41** (open), flow transmitter **34** and flow indicator **35**, temperature transmitter **36** and temperature indicator **37**, as well as shut-off valve **38** (open), which are monitored and controlled by PLC **75**. As a result, the hydrocarbon fuel (optionally together with emulsifier) is mixed with the at least one chemical additive in high shear mixer **1** and circulated back to blend tank **2**.

[0027] Alternatively, both the emulsifier transfer operation and the chemical additive transfer operation may be conducted substantially simultaneously. In this case, the flow of emulsifier and of chemical additive is controlled by pump **31**, shut-off valve **29** (open), shut-off valve **41** (open), flow transmitter **34** and flow indicator **35**, temperature transmitter **36** and temperature indicator **37**, as well as shut-off valve **38** (open), which are monitored and controlled by PLC **75**. Both the emulsifier and the at least one chemical additive are substantially simultaneously mixed with the hydrocarbon fuel in high shear mixer **1**.

[0028] In a next step, water is mixed with the previously obtained hydrocarbon fuel-emulsifier-chemical additive mixture. An antifreeze agent may be used when the process is conducted in an environment where the water may freeze. When used, the antifreeze agent is mixed with water prior to the transfer of water into blend tank **2**. Optionally, the mixing of water with the antifreeze agent may be controlled by the PLC. Optionally, a separate storage and conduit may be foreseen for the anti-freeze for separate addition.

[0029] The mixing of hydrocarbon fuel (plus emulsifier and chemical additive) with water can be conducted in three main possible ways:

1) Batch injection.

[0030] According to this embodiment, high shear mixer **1** is first switched off. Then water is transferred from water storage tank **7** to blend tank **2**. The flow of water from water storage tank **7** to blend tank **2** is controlled by pump shut-off valve **44** (open), pump **45**, flow transmitter **48** and flow indicator **49**, as well as shut-off valve **50** (open), which are monitored and controlled by PLC **75**. Isolation valves **43** and **71** are also open during this operation (while isolation valve **20** can remain open). Once the transfer of water has been completed, high shear mixing **1** is turned on again, and the hydrocarbon fuel-emulsifier-chemical additive mixture and the water are circulated from blend tank **2** to high shear mixer **1** via fifth conduit section **8e** and conduit **21** and back to blend tank **2** via conduit **22**. This circulation is controlled by high shear mixer **1** (on), level transmitter **72** and level indicator **73** which are monitored and controlled by PLC **75**. During this operation, isolation valves **20**, **23**, **57** and **26** are open, while isolation valve **19** is closed.

2) Continuous injection.

[0031] According to this embodiment, water is transferred from water storage tank **7** to blend tank **2** as described above while high shear mixer **1** is still in operation. As a result, water is transferred into blend tank **2** while the content of blend tank **2** is circulated to high shear mixer **1** (where it is subjected to high shear mixing) and back to blend tank **2**.

3) Combined injection.

[0032] According to this embodiment, high shear mixer **1** is first switched off. Part of the water is transferred from water storage tank **7** to blend tank **2** as described in relation with the batch injection embodiment. Preferably, at the end of this stage, blend tank **2** has a water content of from about 0.5 to about 8 wt%, more preferably of from about 1 to about 4 wt%, most preferably of about 1 to about 2 wt%. Then high shear mixer **1** is turned on and the rest of the water is injected as described in the continuous injection embodiment.

[0033] Once all the water has been transferred to blend tank **2**, whether by batch injection, continuous injection or

combined injection, high shear mixer **1** usually stays in operation (as well as circulation through fifth conduit section **8e** and conduits **21** and **22**) for a desired amount of time until a desired emulsion profile of the hydrocarbon fuel-water mixture (aqueous hydrocarbon fuel composition) is obtained.

[0034] An important feature of the invention is that the water phase of the aqueous hydrocarbon fuel composition is preferably 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 about 0.95 micron, and in one embodiment less than about 0.8 micron, and in one embodiment less than about 0.7 micron. In a preferred embodiment, the mean droplet size is in the range of about 0.01 to about 0.95 micron, more preferably about 0.01 to about 0.8 micron, more preferably about 0.01 to about 0.7 micron. In an especially preferred embodiment, the droplet size is in the range of about 0.1 to about 0.7 micron.

[0035] When the desired emulsion profile is obtained, the high shear mixer **1** is turned off, and circulation is stopped in the circulation circuit comprising fifth conduit section **8e** and conduits **21** and **22**. The aqueous hydrocarbon fuel composition is then transferred from blend tank **2** to aqueous hydrocarbon fuel composition storage tank **3**, successively via fifth conduit section **8e**, fourth conduit section **8d**, conduit **51**, second conduit section **8b** and conduit **53**. The flow of aqueous hydrocarbon fuel is controlled by shut-off valve **18** (closed), shut-off valve **52** (open), shut-off valve **10** (closed), pump **11**, flow transmitter **16** and flow indicator **17**, as well as shut-off valve **54** (open), which are monitored and controlled by PLC **75**. During this operation, isolation valves **20**, **19**, **51** and **55** are open while isolation valve **23** is closed.

[0036] In another embodiment, not shown on the drawings, the high-shear mixer may be used as a pump for some of the components to be mixed and added. In this case, conduits are designed so that the storage are connected directly to the high-shear mixer, either before or after, depending on whether the components are to be added to the tank, either at the top or the bottom, or are to be withdrawn from the tank.

[0037] In one embodiment, except for said programming computer, said apparatus of the invention is located at a fuel dispensing location, and said programming computer is located at a location remote from said fuel dispensing location, said programming computer communicating with said programmable logic controller using a telephone modem.

[0038] Making further reference to **Figures 2a to 2c**, blend tank **2** comprises a V-shaped sloping floor **101** and four side walls. Pipe **102** (corresponding to the extremity of conduit **22**) is provided in the top half of blend tank **2** for dispensing an inflow of fluid (hydrocarbon fuel, hydrocarbon fuel-emulsifier-chemical additive mixture or aqueous hydrocarbon fuel composition) from high shear mixer **1** (discharge of the circulation circuit). Pipe **103** (corresponding to the extremity of conduit **8e**) is provided in the bottom half of blend tank **2** for dispensing the initial inflow of hydrocarbon fuel from hydrocarbon fuel storage tank **4** as well as for the subsequent outflow of fluid towards high shear mixer **1**. The suction at the entry of pipe **103** occurs at or near the lowermost part of V-shaped floor **101**. Preferably, pipe **103** is aligned with the central edge of V-shaped floor **101**. Pipe **103** is preferably provided with an elbow in tank **2**. The injection end of pipe **103** preferably curves downwards (most preferably at an angle of about 90° relative to the axis of pipe **103**). Pipe **104** (corresponding to the extremity of conduit **42**) is also provided in the bottom half of blend tank **2** for the inflow of water from water storage tank **7**. Pipe **104** preferably goes through the same side wall of blend tank **2** as pipe **103**. It is preferably positioned under pipe **103** and off-centered, i.e. horizontally shifted (either to the left or to the right) relative to pipe **103**. The injection end **105** of pipe **104** preferably curves downwards (most preferably at an angle of about 45° relative to the axis of pipe **104**).

[0039] All valves used in the present apparatus are preferably classical valves, for example solenoid valves.

[0040] The emulsifier storage tank **5** and the chemical additive storage tank **6** have each a low level alarm switch incorporated into them. When the level in each 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.

[0041] When emulsifier and / or chemical additive is called for in the blending process, pump **31** is started. This pump, which in one embodiment is a volumetric pump, supplies chemical additive to blend tank **2**. 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.

[0042] 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 **7**. For high capacity systems, larger deionizing units may be used, or bulk delivery of water may be used. In one embodiment, water storage tank **7** is a 2080 liters maximum fill, stainless steel tote, or a similarly sized polymeric material tank.

[0043] The water storage tank **7** has a low level alarm switch incorporated into it. When the level in the water storage tank **7** 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.

[0044] The water storage tank **7** 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 7 to automatically control re-filling of the water storage tank 7.

[0045] When water is called for in the blending process, pump 45, which may be a volumetric pump, is started, and water is fed to blend tank 2. 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.

[0046] When fuel is called for in the blending process, pump 11 is started. This pump, which may be a volumetric pump, supplies fuel to blend tank 2. 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.

[0047] In one embodiment, blend tank 2 is made of stainless steel and has a capacity of approximately 7,000 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 2 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 1 and feed pumps. Blend tank 2 includes a conduit and valve which are used for draining the contents of the tank 2.

[0048] The high shear mixer 1 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.

[0049] According to one particular embodiment the high shear mixer 1 is the in-line rotor-stator mixer of the type described in Fig. 4A of US Patent No. 6,368,366, and corresponding disclosure at col. 9, lines 18-67.

[0050] When a dispenser is provided after the aqueous hydrocarbon fuel composition storage tank 3, a dispenser pump may be located on top of the aqueous hydrocarbon fuel composition storage tank. This pump, which in one embodiment may be a 110 liters per minute pump, supplies fuel to the dispenser. Said pump may be started by a nozzle stow switch located on the dispenser. Should a low-level alarm occur in the tank, the pump is locked off by the PLC.

[0051] The 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 hose (e.g., 30 feet 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.

[0052] As now regards the PLC, 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) may monitor the operation of N blending units (Unit 1, Unit 2... Unit N) and a PC2 (personal computer No. 2) may be used to program the operation of each blending unit. PC1 can be operated using Rockwell Software RSSL. 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.

[0053] During operation, a record can be made for each of the aqueous hydrocarbon fuel compositions that is 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.

[0054] 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).

[0055] 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.

[0056] The final aqueous hydrocarbon fuel composition may be as described in US Patent No. 6,368,366, which is incorporated herein by reference.

[0057] The emulsifier may be as described in US Patent No. 6,652,607, which is incorporated herein by reference.

[0058] In particular the emulsifier may be at least one fuel-soluble product (i) made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl-substituted acylating agent having

about 50 to about 500 carbon atoms, this fuel-soluble product (i) being more precisely described in col. 8 1.63 to col. 17 1.31 of US Patent No. 6,652,607.

[0059] The emulsifier may also be at least one of an ionic or non-ionic compound (ii) having a hydrophilic-lipophilic balance of about 1 to about 40, said ionic or non ionic compound (ii) being described in col. 17 1.32 to col. 18 1.63 of US Patent No. 6,652,607.

[0060] The emulsifier may also be a mixture (iii) of the above fuel soluble product (i) and of the above ionic or non ionic compound (ii).

[0061] The emulsifier may also be a water-soluble compound (iv) selected from the group consisting of amine salts, ammonium, azide compounds, nitro compounds, nitrate esters, nitramine, alkali metal salts, alkaline earth metal salts and mixtures thereof in combination with (i), (ii) or (iii), wherein the water soluble compound (iv) is described in col.18 1.64 to col. 19 1.42 of US Patent No. 6,652,607.

[0062] It is another object of the invention to provide a new emulsifier which may be used in the process described above. This new emulsifier is a dehydrated product made by:

(I) reacting (A) a hydrocarbyl substituted succinic acid or anhydride with (B) a polyol, a polyamine, a hydroxyamine, or a mixture of two or more thereof, to form a mixture of reaction water and a first intermediate product comprising: an ester, a partial ester or a mixture thereof when (B) is a polyol; an amide, imide, salt, amide/salt, partial amide or mixture of two or more thereof when (B) is a polyamine; or an ester, partial ester, amide, partial amide, amide/salt, imide, ester/salt, salt or a mixture of two or more thereof when (B) is a hydroxyamine, a mixture of a polyol and a polyamine, a mixture of a polyol and a hydroxyamine, a mixture of a polyamine and a hydroxyamine, or a mixture of a polyol, a polyamine and a hydroxyamine; the hydrocarbyl substituent of said acid or anhydride having an average of about 8 to about 200 carbon atoms; and

(II) heating said mixture (of reaction water and a first intermediate product) at an effective temperature to form a second intermediate product with water of reaction being formed, and separating substantially all of said water of reaction from said second intermediate product to form said dehydrated product, said dehydrated product having a water content of less than about 1 wt%, preferably less than 0.5 wt% and advantageously less than 0.25 wt%, most preferably less than 0.15 wt% and a total acid number of less than about 2, preferably less than about 0.25 mg of KOH/g.

[0063] This invention thus also relates to a process, comprising:

(I) reacting (A) a hydrocarbyl substituted succinic acid or anhydride with (B) a polyol, a polyamine, a hydroxyamine, or a mixture of two or more thereof, to form a mixture of reaction water and a first intermediate product comprising: an ester, partial ester or mixture thereof when (B) is a polyol; an amide, imide, salt, amide/salt, partial amide or mixture of two or more thereof when (B) is a polyamine; or an ester, partial ester, amide, partial amide, amide/salt, imide, ester/salt, salt or a mixture of two or more thereof when (B) is a hydroxyamine; a mixture of a polyol and a polyamine, a mixture of a polyol and a hydroxyamine, a mixture of a polyamine and a hydroxyamine, or a mixture of a polyol, a polyamine and a hydroxyamine; the hydrocarbyl substituent of said acid or anhydride having an average of about 8 to about 200 carbon atoms; and

(II) heating said mixture (of reaction water and a first intermediate product) at an effective temperature to separate substantially all of said water of reaction from said first intermediate product to form said dehydrated product, said dehydrated product having a water content of less than about 1 wt%, preferably less than 0.5 wt% and advantageously less than 0.25 wt%, most preferably less than 0.15 wt% and a total acid number of less than about 2, preferably less than about 0.25 mg of KOH/g.

[0064] This invention also relates to emulsions, comprising: an organic phase; an aqueous phase; and an emulsifying amount of the foregoing dehydrated product.

[0065] As indicated above, the inventive dehydrated reaction products are useful as emulsifiers in formulating emulsions for a wide variety of applications. These include one or more of the following: lubricants or functional fluids; fuels; paints; coatings; inks; caulks or adhesives; fertilizers or agricultural chemicals; refinery or oil-field products; mining products; explosives; commodity chemical manufacturing processes; and the like.

[0066] As used herein, the terms hydrocarbyl substituent, hydrocarbyl group, 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: purely hydrocarbon groups, that is, aliphatic (e.g., alkyl, alkenyl or alkylene), 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).

[0067] The term "lower" when used in conjunction with terms such as alkyl, alkenyl, alkoxy, and the like, is intended

to describe such groups that contain a total of up to 7 carbon atoms.

[0068] 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.

[0069] The term "oil soluble" refers to materials that are soluble in mineral oil to the extent of at least one gram per 100 milliliters of mineral oil at 25°C.

[0070] The term "total acid number" (TAN) refers to a measure of the amount of potassium hydroxide (KOH) needed to neutralize all of the acidity of a product or a composition. The measure is conducted according to the Test Method ASTM D664. This measurement procedure is substantially equivalent to the procedure described in U.S. Pat. Appl. No. 2004/0055677 (\$0021).

[0071] The term "total base number" (TBN) refers to a measure of the amount of acid (perchloric or hydrochloric) needed to neutralize the basicity of a product or a composition, expressed as KOH equivalents. It is measured using Test Method ASTM D 2896.

[0072] The number of "equivalents" of a hydrocarbyl substituted succinic acid or anhydride is dependent on the number of carboxylic functions (e.g., -C(=O)-) present in the acid or anhydride. Thus, the number of equivalents of acid or anhydride will vary with the number of succinic groups present therein. In determining the number of equivalents of acid or anhydride, those carboxylic functions which are not capable of reacting with the polyol, polyamine or hydroxyamine (B) are excluded. In general, however, there are two equivalents of acid or anhydride for each succinic group in the acid or anhydride. Conventional techniques are readily available for determining the number of carboxylic functions (e.g., acid number, saponification number) and, thus, the number of equivalents of the acid or anhydride available to react with component (B).

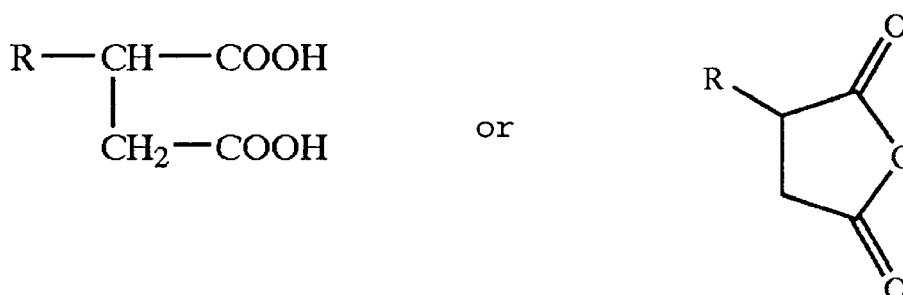
[0073] An "equivalent" of a polyol is that amount of polyol corresponding to the total weight of polyol divided by the total number of hydroxyl groups present. Thus, glycerol has an equivalent weight equal to one-third its molecular weight.

[0074] An "equivalent" of a polyamine is that amount of polyamine corresponding to the total weight of the polyamine divided by the number of nitrogen atoms present which are capable of reacting with a hydrocarbyl substituted succinic acid or anhydride. Thus, octylamine has an equivalent weight equal to its molecular weight; ethylene diamine has an equivalent weight equal to one-half of its molecular weight. The equivalent weight of a commercially available mixture of polyalkylene polyamines can be determined by dividing the atomic weight of nitrogen (14) by the % N contained in the polyamine; thus, a polyalkylene polyamine mixture having a % N of 34 would have an equivalent weight of 41.2.

[0075] An "equivalent" of a hydroxyamine is that amount of hydroxyamine corresponding to the total weight of hydroxyamine divided by the number of hydroxyl groups and nitrogen atoms present which are capable of reacting with a hydrocarbyl substituted succinic acid or anhydride. Thus, diethanolamine has an equivalent weight equal to one-third its molecular weight.

The dehydrated reaction product

[0076] The hydrocarbyl substituted succinic acid or anhydride (A) may be represented by the formulae



wherein in each of the above is a hydrocarbyl group of about 12 to about 200 carbon atoms, and in one embodiment about 12 to about 150 carbon atoms, and in one embodiment about 12 to about 100 carbon atoms, and in one embodiment about 12 to about 75 carbon atoms, and in one embodiment about 12 to about 50 carbon atoms, and in one embodiment about 18 to about 30 carbon atoms. In one embodiment, R is an alkyl or an alkenyl group.

[0077] In one embodiment, a mixture of at least two hydrocarbyl substituted succinic acids or anhydrides is used. The hydrocarbyl substituent of one of the acids or anhydrides has an average of about 12 to about 24 carbon atoms, and in one embodiment about 14 to about 18 carbon atoms, and in one embodiment about 16 carbon atoms. The hydrocarbyl substituent of the other acid or anhydride has an average of about 60 to about 200 carbon atoms, and in one embodiment about 60 to about 150 carbon atoms, and in one embodiment about 60 to about 100 carbon atoms, and in one embodiment

about 60 to about 75 carbon atoms.

[0078] The hydrocarbyl group R in the above formulae may be derived from an alpha-olefin or an alpha-olefin fraction. The alpha-olefins include 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-triacontene, and the like. The alpha olefin fractions that are useful include C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₆ alpha-olefins, C₁₄₋₁₆ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₈₋₂₄ alpha-olefins, C₁₈₋₃₀ alpha-olefins, and the like. Mixtures of two or more of any of the foregoing alpha-olefins or alpha-olefin fractions may be used.

[0079] In one embodiment, R in the above formulae is a hydrocarbyl group derived from an olefin oligomer or polymer. The olefin oligomer or polymer may be derived from an olefin monomer of 2 to about 10 carbon atoms, and in one embodiment about 3 to about 6 carbon atoms, and in one embodiment about 4 carbon atoms. Examples of the monomers include ethylene; propylene; butene-1; butene-2; isobutene; pentene-1; heptene-1; octene-1; nonene-1; decene-1; pentene-2; or a mixture of two of more thereof.

[0080] In one embodiment, R in the above formulae is a polyisobutene group. The polyisobutene group may be made by the polymerization of a C₄ refinery stream having a butene content of about 35 to about 75% by weight and an isobutene content of about 30 to about 60% by weight.

[0081] In one embodiment, R in the above formulae is a polyisobutene group derived from a polyisobutene having a high methylvinylidene isomer content, that is, at least about 50% and in one embodiment at least about 70% methylvinylidenes. Suitable high methylvinylidene polyisobutenes include those prepared using boron trifluoride catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high percentage of the total olefin composition is described in U.S. Pat. Nos. 4,152,499 and 4,605,808, the disclosure of each of which are incorporated herein by reference.

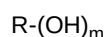
[0082] In one embodiment, the hydrocarbyl-substituted succinic acid or anhydride (A) consists of hydrocarbyl substituent groups and succinic groups. The hydrocarbyl substituent groups are derived from an olefin polymer as discussed above and, in one embodiment, have a number average molecular weight in the range of about 750 to about 3000, and in one embodiment about 900 to about 2000. The hydrocarbyl substituted succinic acid or anhydride is characterized by the presence within its structure of one succinic group for each equivalent weight of the hydrocarbyl substituent.

[0083] For purposes of this invention, the equivalent weight of the hydrocarbyl substituent group of the hydrocarbyl-substituted succinic acid or anhydride 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 acid or anhydride. 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 acid or anhydride is characterized by a total of 20 (40,000/2000=20) equivalent weights of substituent groups.

[0084] The ratio of succinic groups to equivalent of substituent groups present in the hydrocarbyl-substituted succinic acid or anhydride (also called the "succination ratio") may be determined by one skilled in the art using conventional techniques (such as from saponification or acid numbers). For example, the following formula can be used to calculate the succination ratio where maleic anhydride is used: $SR = [M_n \times (\text{Sap. No. of acylating agent})] / [(56100 \times 2) - (98 \times \text{Sap. No. of acylating agent})]$

[0085] 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 which 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.

[0086] In one embodiment, the polyol (B) is a compound represented by the formula

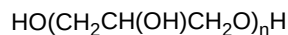


wherein in the foregoing formula, R is an organic group having a valency of m, R is joined to the OH groups through carbon-to-oxygen bonds, and m is an integer from 2 to about 10, and in one embodiment 2 to about 6. The polyol may be a glycol, a polyoxyalkylene glycol, a carbohydrate, or a partially esterified polyhydric alcohol. Examples of the polyols that may be used include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, 1,2-butanediol, 2,3-dimethyl-2,3-butanediol, 2,3-hexanediol, 1,2-cyclohexanediol, pentaerythritol, dipentaerythritol, 1,7-heptanediol, 2,4-heptanediol, 1,2,3-hexanetriol, 1,2,4-hexanetriol, 1,2,5-hexanetriol, 2,3,4-hexanetriol, 1,2,3-butanetriol, 1,2,4-butanetriol, 2,2,6,6-tetrakis-(hydroxymethyl)cyclohexanol, 1,10-decanediol, digitalose, 2-hydroxymethyl-2-methyl-1,3-propanediol-(trimethylolethane), or 2-hydroxymethyl-2-ethyl-1,3-propanediol-(tri-methylpropane), and the like. Mixtures of two or more of the foregoing

can be used.

[0087] In one embodiment, the polyol is a sugar, starch or mixture thereof. Examples of these include erythritol, threitol, adonitol, arabitol, xylitol, sorbitol, mannitol, erythrose, fucose, ribose, xylulose, arabinose, xylose, glucose, fructose, sorbose, mannose, sorbitan, glucosamine, sucrose, rhamnose, glyceraldehyde, galactose, and the like. Mixtures of two or more of the foregoing can be used.

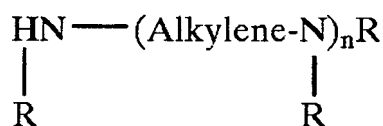
[0088] In one embodiment, the polyol is a compound represented by the formula



wherein n is a number in the range of 1 to about 5, and in one embodiment 1 to about 3. Examples include glycerol, diglycerol, triglycerol, and the like. Mixtures as well as isomers of the foregoing may be used.

[0089] In one embodiment, the polyol is a polyhydric alcohol having at least three hydroxyl groups, wherein some of the hydroxyl groups are esterified with an aliphatic monocarboxylic acid of about 8 to about 30 carbon atoms, but at least two of the hydroxyl groups are not esterified. Examples include monooleate of glycerol, monostearate of glycerol, monooleate of sorbitol, distearate of sorbitol, di-dodecanoate of erythritol, the like. Mixtures of two or more of the foregoing can be used.

[0090] The polyamine (B) may be aliphatic, cycloaliphatic, heterocyclic or aromatic compound. Examples include alkylene polyamines and heterocyclic polyamines. The alkylene polyamines may be represented by the formula



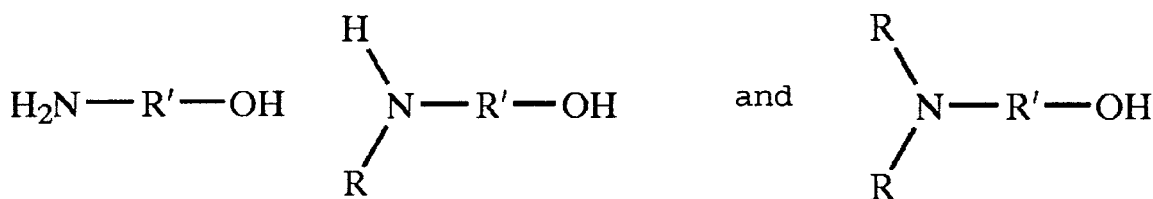
wherein n has an average value between 1 and about 10, and in one embodiment about 2 to about 7, the "Alkylene" group has from 1 to about 10 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms, and each R is independently hydrogen or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms. These alkylene polyamines include ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, etc. The higher homologs and related heterocyclic amines such as piperazines and N-amino alkylsubstituted piperazines are also included. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris-(2-aminoethyl)amine, propylene diamine, trimethylene diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylene hexamine, or a mixture of two or more thereof.

[0091] Ethylene polyamines, such as some of those mentioned above, are useful. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2nd Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Such polyamines are most conveniently prepared by the reaction of ethylene dichloride with ammonia or by reaction of an ethylene imine with a ring opening reagent such as water, ammonia, etc. These reactions result in the production of a complex mixture of polyalkylene polyamines including cyclic condensation products such as piperazines. Ethylene polyamine mixtures are useful.

[0092] The polyamine may also be a heterocyclic polyamine. Among the heterocyclic polyamines are aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetra hydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Useful heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl-substituted piperidines, piperazine, aminoalkyl-substituted piperazines, morpholine, aminoalkyl-substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are useful. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine.

[0093] The hydroxyamine (B) may be a primary, secondary or tertiary amine. The terms "hydroxyamine" and "aminoalcohol" describe the same class of compounds and, therefore, can be used interchangeably. In one embodiment, the hydroxyamine is (a) an N-(hydroxyl-substituted hydrocarbyl) amine, (b) a hydroxyl-substituted poly(hydrocarbyloxy) analog of (a), or a mixture of (a) and (b). The hydroxyamine may be alkanolamine containing from 1 to about 40 carbon atoms, and in one embodiment 1 to about 20 carbon atoms, and in one embodiment 1 to about 10 carbon atoms.

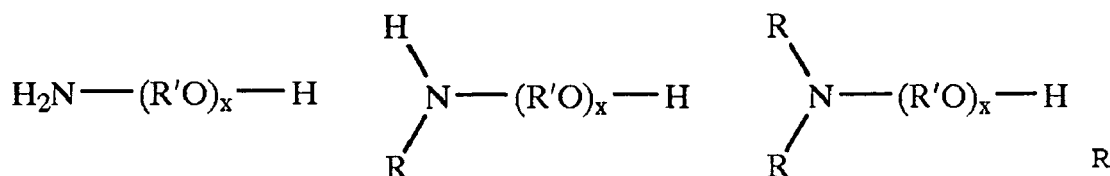
[0094] The hydroxyamine may be a primary, secondary or tertiary alkanol amine, or a mixture of two or more thereof. These hydroxyamines may be represented, respectively, by the formulae:



wherein each R is independently a hydrocarbyl group of one to about eight carbon atoms or hydroxyl-substituted hydrocarbyl group of two to about eight carbon atoms and R' is a divalent hydrocarbon group of about two to about 18 carbon atoms. Typically each R is a lower alkyl group of up to seven carbon atoms. The group -R'-OH in such formulae represents the hydroxyl-substituted hydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group.

[0095] Where two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like.

[0096] The hydroxyamines may be ether N-(hydroxy-substituted hydrocarbyl)amines. These may be hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-described hydroxy amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines may be conveniently prepared by reaction of epoxides with afore-described amines and may be represented by the formulae:



and R' are as described above.

[0097] Polyamine analogs of these hydroxy amines, particularly alkoxyated alkylene polyamines (e.g., N,N-(diethanol)-ethylene diamine) may be used. Such polyamines can be made by reacting alkylene amines (e.g., ethylenediamine) with one or more alkylene oxides (e.g., ethylene oxide, octadecene oxide) of two to about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also be used such as the products made by reacting the afore-described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1:1 or 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

[0098] Specific examples of alkoxyated alkylene polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl)-ethylene-diamine, 1-(2-hydroxyethyl) piperazine, mono(hydroxypropyl)-substituted diethylene triamine, di(hydroxypropyl)-substituted tetraethylene pentamine, N-(3-hydroxy butyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the aforesaid mono- or polyamines are also useful.

[0099] Examples of the N-(hydroxyl-substituted hydrocarbyl) amines include mono-, di-, and triethanolamine, dimethylethanolamine, diethylethanolamine, di-(3-hydroxypropyl)amine, N-(3-hydroxybutyl)amine, N-(4-hydroxybutyl)amine, N,N-di-(2-hydroxypropyl)amine, N-(2-hydroxyethyl)morpholine and its thio analog, N-(2-hydroxyethyl)cyclohexylamine, N-3-hydroxycyclopentyl amine, o-, m- and p-aminophenol, N-(hydroxyethyl) piperazine, N,N'-di(hydroxyethyl) piperazine, and the like.

[0100] Further hydroxyamines are the hydroxy-substituted primary amines described in U.S. Pat. No. 3,576,743 by the general formula $\text{R}_a\text{-NH}_2$, wherein R_a is a monovalent organic group containing at least one alcoholic hydroxy group. The total number of carbon atoms in R_a preferably does not exceed about 20. Hydroxy-substituted aliphatic primary amines containing a total of up to about 10 carbon atoms are useful. The polyhydroxy-substituted alkanol primary amines wherein there is only one amino group present (i.e., a primary amino group) having one alkyl substituent containing up to about 10 carbon atoms and up to about 6 hydroxyl groups are useful. These alkanol primary amines correspond to $\text{R}_a\text{-NH}_2$ wherein R_a is a mono-O or polyhydroxy-substituted alkyl group. It is desirable that at least one of the hydroxyl groups be a primary alcoholic hydroxyl group. Specific examples of the hydroxy-substituted primary amines include 2-

amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, N-(beta-hydroxypropyl)-N'-(beta-aminoethyl)-piperazine, tris-(hydroxymethyl) aminomethane (also known as trimethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethylamine, glucamine, glusoamine, 4-amino-3-hydroxy-3-methyl-1-butene (which can be prepared according to procedures known in the art by reacting isopreneoxide with ammonia), N-3(aminoethyl)-4-(2-hydroxyethyl)-piperazine, 2-amino-6-methyl-6-heptanol, 5-amino-1-pentanol, N-(beta-hydroxyethyl)-1,3-diaminopropane, 1,3-diamino-2-hydroxypropane, N-(beta-hydroxyethoxyethyl)-ethylenediamine, trimethylol aminomethane and the like.

[0101] Hydroxyalkyl alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful. Useful hydroxyalkyl-substituted alkylene polyamines include those in which the hydroxyalkyl group is a lower hydroxyalkyl group, i.e., having less than eight carbon atoms. Examples of such hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl) ethylene diamine, 1-(2-hydroxyethyl)-piperazine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropyl-substituted tetraethylene pentamine, N-(3-hydroxybutyl) tetramethylene diamine, etc. Higher homologs as are obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia and condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water.

[0102] The product of the reaction between components (A) and (B) during step (I) of the inventive process is a first intermediate product. This product may be an ester or a partial ester when component (B) is a polyol. This product may be an amide, imide, salt, amide/salt, partial amide or mixture of two or more thereof when (B) is a polyamine. This product may be an ester, partial ester, amide, partial amide, amide/salt, imide, ester/salt, salt, or a mixture of two or more thereof when component (B) is a hydroxyamine, a mixture of polyol and polyamine, a mixture of polyol and hydroxyamine, or a mixture of polyamine and hydroxyamine. The salt may be an internal salt involving residues of a molecule of the acid or anhydride and the polyamine or hydroxyamine 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. During step (I), components (A) and (B) are mixed together and heated at an effective temperature to form the foregoing first intermediate product. In one embodiment, the temperature is in the range of from about 30°C to about 120°C, and in one embodiment from about 50°C to about 90°C. The reaction time is typically from about 1 to about 120 minutes, and in one embodiment about 1 to about 60 minutes. Components (A) and (B) may be dispersed or dissolved in a normally liquid, substantially inert organic liquid solvent/diluent during the reaction. In one embodiment, components (A) and (B) are reacted in amounts sufficient to provide an equivalent ratio of (A) to (B) from about 3:1 to about 1:2. In one embodiment, this ratio is from about 1:1 to about 1:2, and in one embodiment about 1:1.4 to about 1:1.9.

[0103] During step (II) the mixture of water and first intermediate product from step (I) is heated at a sufficient temperature to separate substantially all of said water and said first intermediate product. The temperature may be in the range of about 130°C to about 210°C, and in one embodiment about 135°C to about 180°C. The reaction time of step (I) and step (II) is typically from about 3 to about 15 hours, and in one embodiment about 5 to about 7 hours. When (B) is a polyol, the second intermediate product comprises one or more bisesters, triesters or low order (about 2 to about 6, and in one embodiment about 2 to about 4) oligomers containing ester, or ester and acid functionality. When (B) is a polyamine, the second intermediate product comprises one or more bisamides, bisimides, amide/imide, or low order (about 2 to about 6, and in one embodiment about 2 to about 4) oligomers containing amide, imide, amide/imide, acid and/or salt functionality. When (B) is a hydroxyamine, the second intermediate product comprises one or more bisamides, bisesters, ester/amides or low order (about 2 to about 6, and in one embodiment about 2 to about 4) oligomers containing ester, amide, acid and/or salt functionality. When (B) is a mixture of a polyol, polyamine and/or hydroxyamine, the second intermediate product comprises one or more of the above-mentioned products depending upon which polyol, polyamine and/or hydroxyamine is used. During step (II) substantially all of the water of reaction is separated from the second intermediate product using known techniques (e.g., distillation, azeotropic removal of water, molecular sieves, etc.) to provide the desired dehydrated product. When component (A) is a succinic anhydride, the amount of water of reaction that is removed is generally from about 1.2 to about 1.3 moles of water per equivalent of succinic anhydride. When component (A) is a succinic acid, the amount of water of reaction that is removed is generally from about 2.2 to about 2.8 moles (for example about 2.5 moles) of water per equivalent of succinic acid.

[0104] The inventive reaction product may be added directly to the inventive emulsion. Alternatively, it may be diluted with a normally liquid organic diluent such as mineral oil, naphtha, benzene, or toluene to form an additive concentrate. The normally liquid organic diluent may be one or more of the precursors or reactants used to make the inventive reaction product, or one or more of the oils or fuels used to make the inventive emulsions described herein. The concentrate usually contains from about 10% to about 90% by weight of the inventive reaction product and may contain, in addition, one or more other additives known in the art or described herein.

[0105] Throughout the specification and in the claims, unless otherwise indicated, all parts and percentages are by

weight, all temperatures are in degrees Celsius (°C), and all pressures are at or near atmospheric.

Water-Blended Fuels

[0106] The inventive reaction products are useful as emulsifiers in making water-blended fuels (sometimes referred to as aqueous hydrocarbon fuels). These water-blended fuels are comprised of a continuous phase of a normally liquid hydrocarbon fuel, a discontinuous aqueous phase, and an emulsifying amount of the inventive reaction product.

[0107] The water used in making these water-blended fuels may be taken from any convenient source. In one embodiment, the water is deionized prior to being mixed with the normally liquid hydrocarbon fuel. In one embodiment, the water is purified using reverse osmosis or distillation. The water may be present in the water-blended fuel at a concentration of about 5 to about 40% by weight, and in one embodiment about 5 to about 30% by weight, and in one embodiment about 5 to about 20% by weight.

[0108] 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 which 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.

[0109] In one embodiment, the normally liquid hydrocarbon fuel is gasoline, that is, a mixture of hydrocarbons having an ASTM distillation range from about 60°C at the 10% distillation point to about 205°C at the 90% distillation point.

[0110] 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 about 300°C to about 390°C, and in one embodiment about 330°C to about 350°C. The viscosity for these fuels typically ranges from about 1.3 to about 24 centistokes at 40°C. 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 about 0.05% by weight (low-sulfur diesel fuel) as determined by the test method specified in ASTM D2622-87.

[0111] The normally liquid hydrocarbon fuel is present in the water-blended fuel compositions of the invention at a concentration of about 50% to about 95% by weight, and in one embodiment about 60% to about 95% by weight, and in one embodiment about 70% to about 95% by weight, and in one embodiment about 80% to about 95% by weight.

[0112] The inventive reaction product may be present in the water-blended fuel at a concentration in the range of about 0.05% to about 15% by weight, and in one embodiment about 0.05% to about 10%, and in one embodiment about 0.05% to about 5%, and in one embodiment about 0.1% to about 2% by weight.

[0113] In addition to the inventive reaction product, other additives which are well known to those of skill in the art may 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. Water-soluble salts capable of forming positive and negative ions in an aqueous solution that do not interfere with the other additives or the hydrocarbon fuel may be added. These include organic amine nitrates, azides, and nitro compounds. Also included are alkali and alkaline earth metal carbonates, sulfates, sulfides, sulfonates, and the like. Particularly useful are the amine or ammonium salts (e.g., ammonium nitrate). These additives may be used at concentrations of up to about 1% by weight based on the total weight of the water-blended fuel compositions, and in one embodiment about 0.01 to about 1% by weight.

[0114] In one embodiment, the water-blended fuel compositions 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 about 10% by weight, and in one embodiment about 0.1% to about 10% by weight of the water-blended fuel composition, and in one embodiment about 1% to about 5% by weight.

[0115] In another embodiment, a cetane improver is used in the fuel emulsions. Said cetane improver is typically an alkyl nitrate such as ethylhexylnitrate.

[0116] The water-blended fuels may be prepared by dissolving the inventive reaction product as well as one or more of the other optional additives referred to above in the fuel phase, and then adding the aqueous phase using high-shear mixing. The antifreeze agent, if used, is typically added to the aqueous phase prior to being blended with the fuel.

EXAMPLES

[0117] The following examples illustrate the invention without limiting it.

Example 1 - process for producing an aqueous hydrocarbon fuel composition

[0118] A batch of an aqueous hydrocarbon fuel composition is prepared with the following contents:

- Diesel fuel about 5600 liters;
- Emulsifier about 210 liters;
- Cetane improver about 60 liters;
- Water about 1000 liters; and
- Antifreeze agent about 110 liters.

[0119] The unit is designed to make a 7000 liters batch in 2.5 hours. The high shear mixer is a Silverson 500/700 multi-stator. A filter at the mixer inlet traps solid particles and protects the mixer. The manufacturing operation consists of:

- 1) transferring all the diesel fuel to the blend tank and then switching on the high shear mixer and the circulation from the blend tank to the high shear mixer and back to the blend tank (about 10 min);
- 2) injecting all emulsifier and cetane improver into the diesel fuel and then stopping the high shear mixer and the circulation (about 4 min);
- 3) injecting water + antifreeze agent until a concentration of 2% water in the blend tank is reached (about 1 min);
- 4) switching on the high shear mixer and the circulation from the blend tank to the high shear mixer and back to the blend tank while injecting the rest of the water + antifreeze agent (about 5 min) ;
- 5) continuing the circulation (from 1 to 2 hours);
- 6) optionally, controlling the quality of the blend manually by running a laboratory stability test (e.g. each every 10 min);
- 7) transferring the blend to storage (about 12 min).

[0120] Accordingly, approximately 6995 liters may be prepared in approximately 2.5 h, hence a 2798 liters/h production rate.

Example 2 - characterization of the aqueous hydrocarbon fuel composition obtained through the process of the invention

[0121] An emulsifier is prepared by the following process. A PIBSA of a molecular weight of about 950-1000, and with 80-90% of the double bond of PIB being reactive is used in the synthesis. It is reacted with TEPA reacted with TEPA at a molar ratio of about 1:1.3. Reaction is carried out at reflux under distillation conditions to distill off about 2.5 moles of water. The final reaction product has a final water content from 0.69% to 0.13%, thus from 6900 to 1300ppm of water. The TAN number is equal to or below 0.25mg KOH/g.

[0122] An emulsion based on diesel fuel, water (9 wt%), monoethyleneglycol (1.6 wt%) and the above emulsifier was prepared. A procetane additive was used at a final amount of 0.29% by weight. A further surfactant (ethoxylated vegetable oil with about 30 EO units) was used at an amount of 0.48% by weight in the final emulsion. Four compositions A1 to A4 were prepared, wherein the above emulsifier varied from each composition to the next. The above emulsifier is weighed, then diesel fuel was added and mixed with UltraTurrax (10,000 rpm) during 5-10 seconds. The water/monoethyleneglycol mix was rapidly added (with UltraTurrax on) and mixed during 10 minutes.

[0123] The resulting emulsions were assayed by centrifugation and particle size analysis. The results are presented in **Table 1** below. Furthermore, the stability of the emulsion was visually assayed for three different temperatures of conservation: 75°C, ambient temperature and -10°C. The results are presented in **Table 2** below.

[0124] The centrifugation assay corresponds to standard NF M 07-101 (with a reproducibility of 3.33% v/v absolute).

[0125] The particle size analysis was made by laser according to standard NF ISO 13320-1. The results indicated correspond to the DV90 (i.e. in the case of A1 for example, 90 % of the droplets have a diameter lower than 1.08 µm).

[0126] Two series of tests (centrifugation and particle size analysis) were conducted for each of the samples A1 to A4.

[0127] Stability at 75°C was investigated in a 500 ml flask. The volume of free water indicated is an average over two flasks. A visual inspection of the samples revealed that samples A2 to A4 have a similar aspect, unlike sample A1.

[0128] Stability at ambient temperature was assessed at 45 days after making the samples. Stability at -10°C was assessed at 10 days after making the samples (each sample had a volume of 100 ml). In the table, the amount of emulsifier is expressed as % by weight and between parenthesis the % of active of said emulsifier. The amount of "active" emulsifier thus has the following values for samples A1-A4: 0.736%; 0.752%; 0.733% and 0.714%.

Table 1 - Analysis of the samples

Sample	wt% of water in emulsifier	Emulsifier amount (%)	Centrifugation 2 min/5 min/ 10 min	Particle size analysis
A1	0.69	0.89% (82.73%)	3.7 / 7.5 / 10.7 4.8 / 8.8 / 10.5	1.08 μm 1.59 μm
A2	0.32	0.89% (84.47%)	3.5 / 7 / 9.8 4.3 / 8.1 / 10.5	0.97 μm 1.06 μm
A3	0.19	0.88% (83.35%)	3.5 / 6.5 / 9.4 3.8 / 7.5 / 10	0.96 μm 1.02 μm
A4	0.13	1.43% (49.90%)	3 / 6.1 / 8.7 4.3 / 7.8 / 10.6	0.89 μm 1.02 μm

Table 2 - Stability of the samples

Sample	Stability at 75°C	Stability at ambient T	Stability at -10°C.
A1	Phase separation at 30 days; free water: 1.9 ml	A few drops of free water (<0.05% vol)	Solid phase - 5 to 10 % vol
A2	Phase separation at 37 days; free water: 0.37 ml	A few drops of free water (<0.05% vol)	NTR
A3	Phase separation at 37 days; free water: 0.25 ml	NTR	NTR
A4	Phase separation at 43 days; free water: 0.3 ml	NTR	NTR
NTR = nothing to report.			

Claims

1. An apparatus for making an aqueous hydrocarbon fuel composition, comprising:

- a blend tank and a high shear mixer, for mixing a hydrocarbon fuel with an emulsifier and optionally a chemical additive to form a hydrocarbon fuel-emulsifier-optionally chemical additive mixture, and for mixing said hydrocarbon fuel-emulsifier-optionally chemical additive mixture with water to form said aqueous hydrocarbon fuel composition;
- an emulsifier storage tank and optionally a chemical additive storage tank and at least one pump and conduits for transferring said emulsifier from said emulsifier storage tank to said high shear mixer and optionally said chemical additive from said chemical additive storage tank to said high shear mixer;
- a conduit for transferring said hydrocarbon fuel from a hydrocarbon fuel source to said blend tank;
- conduits and actuated valves for circulating said hydrocarbon fuel, said hydrocarbon fuel-emulsifier-optionally chemical additive mixture, and said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank;
- a water conduit for transferring said water from a water storage tank into said blend tank;
- an aqueous hydrocarbon fuel composition storage tank for storing said aqueous hydrocarbon fuel composition;
- a conduit for transferring said aqueous hydrocarbon fuel composition from said blend tank to said aqueous hydrocarbon fuel composition storage tank.

2. The apparatus of claim 1 wherein said water conduit is arranged to provide for the initial mixing of the hydrocarbon fuel-emulsifier-chemical additive mixture and water in the blend tank.

3. The apparatus of claim 1 or 2, further comprising:

- a programmable logic controller for controlling: (i) the transfer of said hydrocarbon fuel from said hydrocarbon fuel source to said blend tank; (ii) the transfer of said emulsifier and optionally chemical additive from said emulsifier storage tank and optionally said chemical additive storage tank to said high shear mixer; (iii) the circulation of said hydrocarbon fuel and said emulsifier and optionally said chemical additive to said high shear mixer and back to said blend tank; (iv) the transfer of water from said water storage tank to said blend tank; (v) the circulation of said hydrocarbon fuel-emulsifier-optionally chemical additive mixture and water from said blend tank to said high shear mixer and back to said blend tank and the mixing in said high shear mixer of said hydrocarbon fuel-emulsifier-optionally chemical additive mixture and said water; and (vi) the transfer of said aqueous hydrocarbon fuel composition from said high shear mixer to said aqueous hydrocarbon fuel composition storage tank.

4. The apparatus of any one of claims 1 to 3, wherein said high shear mixer is a rotor-stator mixer.

5. The apparatus of any one of claims 1 to 4, wherein the emulsifier is selected from the group consisting of at least one fuel-soluble product (i) made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl-substituted acylating agent having about 50 to about 500 carbon atoms, this fuel-soluble product, (ii) at least one of an ionic or non-ionic compound (ii) having a hydrophilic-lipophilic balance of about 1 to about 40, or (iii) a mixture of the above fuel soluble product (i) and of the above ionic or non ionic compound (ii)..

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

(A) flowing a stream of hydrocarbon fuel to a blend tank;

(B) circulating the hydrocarbon fuel from said blend tank to a high shear mixer and back to said blend tank, flowing a stream of emulsifier and optionally chemical additive to said high shear mixer, and mixing said emulsifier and optionally chemical additive with said hydrocarbon fuel, to form a hydrocarbon fuel-emulsifier-optionally chemical additive mixture;

(C) flowing a stream of water to said blend tank and mixing it with said hydrocarbon fuel-emulsifier-chemical additive mixture to form said aqueous hydrocarbon fuel composition;

(D) circulating said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank, and mixing it in said high shear mixer, until a desired stability is obtained;

(E) transferring said aqueous hydrocarbon fuel composition from said blend tank to an aqueous hydrocarbon fuel composition storage tank;

wherein said process is carried out in an apparatus of any one of claims 1 to 10.

7. The process of claim 6, wherein the flowing of said stream of water of step (C) is conducted while said hydrocarbon fuel-emulsifier-chemical additive mixture remains in said blend tank.

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

(A) flowing a stream of hydrocarbon fuel to a blend tank;

(B) circulating the hydrocarbon fuel from said blend tank to a high shear mixer and back to said blend tank, flowing a stream of emulsifier and optionally chemical additive to said high shear mixer, and mixing said emulsifier and optionally chemical additive with said hydrocarbon fuel, to form a hydrocarbon fuel-emulsifier-optionally chemical additive mixture;

(C) flowing a stream of water to said blend tank and mixing it with said hydrocarbon fuel-emulsifier-chemical additive mixture to form said aqueous hydrocarbon fuel composition;

(D) circulating said aqueous hydrocarbon fuel composition from said blend tank to said high shear mixer and back to said blend tank, and mixing it in said high shear mixer, until a desired stability is obtained;

(E) transferring said aqueous hydrocarbon fuel composition from said blend tank to an aqueous hydrocarbon fuel composition storage tank;

wherein the flowing of said stream of water of step (C) comprises successively:

(C1) flowing a first portion of said stream of water while said hydrocarbon fuel-emulsifier-optionally chemical additive mixture remains in said blend tank;

(C2) flowing a second portion of said stream of water while said hydrocarbon fuel-emulsifier-optionally chemical additive mixture is circulated from said blend tank to said high shear mixer and back to said blend tank.

9. The process of any of claims 6 to 8, wherein the emulsifier is:

- at least one fuel-soluble product (i) made by reacting at least one hydrocarbyl-substituted carboxylic acid acylating agent with ammonia or an amine, the hydrocarbyl-substituted acylating agent having about 50 to about 500 carbon atoms; or
- at least one of an ionic or non-ionic compound (ii) having a hydrophilic-lipophilic balance of about 1 to about 40; or
- a mixture (iii) of the fuel soluble product (i) and of the ionic or non ionic compound (ii); or
- a water-soluble compound (iv) selected from the group consisting of amine salts, ammonium, azide compounds, nitro compounds, nitrate esters, nitramine, alkali metal salts, alkaline earth metal salts and mixtures thereof in combination with (i), (ii) or (iii).

10. The process of any of claims 6 to 9, wherein the emulsifier is a dehydrated product made by: (I) reacting (A) a hydrocarbyl substituted succinic acid or anhydride with (B) a polyol, a polyamine, a hydroxyamine, or a mixture of two or more thereof, to form a mixture of reaction water and a first intermediate product comprising: an ester, partial ester or a mixture thereof when (B) is a polyol; an amide, imide, salt, amide/salt, partial amide or mixture two or more thereof when (B) is a polyamine; or an ester, partial ester, amide, partial amide, amide/salt, imide, ester/salt, salt or a mixture of two or more thereof when (B) is a hydroxyamine, a mixture of a polyol and a polyamine, a mixture of polyol and a hydroxyamine, a mixture of a polyamine and a hydroxyamine, or a mixture of a polyol, a polyamine and a hydroxyamine; the hydrocarbyl substituent of said acid or anhydride having an average of about 8 to about 200 carbon atoms; and (II) heating said mixture at an effective temperature to separate substantially all of said water from said mixture and to form said dehydrated product, said dehydrated product having a water content of less than about 1 wt%, preferably less than 0.5 wt% and advantageously less than 0.25 wt%, most preferably less than 0.15 wt% and a total acid number of less than about 2, preferably less than about 0.25 mg of KOH/g.

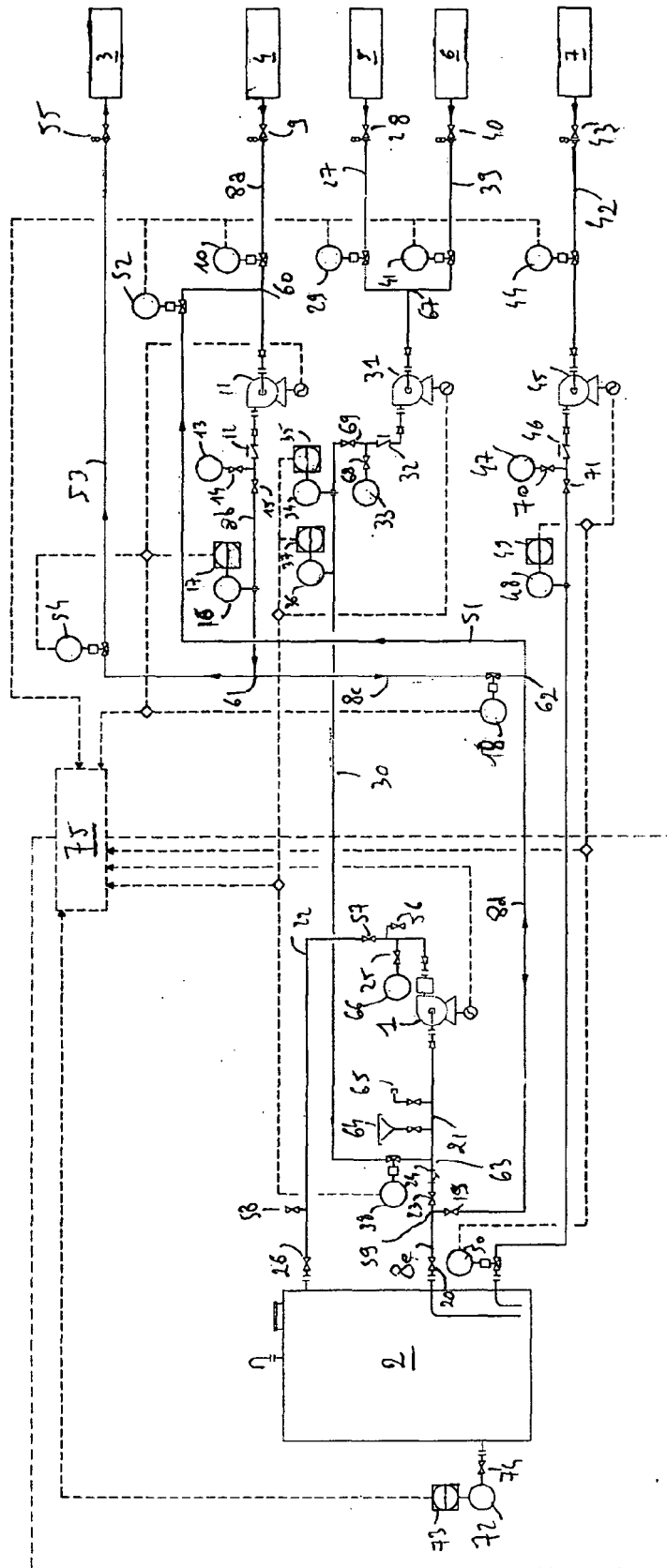


Figure 1

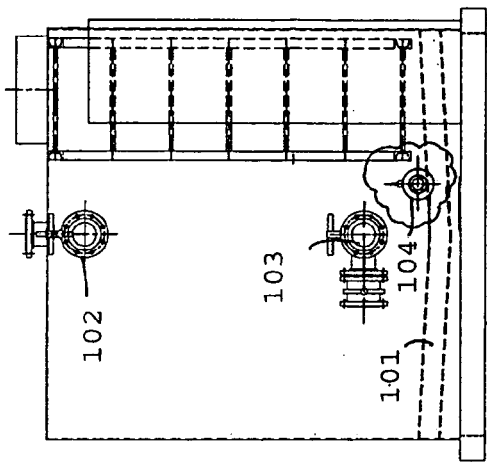


Figure 2c

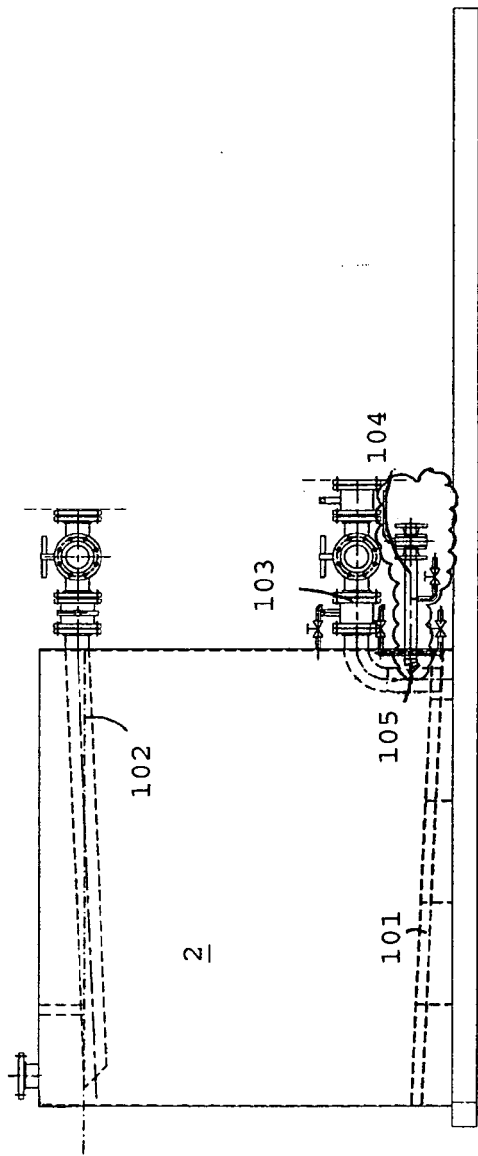


Figure 2a

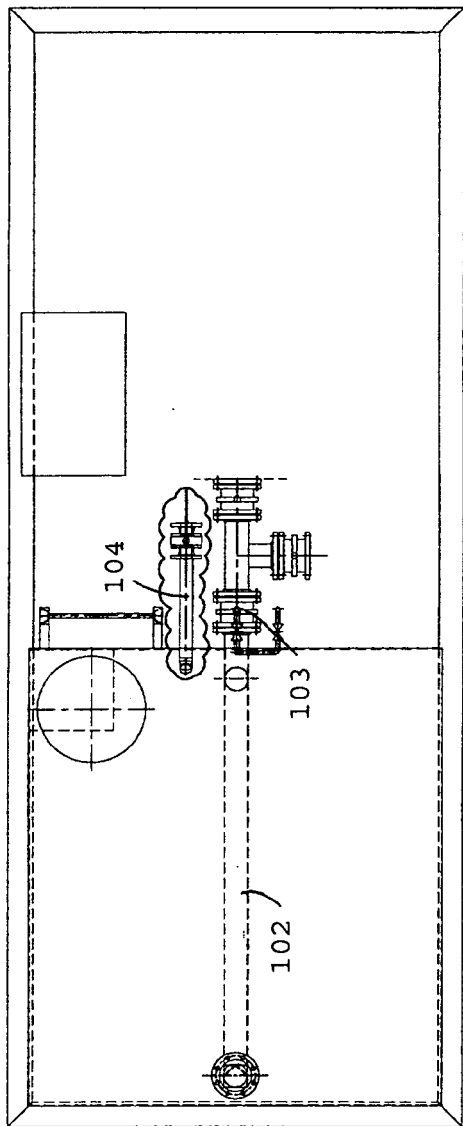


Figure 2b



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 29 1633

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,X	US 6 368 366 B1 (LANGER DEBORAH A [US] ET AL) 9 April 2002 (2002-04-09) * column 3, line 41 - column 5, line 48 * * column 9, lines 18,19 * * column 12, line 60 - column 13, line 10 * * column 14, line 58 - column 17, line 7; figure 1 * -----	1-10	INV. B01F3/08 C10L1/32
			TECHNICAL FIELDS SEARCHED (IPC) B01F C10L
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 2 April 2007	Examiner Bertrand, Samuel
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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