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(54) Title: METHODS AND COMPOSITIONS FOR REMOVING SOLIDS FROM HYDROCARBON STREAMS

(57) Abrégé/Abstract:
A demulsifying agent may be added to a hydrocarbon stream in an effective amount where the hydrocarbon stream includes a plurality of solids. The demulsifying agent may be added to the hydrocarbon stream at a location that is upstream from a desalter. The demulsifying agent may water-wet at least a portion of the solids for subsequent separation of the solids from the hydrocarbon stream. The demulsifying agent may be or include but is not limited to at least one maleic acid derivative, such as di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl pheno succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1 -icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof.

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METHODS AND COMPOSITIONS FOR REMOVING SOLIDS FROM HYDROCARBON STREAMS

TECHNICAL FIELD

[0001] The present invention relates to methods and compositions for separating solids from a hydrocarbon stream, and more particularly relates, in one non-limiting embodiment, to a demulsifying agent added to a hydrocarbon stream for separating at least a portion of the solids from the hydrocarbon stream where the demulsifying agent may be or include at least one maleic acid derivative.

BACKGROUND

[0002] Hydrocarbon streams, such as crude oils, asphalt, bitumens, etc typically carry varying amounts of solids within the hydrocarbon stream. Additional solids from the sludge of a crude storage tank may also be incorporated into the hydrocarbon stream once the hydrocarbon stream enters the crude storage tank. The solids and/or sludge include inorganic solids, paraffin wax, and the like. Depending on the quality of the crude oils and the length of time and/or whether the crude storage tank has been in storage, the amount of solids may vary from about 20 pounds per thousand barrels (ptb) (about 11 kilograms per thousand barrels) to about 2500 ptb (about 1133 kg per thousand barrels), or in the case of sludge, the sludge accumulation may range from several centimeters to over one meter deep. A layer of sludge typically forms at the bottom of a crude storage tank as crude oil is discharged into the crude storage tank and later discharged from the crude storage tank. This sludge appears to be a complex emulsion stabilized by inorganic and/or organic solids within the emulsion. The salty sludge is picked up from the bottom of the crude storage tank by the velocity of the crude oil. The specific gravity of the sludge within the crude storage tank is lighter than water and is easily dispersed into the hydrocarbon stream.

[0003] As noted, the sludge is a complex emulsion of hydrocarbon, brine, and inorganic solids, and paraffin wax. The inorganic solids may include iron oxides, sulfides, sand, silt, clay, and the like. These solids arise from several sources, such as brine contamination as a result of the brine associated with the oil in the formation. Most minerals, clay, silt, and sand come from the formation around the oil wellbore. The iron oxides and iron sulfides are a result of corrosion during production, transport, and/or storage of the crude oil. The sludge poses several problems, such as reducing the volume of the working crude storage tank and crude unit upsets. When the crude storage tank is taken off-line for inspection and/or needs to be repaired, the sludge poses additional concerns related to worker safety, environmental release of the sludge, disposal costs, cost to remove the sludge, downtime, etc.

[0004] Regardless of the source of the solids within the hydrocarbon stream, several treatment approaches have been made to reduce or remove the total amount of solids, but these have traditionally centered on the removal of solids at the desalter unit. Desalting or removing the solids, or at least reducing their presence, is necessary prior to further processing since these solids would otherwise cause fouling and deposits in downstream heat exchanger equipment and/or the solids would be detrimental to crude oil processing equipment. Effective crude oil desalting can help minimize the effects of these contaminants on the crude unit and downstream operations. However, some types of crude oil have higher levels of solids that stabilize the emulsion, and this poses a problem for removal of a high level of solids by the desalter alone.

[0005] It would be desirable if methods were devised that would at least partially remove solids from the hydrocarbon stream prior to the injection of the hydrocarbon stream into the desalter, which would allow for better efficiency and use of the desalter.

SUMMARY

[0006] There is provided, in one form, a method for separating at least a portion of solids from a hydrocarbon stream having a plurality of solids therein. A demulsifying agent may be added to the hydrocarbon stream for subsequent separation of the solids from the hydrocarbon stream in an effective amount to water-wet at least a portion of the solids. The demulsifying agent may be or include, but is not limited to, at least one maleic acid derivative.

[0007] There is further provided in another non-limiting embodiment, a method for separating at least a portion of solids from an oil phase of an oil/water emulsion having a plurality of solids therein. A demulsifying agent may be added to the emulsion in an amount ranging from about 0.1 ppm to about 30 ppm to water-wet at least a portion of the solids. The demulsifying agent may be or include at least one maleic acid derivative. The demulsifying agent may be added to the emulsion at a location upstream from a desalter. The water-wet solids may then separate from the oil phase of the emulsion for subsequent removal of the solids.

[0008] In another non-limiting embodiment, a treated hydrocarbon stream in a crude storage tank is described. The treated hydrocarbon stream may include a plurality of water-wet solids and a demulsifying agent. The demulsifying agent may be or include, but is not limited to at least one maleic acid derivative. The amount of the demulsifying agent may range from about 0.1 ppm to about 30 ppm. The plurality of water-wet solids are more water-wet as compared to a plurality of solids within a hydrocarbon stream in the absence of the demulsifying agent.

[0009] The demulsifying agent appears to water-wet the solids in such a way to allow the solids to separate from a hydrocarbon stream or oil phase of an emulsion, and then the solids may be removed or incorporated into a water phase.

[0009a] Accordingly, in one aspect of the present invention there is provided a method for separating at least a portion of solids from a hydrocarbon fluid having solids therein comprising:

adding an agent to the hydrocarbon fluid in an effective amount for subsequent separation of at least a portion of the solids from the hydrocarbon fluid, where the solids are present as solids prior to adding the demulsifying agent, and where the agent rests with the hydrocarbon fluid for about 24 hours to about 36 hours prior to the hydrocarbon fluid being delivered to a desalter;

the agent water-wetting at least a portion of the solids; wherein the agent is selected from the group consisting of di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl phenyl succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof; and

separating at least a portion of the solids from the hydrocarbon fluid.

[0009b] According to another aspect of the present invention there is provided a method for separating at least a portion of solids from an oil phase of an emulsion, wherein the method comprises:

adding an agent to the emulsion in an amount ranging from about 0.1 ppm to about 200 ppm based on the emulsion, where the solids are present as solids prior to adding the agent, and where the agent rests with the emulsion for about 24 hours to about 36 hours prior to the hydrocarbon fluid being delivered to a desalter;

the agent water-wetting a plurality of solids within the emulsion; wherein the agent is selected from the group consisting of di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl phenyl succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof; and

separating the water-wet solids from the oil phase of the emulsion; wherein the water-wet solids, after contact with the agent, are then carried into a water phase of the emulsion.

[0009c] According to yet another aspect of the present invention there is provided a method for separating at least a portion of solids from an oil phase of an emulsion, wherein the method comprises:

adding an agent to the emulsion in an amount ranging from about 0.1 ppm to about 200 ppm based on the emulsion, where the solids are present as solids prior to adding the agent, and where the agent rests with the emulsion for about 24 hours to about 36 hours prior to the hydrocarbon fluid being delivered to a desalter;

the agent water-wetting a plurality of solids within the emulsion; wherein the agent is selected from the group consisting of di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl phenyl succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof; and

separating the water-wet solids from the oil phase of the emulsion; wherein the water-wet solids, after contact with the agent, are then carried into a water phase of the emulsion;

wherein the oil phase is selected from the group consisting of crude oil, asphalt, bitumen, shale condensates, decant oil, and combinations thereof; and

wherein the solids are inorganic solids selected from the group consisting of metal oxides, metal dioxides, metal sulfides, metal sulfates, metal carbonates, sand, silt, clay, paraffin wax, dolomite, coke fines, zinc compounds and combinations thereof, where the metals are selected from the group consisting of iron, copper, manganese, zinc, nickel, and combinations thereof.

DETAILED DESCRIPTION

[0010] It has been discovered that adding a chemical, such as a demulsifying agent, as a pre-treatment or preconditioning for a hydrocarbon stream when the chemical is added to the hydrocarbon stream for better mixing of the demulsifying agent with the hydrocarbon stream, and therefore better separation of the solids by the time the hydrocarbon stream reaches the desalter. The demulsifying agent may be added to a tank having the hydrocarbon stream; alternatively, the demulsifying agent may be added to the hydrocarbon stream at a location upstream from a desalter. The chemical may be added directly to the desalter for separating solids from the hydrocarbon stream; however, the chemical has more contact time and therefore better performance by the chemical when it is added as a pre-treatment to the hydrocarbon stream upstream from the desalter. Such a pre-treatment allows the chemical to have more contact time with the solids and thereby better separation of the solids as well as other functions, such as but not limited to solids wetting capabilities, better surface tension and improved oil-water partition, etc. 'Upstream from the desalter' means the demulsifying agent may be added to the hydrocarbon stream at any point prior to feeding the hydrocarbon stream into the desalter.

[0011] The added amount of time by using the chemical as a pre-treatment instead of adding the chemical directly to a desalter allows for improved resolution of micro-emulsions that can be present within the hydrocarbon stream, as well as provide solids separation from a solids laden sludge that is carried with the normal crude feed. Many potential secondary benefits include fewer crude unit upsets, better desalter operation, less crude unit preheat system fouling, improved crude unit corrosion control, reduced water slugs, and combinations thereof. This type of pre-treatment allows for reduced time for crude storage tank maintenance, lower sludge disposal costs, and better quality raw crude oil charged to the crude storage tank.

[0012] 'Pre-treatment' is defined herein to mean that the chemical is added to the hydrocarbon stream and the chemical rests with the hydrocarbon

stream for a specified amount of time prior to the injection of the hydrocarbon stream into the desalter. For example, the pre-treatment chemical may rest with the hydrocarbon stream for a period of about 10 minutes independently to about 7 days prior to the injection of the pre-treated hydrocarbon stream into the desalter, alternatively from about 30 minutes independently to about 5 days, or from about 30 minutes independently to about 120 hours. Similarly, a 'pre-treated' hydrocarbon stream is defined herein to be a hydrocarbon stream that has the chemical therein where the chemical has rested with the hydrocarbon stream for a period of time that falls within at least one of the given ranges above. As used herein with respect to a range, “independently” means that any lower threshold may be used together with any upper threshold to give a suitable alternative range.

[0013] The hydrocarbon stream may be part of an oil-in-water emulsion and/or a water-in-oil emulsion (hereinafter referred to as ‘the emulsion’), and the demulsifying agent may be added to either the oil phase, the water phase, or both of the emulsion. The amount of water within the emulsion may be greater than 50 vol%, or range from about 2 vol % independently to about 95 vol%, alternatively from about 0.01 vol % independently to about 20 vol%. The hydrocarbon stream may be or include, but is not limited to crude oil, asphalt, bitumen, shale condensates, decant oil (also known as treated slop oil), and combinations thereof. The types of crude oil may be or include heavy Canadian crudes, bitumen, shale oils, heavy Californian crudes, South American crudes, Russian crudes, topped crudes, West Texas intermediate crude(WTI), and combinations thereof. For example, specific crudes may include crudes produced by Steam Assisted Gravity Drainage (SAGD) or PFT, Dillbit (diluted bitumen also known as Synbit), and conventional crudes. 'Heavy' as used in the context of crudes is a crude that has an API gravity less than about 30; API gravity is a measure of how heavy or light a petroleum liquid is when compared to water.

[0014] The solids may be or include inorganic solids, such as but not limited to metal oxides, metal dioxides, metal sulfides, metal sulfates, metal

carbonates, sand, silt, clay, paraffin wax, dolomite, coke fines, zinc compounds and combinations thereof. Particular non-limiting examples of the metal oxides may be or include iron oxides (FeO, Fe_2O_3, Fe_3O_4, Fe_2O_3), copper oxides (Cu_2O and/or CuO), manganese oxides (MnO, Mn_3O_4, Mn_2O_3, MnO_2, and Mn_2O_7), zinc oxides, nickel oxides, and combinations thereof; a non-limiting example of metal dioxides may be or include titanium dioxide. Non-limiting examples of the sulfides, sulfates, and carbonates may be or include iron sulfides (e.g. FeS, FeS_2, Fe_3S_4) and the like. The size of the solids may be less than about 0.45 microns, alternatively from about 0.1 microns independently to about 5 microns.

[0015] The demulsifying agent may be injected into the hydrocarbon stream as it enters into the crude storage tank, e.g. one injection location may be the suction of the crude transfer pump or injection pump, or the demulsifying agent may be added to the hydrocarbon stream once the hydrocarbon stream is already in the crude storage tank. The demulsifying agent may be or include, but is not limited to maleic acid derivatives, which may be used in conjunction with naphthalene sulfonates, alkyl diphenyloxide disulfonate, and combinations thereof. The naphthalene sulfonates may have from 1 aromatic ring to 4 aromatic rings; alternatively, the naphthalene sulfonate may have 2 aromatic rings. Non-limiting examples of the naphthalene sulfonate include mono-alkyl substituted naphthalene sulfonates, di-alkyl substituted naphthalene sulfonates (e.g. di-isopropyl naphthalene sulfonate), methanolamine dibutyl naphthalene sulfonate, sodium benzyl naphthalene sulfonate, and the like. A non-limiting example of the alkyl diphenyloxide disulfonate is Dowfax 2A1TM, which is supplied by Dow Chemical Company.

[0016] In one non-limiting embodiment, at least one maleic acid derivative may be used as the demulsifying agent; in one non-limiting embodiment, two or more maleic acid derivatives may be used as the demulsifying agent. The maleic acid derivative may be a sulfosuccinate having a C_6-C_{18} sulfosuccinate, and the maleic acid derivative may be a sodium salt, an amine salt, a potassium salt, an ammonium salt, and combinations thereof.

Maleic acid derivatives include, but are not necessarily limited to, di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl pheno succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof. In one non-limiting embodiment, the succinate may be a sulfosuccinate. The maleic acid derivative may be used in conjunction with an alkali salt, such as sodium, in one non-limiting embodiment.

[0017] In one non-limiting embodiment, the demulsifying agent includes at least one maleic acid derivative, e.g. dioctyl sulfosuccinate, and at least one naphthalene sulfonate, even though the maleic acid derivative is effective when used alone. Particular ratios of the maleic acid derivative and the naphthalene sulfonate that are beneficial range from about a 50/50 ratio of maleic acid derivative to naphthalene sulfonate independently to about a 95/5 ratio of maleic acid derivative to naphthalene sulfonate. Alternative ratios may include an 80/20 ratio of maleic acid derivative to naphthalene sulfonate, a 90/10 ratio of maleic acid derivative to naphthalene sulfonate, and the like.

[0018] A primary demulsifier may also be used with the demulsifying agent to promote the activity by the demulsifying agent. The primary demulsifier may be mixed with the demulsifying agent for injection of the primary demulsifier at the same time as the demulsifying agent. Alternatively, the primary demulsifier may be injected at a different location altogether from the demulsifying agent. As long as a primary demulsifier is used with the demulsifying agent, regardless of whether it is injected at the same time or a different time as the demulsifying agent, the demulsifying agent will be capable of performing its functions. Non-limiting examples of primary demulsifiers may be or include alkoxylated resins, alkoxylated dipropylene glycols, maleic esters, cross-linked alkoxylated resins, alkoxylated glycols, alkoxylated glycerins, and trisaminoemethane alkoxylates, and combinations thereof. However, the

specific primary demulsifier to be used will depend on the composition and amount of the demulsifying agent used.

[0019] The solids may be suspended in the hydrocarbon stream or oil phase of the emulsion. Adding the demulsifying agent to the hydrocarbon stream or oil phase of the emulsion allows for the demulsifying agent to rest with the hydrocarbon stream and separate the solids therefrom prior to the injection of the hydrocarbon stream into a desalter, even if there is no sludge present in the crude storage tank. The demulsifying agent destabilizes the solids from the emulsion and affects rapid coalescence of water and preferentially water wets the solids. The water-wet solids are then carried into the water phase of the emulsion, thereby providing a reduced amount of solids within the hydrocarbon stream or oil phase of the emulsion. The water and the water-wet solids may then be removed for proper recovery of the hydrocarbon components with fewer solids. Overall, removal of the solids prior to the injection of the hydrocarbon stream causes fewer problems in the refinery and other processing downstream.

[0020] One non-limiting example of this occurs in the crude storage tank where the hydrocarbon stream or crude oil in the top of the crude storage tank is sufficiently low in solids, and the water containing the water-wet solids may be drained from the crude storage tank. Over a period of weeks to months, significant reductions in sludge volume may be achieved. Exposure of the bottom sludge from the crude storage tank to a crude oil treated with the demulsifying agent slowly reduces the level of sludge in the crude storage tank.

[0021] The introduction of the demulsifying agent into the hydrocarbon stream by itself may be sufficient mixing, or there may be an additional process for intentional mixing, such as a paddle stirrer or the like as one non-limiting example. Subsequently, the hydrocarbon stream is kept still or held quiescent in the crude storage tank for enough time to allow or permit the solids to water-wet by the demulsifying agent. In the instance of sludge removal, the water-wet solids may settle to the bottom of the crude storage tank under the influence of gravity.

[0022] A goal of the method is to reduce the solids content in the hydrocarbon stream to an acceptable level for the hydrocarbon stream to be processed in a refinery. Said differently, complete separation of the solids from the hydrocarbon stream is desirable, but it should be appreciated that complete separation is not necessary for the methods discussed herein to be considered effective. Success is obtained if more solids are separated using the demulsifying agent than in the absence of the demulsifying agent.

[0023] In one non-limiting embodiment, the methods described are considered successful if a majority of the solids are separated, i.e. greater than 50 wt%, alternatively from about 60 wt% independently to about 90 wt% of the solids are separated, or from about 80 wt% independently to about 90 wt% in another non-limiting embodiment. By "separating" solids from the hydrocarbon stream is defined herein to mean any and all partitioning, sequestering, removing, transferring, eliminating, dividing, removing, dropping out of the solids from the hydrocarbon or crude oil to any extent.

[0024] In one non-limiting embodiment, the hydrocarbon stream would be treated with the demulsifying agent until a predetermined target concentration is reached. In another non-restrictive version, there may be a fixed amount of time before the hydrocarbon stream must be processed in the refinery. Thus, the dosage of the demulsifying agent would be adjusted to accomplish yielding a hydrocarbon stream with the necessary amount of solids content, types of solids, and/or size of solids threshold in the time required. However, it should be realized that the exact dosage will be very dependent upon the particular hydrocarbon stream and the needs of the particular refinery. Optimum dosages will have to be developed with experience and would be very difficult to predict in advance.

[0025] The amount of the demulsifying agent may range from about 0.1 ppm independently to about 200 ppm, alternatively from about 2 ppm independently to about 100 ppm, or from about 3.5 ppm independently to about 25 ppm in another non-limiting embodiment. However, it is difficult to determine the exact amount of the demulsifying agent to be added for optimum separation

of the solids from the hydrocarbon stream because the amount depends on many variables, such as but not limited to the type of results desired, the type of hydrocarbon stream being processed, the amount of mixing, the temperature of the crude storage tank, the amount of settling time, the geometry of the crude storage tank, injection points, and constituency of the emulsion, etc. For example, if the treated hydrocarbon stream is to be stored in the crude storage tank for several hours, e.g. 10 hours, the treatment dosage of the demulsifying agent may be much lower than the treatment dosage for a hydrocarbon stream that is to be stored in a crude storage tank for about 3-5 hours. A higher dosage may provide better resolution of the emulsion in a shortened time period.

[0026] The amount of the demulsifying agent may also depend on the rate at which it is injected into the hydrocarbon stream and/or the crude storage tank. This amount may be adjusted as the crude flow rate changes to assure the refiner that all of the hydrocarbon stream receives the correct amount of demulsifying agent. One method of doing this is to use a variable speed chemical injection pump where a signal from an in-line flow sensor automatically adjusts the chemical injection rate as the flow rate of the hydrocarbon stream changes.

[0027] Settling agents may also be useful in facilitating the settling of various solids to the bottom of the crude storage tank. Suitable settling agents include, but are not necessarily limited to alkyoxylated phenolic resins; oxyalkylated polyamines, including, but not necessarily limited to ethoxylated and/or propoxylated 1,2-ethanediamine, N1-(2-aminoethyl)-N2-[2-[(2-aminoethyl)amino]ethyl]-, and polymers with 2-methyloxirane and oxirane; oxyalkylated alkanol amines, including, but not necessarily limited to, ethoxylated and/or propoxylated 1,3-propanediol, 2-amino-2-(hydroxymethyl)-1,3-propanediol, and again polymers with 2-methyloxirane and oxirane; Mannich reaction condensation products of alkyl phenols and polyamines and mixtures thereof. Amines suitable to make these settling agents may range from ethylene diamine to tetraethylene pentamine or higher. Suitable alkyl

phenols for use in these settling agents may be those having one or more R group substituent, where R may be defined from C1 to C36 linear, branched, cyclic alkyl groups and combinations of these. The amounts of such settling agents may range from about 5 ppm independently to about 1000 ppm; alternatively from about 50 ppm independently to about 250 ppm.

[0028] Other additives may be added to the hydrocarbon stream including, but not necessarily limited to, corrosion inhibitors, demulsifiers, pH adjusters, metal chelants, scale inhibitors, hydrocarbon solvents, and mixtures thereof. As noted, in one non-limiting embodiment, the method is practiced ahead of a refinery desalting process that involves washing the crude emulsion with wash water.

[0029] In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been described as effective in providing methods and compositions for separating solids from a hydrocarbon stream having solids therein. However, it will be evident that various modifications and changes can be made thereto without departing from the broader scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, hydrocarbon streams, crude oils, demulsifying agents, and solids falling within the claimed parameters, but not specifically identified or tried in a particular composition or method, are expected to be within the scope of this invention.

[0030] The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, the method may consist of or consist essentially of separating at least a portion of solids from a hydrocarbon stream having solids therein by adding a demulsifying agent to the hydrocarbon stream in an effective amount, where the demulsifying agent may be or include at least one maleic acid derivative, and the demulsifying agent water-wets at least a portion of the solids.

[0031] Alternatively, the composition may consist of or consist essentially of a treated hydrocarbon stream in a crude storage tank including, but not limited to a demulsifying agent comprising at least one maleic acid derivative, in an amount ranging from about 0.1 ppm to about 200 ppm. The treated stream may further include a plurality of water-wet solids within the hydrocarbon stream where the plurality of solids are more water-wet as compared to a plurality of solids within the hydrocarbon stream in the absence of the demulsifying agent.

[0032] The words "comprising" and "comprises" as used throughout the claims, are to be interpreted to mean "including but not limited to" and "includes but not limited to", respectively.

CLAIMS

What is claimed is:

1. A method for separating at least a portion of solids from a hydrocarbon fluid having solids therein comprising:

adding an agent to the hydrocarbon fluid in an effective amount for subsequent separation of at least a portion of the solids from the hydrocarbon fluid, where the solids are present as solids prior to adding the demulsifying agent, and where the agent rests with the hydrocarbon fluid for about 24 hours to about 36 hours prior to the hydrocarbon fluid being delivered to a desalter;

the agent water-wetting at least a portion of the solids; wherein the agent is selected from the group consisting of di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl phenyl succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof; and

separating at least a portion of the solids from the hydrocarbon fluid.

2. The method of claim 1, wherein the agent further comprises a second component selected from the group consisting of naphthalene sulfonate, alkyl diphenyloxide disulfonate, and combinations thereof.

3. The method of claim 1, wherein an emulsion comprises an oil phase and a water phase; and wherein the oil phase comprises the hydrocarbon fluid; and wherein the adding of the agent is added to a phase selected from the group consisting of the oil phase, the water phase, and combinations thereof; and wherein the water-wet solids, after contact with the agent, are then carried into the water phase of the emulsion.

4. The method of claim 1, wherein the effective amount of the agent ranges from about 0.1 ppm to about 200 ppm based on the hydrocarbon fluid.

5. The method of claim 1, wherein the adding the agent is added to hydrocarbon fluid at a location selected from the group consisting of a crude storage tank, the suction of a transfer pump for subsequent injection into a crude storage tank, and combinations thereof.

6. The method of claim 1, wherein the solids are inorganic solids selected from the group consisting of metal oxides, metal dioxides, metal sulfides, metal sulfates, metal carbonates, sand, silt, clay, paraffin wax, dolomite, coke fines, zinc compounds and combinations thereof, where the metals are selected from the group consisting of iron, copper, manganese, zinc, nickel, and combinations thereof.

7. A method for separating at least a portion of solids from an oil phase of an emulsion, wherein the method comprises:

adding an agent to the emulsion in an amount ranging from about 0.1 ppm to about 200 ppm based on the emulsion, where the solids are present as solids prior to adding the agent, and where the agent rests with the emulsion for about 24 hours to about 36 hours prior to the hydrocarbon fluid being delivered to a desalter;

the agent water-wetting a plurality of solids within the emulsion; wherein the agent is selected from the group consisting of di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl phenyl succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof; and

separating the water-wet solids from the oil phase of the emulsion; wherein the water-wet solids, after contact with the agent, are then carried into a water phase of the emulsion.

8. The method of claim 7, wherein the agent further comprises a second component selected from the group consisting of naphthalene sulfonate, alkyl diphenyloxide disulfonate, and combinations thereof.

9. The method of claim 7, wherein the agent is added to the oil phase of the emulsion.

10. The method of claim 7, wherein the oil phase is selected from the group consisting of crude oil, asphalt, bitumen, shale condensates, decant oil, and combinations thereof.

11. The method of claim 7, wherein the solids are inorganic solids selected from the group consisting of metal oxides, metal dioxides, metal sulfides, metal sulfates, metal carbonates, sand, silt, clay, paraffin wax, dolomite, coke fines, zinc compounds and combinations thereof, where the metals are selected from the group consisting of iron, copper, manganese, zinc, nickel, and combinations thereof.

12. A method for separating at least a portion of solids from an oil phase of an emulsion, wherein the method comprises:

adding an agent to the emulsion in an amount ranging from about 0.1 ppm to about 200 ppm based on the emulsion, where the solids are present as solids prior to adding the agent, and where the agent rests with the emulsion for about 24 hours to about 36 hours prior to the hydrocarbon fluid being delivered to a desalter;

the agent water-wetting a plurality of solids within the emulsion; wherein the agent is selected from the group consisting of di-lauryl succinate, dioctyl succinate, di-hexyl succinate, octyl phenyl succinate, dodecyl diphenyl succinate, ditridecyl succinate, dioctyl sulfosuccinate, disodium laureth sulfosuccinate, diammonium 1-icosyl 2 sulfosuccinate, ammonium 1,4 didecyl sulfosuccinate, dihexyl sodium sulfosuccinate, sodium dinonyl sulfosuccinate, sodium lauryl sulfoacetate, salts thereof, and combinations thereof; and

separating the water-wet solids from the oil phase of the emulsion; wherein the water-wet solids, after contact with the agent, are then carried into a water phase of the emulsion;

wherein the oil phase is selected from the group consisting of crude oil, asphalt, bitumen, shale condensates, decant oil, and combinations thereof; and

wherein the solids are inorganic solids selected from the group consisting of metal oxides, metal dioxides, metal sulfides, metal sulfates, metal carbonates, sand, silt, clay, paraffin wax, dolomite, coke fines, zinc compounds and combinations thereof, where the metals are selected from the group consisting of iron, copper, manganese, zinc, nickel, and combinations thereof.

13. The method of claim 12, wherein the agent is added to the oil phase of the emulsion.