Title: ALKALINE SOLUTION CONTACT PROCESS AND APPARATUS RELATING THERETO

Abstract: One exemplary embodiment can be a process for contacting an alkaline solution with kerosene or diesel. The process can include providing a stream of kerosene or diesel and at least one of a naphthenic acid and a salt thereof, with an additional alkaline solution to a prewash vessel, forming an emulsion interface between a kerosene or diesel phase and an alkaline phase in the prewash vessel, controlling an amount of the emulsion interface by withdrawing at least a portion of the emulsion interface between the two phases, and adding an acid to a withdrawn emulsion.
ALKALINE SOLUTION CONTACT PROCESS
AND APPARATUS RELATING THERETO

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 14/020,629 which was filed September 06, 2013, the contents of which are hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention generally relates to a process for contacting an alkaline solution with kerosene or diesel.

DESCRIPTION OF THE RELATED ART

[0003] Generally, a hydrocarbon feed, such as kerosene or diesel, is treated, and accompanying acidic components removed or reduced, in a prewash zone which is upstream of a mercaptan oxidation reactor vessel, a water wash column, a salt filter vessel, and a clay filter vessel for sweetening the hydrocarbon feed. Such vessels can be disclosed in, e.g., US 7,223,332.

[0004] As the quality of crude oil decreases and refiners move to processing lower quality hydrocarbon feedstocks, the concentrations of naphthenic and other acids in kerosene, diesel and other hydrocarbon cuts may increase. This increased acidic concentration can express itself, with a kerosene feed for example, as Total Acid Numbers (hereinafter may be referred to as "TAN") of above 0.15 mg caustic consumed/gram kerosene. In some instances, refining operations have observed TAN numbers of up to 0.45 in the field, which can result in greater corrosion within the crude refinery.

[0005] Furthermore, the presence of acid in a hydrocarbon feed, such as kerosene or diesel, can deactivate downstream catalysts, such as, e.g., the downstream catalyst used to sweeten kerosene to jet fuel. Such catalysts often have an activated carbon base that may be susceptible to deactivation by plugging of the carbon pores by an acid salt formed by the reaction of the acid with strong caustic. Although the plugging is reversible, it would clearly be desirable not to have such acid salts present in downstream processes. These acid salts such as sodium naphthenate can lead to increased water and caustic in the product, which can
increase salt and clay consumption and potentially lead to product failing to meet specifications.

[0006] A dilute caustic solution can be used to remove naphthenic acids from a kerosene or diesel feed by adding the caustic solution to the feed, mixing the two phases, and passing the mixture through an electrostatic coalescer or electrostatic coalescer precipitator, which may also be referred to as "ECP". Typically, the caustic coalesces and separates from the hydrocarbon, resulting in a very thick emulsion, sometimes referred to as a "rag layer" by operators, at an interface of the caustic and kerosene in the electrostatic coalescer. In the case of a feed with a high TAN with limited equipment or flexibility, such as insufficient control of the valves or caustic strength, the formed rag layer may grow in thickness and shorting of the ECP grids and potentially pass in the effluent from the ECP. Emulsion formation after caustic treatment can be of concern because emulsion formation and accumulation can impede sweetening of the mercaptan in the downstream reactor by deactivating the catalyst in the reactor, increasing consumption of salt for drying and clay treatments, and possibly causing product to not meet specification. To avoid this situation, the emulsion layer is manually drained and sent to a water treatment plant. Typically, water treatment plants have difficulty processing this heavy emulsion layer, resulting in a reduction in the processing capabilities that can ultimately cause complications with the entire refinery operation.

[0007] Generally, a dilute caustic is used to minimize emulsion formation after treatment of the kerosene or diesel feed. A dilute ammonia solution may also be used to remove the naphthenic acids in an electrostatic coalescer. Although ammonia is generally a weaker base, emulsion concerns can still persist.

[0008] Accordingly, there is a need in the art for a method and apparatus providing a single stage for naphthenic acid and similar acid removal while controlling or treating emulsions independent of the strength of the solutions, such as caustic, involved.

SUMMARY OF THE INVENTION

[0009] One exemplary embodiment can be a process for contacting an alkaline solution with kerosene or diesel. The process can include providing a stream of kerosene or diesel and at least one of a naphthenic acid and a salt thereof, with an additional alkaline solution to a prewash vessel, forming an emulsion interface between a kerosene or diesel phase and an
alkaline phase in the prewash vessel, controlling an amount of the emulsion interface by withdrawing at least a portion of the emulsion interface between the two phases, and adding an acid to a withdrawn emulsion.

[0010] Another exemplary embodiment can be a process for contacting an alkaline solution with kerosene or diesel. The process can include providing a stream including the kerosene or diesel and at least one of a naphthenic acid and a salt thereof and the alkaline solution to a prewash vessel, forming an emulsion interface between a kerosene or diesel phase and an alkaline phase in the prewash vessel, detecting the emulsion interface, and withdrawing at least a portion of the emulsion interface.

[0011] A further exemplary embodiment can be a process for contacting an alkaline solution with kerosene or diesel. The process can include providing a stream of kerosene or diesel and at least one of a naphthenic acid and a salt thereof and the alkaline solution to a prewash vessel. An emulsion interface can form between a kerosene or diesel phase and an alkaline phase in the prewash vessel. The process may further include detecting the emulsion interface, measuring the emulsion interface prior to withdrawal, comparing the measured emulsion interface with a setpoint, sending a first signal to a first control valve for withdrawing at least a portion of the emulsion interface, sending a second signal to a second control valve for releasing an acid for contacting the portion of the withdrawn emulsion interface to form a hydrocarbon phase and an alkaline phase, and withdrawing at least a portion of at least one of the hydrocarbon phase and the alkaline phase.

[0012] The embodiments herein can treat a hydrocarbon stream, such as diesel or kerosene that has one or more naphthenic or similar acids and at least one salt thereof, by treating the stream with an alkaline solution, thereby neutralizing the acidic components. These embodiments may provide a practical method for purifying and substantially separating the hydrocarbon stream from other less desirable acidic components, improving the quality of the hydrocarbon product with greater efficiency and cost savings. Furthermore, a greater variety of hydrocarbon feeds, particularly those with higher acid numbers, e.g., above 0.3 mg KOH/g, can be processed, and higher strength caustics, such as NaOH, can be used thereby reducing volume used and corresponding waste.
DEFINITIONS

[0013] As used herein, the term "stream" can include various hydrocarbon molecules, such as straight-chain, branched, or cyclic alkanes, alkenes, alkadienes, and alkynes, and optionally other substances such as impurities, including heavy metals, and sulfur and nitrogen compounds. The stream can also include aromatic and non-aromatic hydrocarbons. Moreover, the hydrocarbon molecules may be abbreviated CI, C2, C3...Cn where "n" represents the number of carbon atoms in the one or more hydrocarbon molecules. Furthermore, a superscript "+" or "-" may be used with an abbreviated one or more hydrocarbons notation, e.g., C8+ or C8-, which is inclusive of the abbreviated one or more hydrocarbons. As an example, the abbreviation "C8+" means one or more hydrocarbon molecules of eight carbon atoms and/or more. In addition, the term "stream" may be applicable to other fluids optionally without having one or more hydrocarbons, such as aqueous and non-aqueous solutions of alkali, such as sodium hydroxide, and at least one acid in an aqueous solution.

[0014] As used herein, the term "zone" can refer to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include one or more reactors or reactor vessels, heaters, exchangers, pipes, pumps, compressors, and controllers. Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones.

[0015] As used herein, the term "rich" can mean an amount of generally at least 50%, and preferably 70%, by mole, of a compound or class of compounds in a stream. If referring to a solute in solution, e.g., one or more naphthenic acids and salts thereof in an alkaline solution, the term "rich" may be referenced to the equilibrium concentration of the solute. As an example, 5%, by mole, of a solute in a solvent may be considered rich if the concentration of solute at equilibrium is 10%, by mole.

[0016] As used herein, the term "substantially" can mean an amount of at least generally 80%, preferably 90%, and optimally 99%, by weight, of a compound or class of compounds in a stream.

[0017] As used herein, the term "parts per million" may be abbreviated herein as "ppm" and "weight ppm" may be abbreviated herein as "wppm". Generally, parts per million is based on weight unless otherwise indicated.
As used herein, the terms "mercaptan" and "thiol" may be used interchangeably.

As used herein, the terms "acid value" or "total acid number (TAN)" can be a mass of potassium hydroxide in milligrams required to neutralize one gram of a hydrocarbon, e.g., kerosene or diesel containing, e.g., one or more naphthenic acid compounds. Generally, the mass of acid value can be abbreviated "mg KOH/g" and may be measured by UOP Method 565-05, Procedure C, ASTM D3242-11 for acid numbers no greater than 0.1 and ASTM D664-1 la, Test Method A for acid numbers of at least 0.1.

As used herein, the term "alkali" can mean any substance that in solution, typically a water solution, has a pH value greater than 7.0, and exemplary alkali can include sodium hydroxide, potassium hydroxide, or ammonia. Such an alkali in solution may be referred to as an alkaline solution or an alkaline.

As used herein, the term "caustic" can mean an alkaline solution, such as, e.g., a solution of sodium hydroxide.

As used herein, the term "kerosene" can mean a fluid having one or more C8-C15 hydrocarbons and boiling at 160 - 275° C at atmospheric pressure.

As used herein, the term "diesel" can mean a fluid having one or more C8-C21 hydrocarbons and boiling at 250 - 340° C at atmospheric pressure.

As used herein, the term "naphthenic acid" can mean a cycloalkyl, typically cyclopentyl, moiety having at least one bridging group, typically an alkyl group having 5 to 20 carbon atoms, terminating in a carboxyl substituent. A salt of a naphthenic acid can have one or more cations, such as sodium or potassium, replacing the hydrogen of at least one carboxyl group.

As used herein, the term "kilopascal" may be abbreviated herein as "KPa".

As depicted, process flow lines in the figures can be referred to interchangeably as, e.g., lines, pipes, liquids, solutions, alkalines, alkaline solutions, caustic, acid solutions, feeds, products, or streams.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a schematic, partial cross-sectional depiction of an exemplary apparatus.
DETAILED DESCRIPTION

[0029] Referring to the FIGURE, an exemplary alkaline solution contact apparatus 100 is shown. The apparatus 100 can include a pre-wash vessel 110, a piping network 150, and a vessel 200 for separating emulsion products after treatment.

[0030] In one preferred embodiment, a stream 10 comprised substantially of kerosene, diesel or both, and impurities typically of at least one of a naphthenic acid and a salt thereof, is provided. Usually, the stream 10 includes the naphthenic acid with the salt of the naphthenic acid only present at equilibrium levels. Often, the salt of the naphthenic acid is a sodium and/or potassium salt thereof, although additional or different acids or salts may be present. Preferably, the naphthenic acid and salt thereof includes a cyclopentyl moiety having an alkyl group of 5 to 20 carbon atoms, and preferably the naphthenic acid and salt thereof are present at a concentration of 0.015 - 1.2 mg KOH/g of kerosene also known as diesel acid value. Alternatively, the naphthenic acid and salt may be present at a concentration of at least 50 - 1,000 wppm. In an effort to simplify the discussion, the stream 10 and its downstream derivatives, such as a phase or product stream, can be referred to as a "kerosene stream" or including kerosene, but it should be understood that the stream 10 and its downstream derivatives can include or be substituted with any suitable hydrocarbon, including diesel.

[0031] Generally, the kerosene stream 10 combines with an alkaline stream 20 to form a combined stream 30. The alkaline stream 20 can be comprised of a caustic, and in preferred embodiments, is comprised of sodium hydroxide, an ammonia, a potassium hydroxide, or a combination thereof. Preferably, the alkaline stream 20 has a concentration of alkali of at least 1 - 10%, by weight, based on the weight of the solution.

[0032] When the kerosene stream 10 and alkaline stream 20 combine, the alkaline stream 20 may neutralize and separate the acidic components from the hydrocarbon portion of the stream. Although not wanting to be bound by theory, the acidic impurities such as naphthenic acid typically convert to a salt or salts after contacting the alkaline stream 20. Optionally, some of the acid or salt may be present before or after contacting.

[0033] Generally, the combined stream 30 enters a pre-wash vessel 110, in which the components of the combined stream separate, generally, into a kerosene phase 114 at the upper end of the pre-wash vessel 110, and an alkaline phase 122 at the lower end of the pre-
wash vessel 110. In a preferred embodiment, the prewash vessel 110 is an electrostatic coalescer precipitator.

[0034] Sometimes a rag or an emulsion layer or emulsion interface 118 may form between the separated kerosene phase 114 and alkaline phase 122. Usually, the rag layer 118 has a thick consistency, roughly that of mayonnaise, and is comprised of materials that do not separate out into either the kerosene phase 114 or alkaline phase 122. The rag layer 118 typically has a pH greater than 10 and can include water, hydrocarbons such as kerosene, an acid such as naphthenic acid, a sodium naphthanate, a sodium phenylate, and a sodium hydroxide.

[0035] After separation, a kerosene product stream 140 can exit a top and a spent alkali stream 144, which may include one or more naphthenic salts, can exit a bottom of the prewash vessel 110. The kerosene product stream 140 is typically obtained with a lowered content of the naphthenic or other acids and/or at least one salt thereof, of less than 100 ppm, by weight. The kerosene product stream 140 can optionally be sent downstream for further processing. Generally, the kerosene product stream 140 can have an acid value of no more than 0.015 mg KOH/g of kerosene. The spent alkali stream 144 can be comprised of caustic salts, such as a potassium or sodium naphthenic salt, and be sent for waste water treatment for processing or to spent alkali disposal.

[0036] The piping network 150 can include several lines 160, 164, 168, 172, and 176 that may form branches that can be combined into a main or combined line 182. In this embodiment, the set of lines 160, 164, 168, 172, and 176 is comprised of five lines. Each line 160, 164, 168, 172, and 176 may have a corresponding control valve 162, 166, 170, 174, and 178 and be at a different elevation on the prewash vessel 110. Each control valve 162, 166, 170, 174 and 178 can be considered, independently, a first control valve. In an alternative embodiment, the lines 164, 168, and 172 can have respective control valves, and the lines 160 and 176 may have manual valves. In a further embodiment, the line 168 may have a control valve, the other lines 160, 164, 172, and 178 can have manual valves. In yet another embodiment, the lines 160, 164, 168, 172, and 176 can all have manual valves. However, it should be understood that any suitable number of lines and valves are optional with no or one or more control valves.
The depth, location and width of the rag layer 118 can vary somewhat within the pre-wash vessel 110, based upon factors such as the relative amounts of the kerosene phase 114 and alkaline phase 122 within the pre-wash vessel 110 at any given time. Accordingly, at least a portion of the rag layer 118 is drawn off by one or more of the lines 160, 164, 168, 172, and 176 positioned at various heights along the pre-wash vessel 110. The lines can be of any number and be suitable for drawing off the rag layer 118 within the pre-wash vessel 110. The flow of each stream through each of the lines 160, 164, 168, 172, and 176 can be controlled by the control valves 162, 166, 170, 174, and 178. Each of the first set of control valves 162, 166, 170, 174, and 178 can be opened, closed, or left in some suitable intermediate position based upon applicable factors, such as the location and thickness of the rag layer 118. The control valves 162, 166, 170, 174, and 178 can be regulated by a level controller 130, which upon detecting the rag layer 118 can send a signal 132. The signal 132 may pass to point "A" and be received at point "A" at the control valves 162, 166, 170, 174, 178, and 184. Point "A" is provided in the FIGURE to illustrate communicating the level controller 130 with the control valves 162, 166, 170, 174, 178, and 184 and to not unduly clutter the FIGURE with excessive lines. In a preferred embodiment, the level controller 130 measures the level and thickness of the rag layer 118, compares the measured rag layer 118 with a setpoint, and sends the signal to one or more control valves 162, 166, 170, 174, and 178, which can be independently opened. Any suitable level controller 130 can be utilized. One level controller is sold under the trade designation ID-201 Interface Detector by Agar Corporation Inc. of Houston, Texas. Another level controller may use an ultrasonic level measurement.

As an example, if there is a relatively small amount of the upper kerosene phase 114 relative to the alkaline phase 122, then the emulsion interface 118 would be found to be relatively high within the pre-wash vessel 110. Upon a signal 132, the level controller 130 can open the uppermost first control valve 162 and the lower valves 166, 170, 174, and 178 can remain closed, such that the rag layer 118 would be drawn off only by the line 160. Alternatively, if the rag layer 118 is centered in the pre-wash vessel 110, the control valve 170 may be opened to drain the rag layer 118 through the line 168, as depicted in the FIGURE.
[0040] The stream or streams from the lines 160, 164, 168, 172, and 176 can be joined into the main line 182. Generally, the stream in the combined line 182 has a high pH, and to treat the main stream 182 and break down the emulsion into a hydrocarbon phase and an alkaline phase, an acid stream 180 can be added. The acid stream 180 can be comprised of any suitable acid, preferably an organic and/or a mineral acid, such as acetic acid, carboxylic acid, hydrochloric acid, or sulfuric acid; and in one preferred embodiment, is comprised of a carboxylic acid, acetic acid or both.

[0041] The acid stream flow to the combined stream 182 can be regulated by a control valve 184, which may be considered a second control valve. The control valve 184 can be, in turn, actuated by the signal 132, as previously discussed. Namely, once the level controller 130 detects the rag layer 118, the signal 132 may be sent to the control valve 184 to release the acid stream 180.

[0042] The components of the combined stream 182 can be added to the acid stream 180 to form a merged stream 188. The fluids of the merged stream 188 may proceed through an inline static mixer 190, which more thoroughly mixes the merged stream 188. The alkaline components of the combined stream 182 are broken down by the added acid stream 180, which can result in a stream having a pH of less than 7, or even no more than 2. Usually, the inline static mixer 190 has a pressure drop of less than 21 KPa. As a result, the merged stream 188 can become much less viscous and liquefy.

[0043] The resulting mixed stream 192 enters a vessel 200. The addition of the acid stream 180 can result in two phases, an aqueous or alkaline phase and a hydrocarbon phase, which may separate within the vessel 200. The hydrocarbon phase, which can be comprised of hydrocarbons such as naphthenic acids, phenols, and residual kerosene, may be withdrawn from the upper portion of the vessel 200 as a hydrocarbon stream 202 and may proceed for further processing, such as, e.g., slops, and typically sent on to a main crude tower. Often, the aqueous or alkaline phase, which may contain acid salts such as sodium chloride, is withdrawn from the lower portion of the vessel 200 as an aqueous stream 210 and proceeds to a water treatment system.
SPECIFIC EMBODIMENTS

[0044] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0045] A first embodiment of the invention is a process for contacting an alkaline solution with kerosene or diesel, comprising A) providing a stream comprising the kerosene or diesel and at least one of a naphthenic acid and a salt thereof and the alkaline solution to a prewash vessel; B) forming an emulsion interface between a kerosene or diesel phase and an alkaline phase in the prewash vessel; C) controlling an amount of the emulsion interface by withdrawing at least a portion of the emulsion interface between the two phases; and D) adding an acid to a withdrawn emulsion. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the alkaline solution comprises an alkali, in turn comprising at least one of a sodium hydroxide and an ammonia. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the alkali comprises the sodium hydroxide. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the sodium hydroxide in a solution has a concentration of at least 1%, by weight, based on the weight of the solution. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the sodium hydroxide in a solution has a concentration of no more than 10%, by weight, based on the weight of the solution. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein at least one of the naphthenic acid and the salt thereof comprises a cyclopentyl moiety having an alkyl group of 5 to 20 carbon atoms. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein a spent second stream comprises a potassium or sodium naphthenic salt. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the at least one of the naphthenic acid and the salt is comprised at a concentration of no more 1,000 ppm, by weight. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up
through the first embodiment in this paragraph, further comprising providing a level controller to measure the emulsion interface. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the acid comprises a carboxylic acid. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the acid comprises an acetic acid. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the alkaline solution comprises an alkali, in turn comprising a sodium hydroxide. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising passing the acid and withdrawn emulsion through a static mixer and into a vessel. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the kerosene or diesel comprises at least one of a naphthenic acid and a salt comprised at a concentration of 0.015 - 1.2 mg KOH/g of kerosene or diesel.

[0046] A second embodiment of the invention is a process for contacting an alkaline solution with kerosene or diesel, comprising A) providing a stream comprising the kerosene or diesel and at least one of a naphthenic acid and a salt thereof and the alkaline solution to a prewash vessel; B) forming an emulsion interface between a kerosene or diesel phase and an alkaline phase in the prewash vessel; C) detecting the emulsion interface; and D) withdrawing at least a portion of the emulsion interface. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising measuring the emulsion interface prior to withdrawal. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising sending a signal to a control valve for withdrawing at least a portion of the emulsion interface by comparing the measured emulsion interface with a setpoint. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising sending another signal to another control valve for releasing an acid for contacting the portion of the withdrawn emulsion interface. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the acid comprises an acetic acid.
A third embodiment of the invention is a process for contacting an alkaline solution with kerosene or diesel, comprising:

A) providing a stream comprising the kerosene or diesel and at least one of a naphthenic acid and a salt thereof and the alkaline solution to a prewash vessel;  
B) forming an emulsion interface between a kerosene or diesel phase and an alkaline phase in the prewash vessel;  
C) detecting the emulsion interface;  
D) measuring the emulsion interface prior to withdrawal;  
E) comparing the measured emulsion interface with a setpoint;  
F) sending a first signal to a first control valve for withdrawing at least a portion of the emulsion interface;  
G) sending a second signal to a second control valve for releasing an acid for contacting the portion of the withdrawn emulsion interface to form a hydrocarbon phase and an alkaline phase; and  
H) withdrawing at least a portion of at least one of the hydrocarbon phase and the alkaline phase.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.
CLAIMS

1. A process for contacting an alkaline solution with kerosene or diesel, comprising:
   A) providing a stream comprising the kerosene or diesel and at least one of a naphthenic acid and a salt thereof and the alkaline solution to a prewash vessel;
   B) forming an emulsion interface between a kerosene or diesel phase and an alkaline phase in the prewash vessel;
   C) controlling an amount of the emulsion interface by withdrawing at least a portion of the emulsion interface between the two phases; and
   D) adding an acid to a withdrawn emulsion.

2. The process according to claim 1, wherein the alkaline solution comprises an alkali, in turn comprising at least one of a sodium hydroxide and an ammonia.

3. The process according to claim 2, wherein the alkali comprises the sodium hydroxide.

4. The process according to claim 3, wherein the sodium hydroxide in a solution has a concentration of at least 1%, by weight, based on the weight of the solution.

5. The process according to claim 3, wherein the sodium hydroxide in a solution has a concentration of no more than 10%, by weight, based on the weight of the solution.

6. The process according to claim 1 or 2, wherein at least one of the naphthenic acid and the salt thereof comprises a cyclopentyl moiety having an alkyl group of 5 to 20 carbon atoms.

7. The process according to claim 1 or 2, wherein a spent second stream comprises a potassium or sodium naphthenic salt.

8. The process according to claim 1 or 2, wherein the at least one of the naphthenic acid and the salt is comprised at a concentration of no more 1,000 ppm, by weight.
9. The process according to claim 1 or 2, further comprising providing a level controller to measure the emulsion interface.

10. The process according to claim 1 or 2, wherein the acid comprises a carboxylic acid.
### INTERNATIONAL SEARCH REPORT

#### International application No.

PCT/US2014/052610

#### CLASSIFICATION OF SUBJECT MATTER

CIOG 19/02(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

#### FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOG 19/02; CIOG 19/00; CIOG 27/10; G01N 9/26; C07C 5/1/02; CIOG 17/00; B01D 17/06; C07C 51/42; B01D 17/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & keywords: kerosene, diesel, naphthenic acid, alkaline solution, prewash, emulsion interface, phase, controller, valve, signal

#### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>Y</td>
<td>US 2002-0125175 A (IAN RALPH COLLINS et al.) 12 September 2002</td>
<td>1-10</td>
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<tr>
<td></td>
<td>See abstract; paragraphs [0003], [0059-0066]; claims 1-3, 15-18; figures 1, 2.</td>
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<tr>
<td>Y</td>
<td>CN101255106 B (SHANDONG UNIVERSITY) 16 March 2011</td>
<td>1-10</td>
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<td>See abstract; paragraphs [0004], [0005], [0013]; claim V, figure 1.</td>
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<td>A</td>
<td>US 2002-0033356 A (TATSUHI HONDA et al.) 21 March 2002</td>
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<td></td>
<td>See abstract; paragraphs [0033], [0066]-[0065], [0077]; claims 1-5; figures 2, 4, 5.</td>
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<td>A</td>
<td>US 6531055 B (MARK ALAN GREANEY) 11 March 2003</td>
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<td>See abstract; column 2, lines 30-34; column 2, lines 59-62; column 4, lines 34-55; claim 1, 2, 4.</td>
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<td>US 05612490 A (EDWIN D. CARLSON et al.) 18 March 1997</td>
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<td></td>
<td>See abstract; column 6, line 18, column 8, line 25; claims 1-8; figures 1A, 1B.</td>
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<td>A</td>
<td>US 05039398 A (LAURENCE G. STINE et al.) 13 August 1991</td>
<td>1-10</td>
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<tr>
<td></td>
<td>See abstract; column 9, lines 3-41; claims 1-8; figure 2.</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
  - **A** document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search: 13 February 2015 (13.02.2015)

Date of mailing of the international search report: 16 February 2015 (16.02.2015)

Name and mailing address of the ISA/KR

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Korean Intellectual Property Office
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