

A METHOD OF TREATING OILY SOLID PARTICLES**Field Of Invention**

5 The present invention relates to a method of treating oily solid particles entrapping particularly heavy crude oil and the like. Specifically, the disclosed method conditions the oily solid particles to a preferred state and reacts the oily solid particles with a specially formulated emulsified composition to remove the entrapped crude oil from the surface of the solids.

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Background Of The Invention

Treatment of oily waste material or oily solids derived majorly from oil drilling and refinery activities remain one of the biggest challenges in the oil and gas industry. These oily solid or oily waste materials can refer to oil sludge, drill cuttings, contaminated soils, contaminated sands/minerals and the like generated from various areas in the industry. It is a mixture majorly composed of sands, clay, minerals, and oil (crude oil or base oil from drilling fluid) presented in the mixture. It is crucial to at least remove or recover the crude oil from the solids prior to disposing the waste material to reduce its impact towards the environment. Presence of complex elements in the oily solids poses great hurdles towards the attempt to effectively separate the oil fragments from the solid phase and various approaches have been proposed along the years to tackle the problems. For example, in early year, sole water extraction using water jet to de-oil the oily solids is described in the United States patent application no. 3764008. While solvent extraction method in conjunction with special pre-treatment on the oil waste can be found in United States patent application no. 4260489, 4931161, 5347069 and 2009078612 respectively. Gary *et al.* describes another approach in United States patent application no. 4775457 which mix the oily solid waste with perlite following by burning the mixture to rid the oil fragment. With the advance in surfactant technologies, oil separation methods based on the use of emulsified composition and surfactants are developed to yield better separation of the oil from the solid particles. Donald offers a method of cleaning oil contaminated substrates by using two different surfactants with different HLB value and the difference in between the HLB value is at least 3. Cordova claims another method of treating oil-contaminated

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substrate by pre-treating the substrate with an emulsion breaker with subsequent steam distillation treatment to recover the oil phase from the substrate. Further, French patent application no. 2814385 provides a method to wash off the oil covered-particles using a lighter oil phase containing non-ionic surfactant and further separating the reactants into at least three different layers through decantation. Use of surfactant and aqueous polymer mixture for de-oiling oil contaminated substrate can be found in WO2005033469.

Summary Of The Invention

The present invention aims to disclose a method of treating oily solid waste or material. The oily solid particles preferably entrap high content of crude oil and the like in between the surface of the solid particles.

Another object of the present invention is to offer a method of treating oily solid particles using a specially formulated emulsified composition to effectively repel the oil phase off the surface of the oily solid particles.

Further object of the present invention is to offer an effective method of treating oily solid particles by preparing or pre-treating the oily solid particles to a suitable condition to be readily reacted with the emulsified composition.

At least one of the preceding objects is met, in whole or in part, by the present invention, in which one of the embodiments of the present invention is a method of cleaning oily mass having heavy oil adsorbed onto solid particles comprising the steps of creating electrostatic repulsion in between the surface of the solid particles and the adsorbed heavy oil using a basic solution; reacting the oily mass with an emulsified composition containing light hydrocarbon in the presence of the basic solution to displace the adsorbed heavy oil from the surface of the solid particles using the light hydrocarbon; separating the reacted oily mass into a liquid phase and a solid phase; and removing residues of the emulsified composition from solid phase, wherein the emulsified composition comprises a surfactant in 2 to 40% by weight of total composition selected from alkyl polyglycosides, glyceryl-based surfactant, polyglyceryl-based surfactant, sucrose-based surfactant, sorbitol fatty acid esters, sulfofatty acid methyl esters, acylated aminoacids, acyl glutamates, acyl glycinate,

acyl alaninates, lauroyl sarcosinate, nopol alkoxylates; a co-surfactant in 1 to 30% by weight of total composition selected from the group consisting of C3 to C18 alcohols, C3 to C18 alkyl lactates, lecithins, C3 to C18 fatty acids, diols, amino acids and any mixtures thereof; an oil phase in 15 to 90% by weight of total composition; and an aqueous phase in 5 0.5 to 20% by weight of total composition. Preferably, the disclosed method includes additional steps of recovering oil from the liquid phase.

In one aspect, the disclosed method has the oily mass dispersed within the basic solution in the creating and reacting steps to assist dissociation of the oil phase and increase surface 10 area of the oily mass to be reacted with the basic solution of the emulsified composition. Preferably, the emulsified composition constitutes 0.01 to 15% wt of the basic solution.

In one aspect, the removing step is washing the solid phase with a solvent mixture of an aqueous solution containing a co-solvent at least one time followed by separating the 15 washed solid phase from the solvent mixture that the co-solvent is ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, diprolyene glycol, methanol, ethanol, propanols, butanols, butoxyethanol or any combination derived thereof. Apart from that, aqueous solution is employed as the sole washing agent without any co-solvent in another embodiment of the disclosed invention.

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To further reduce oil content of the acquired solid phase, the removing step also includes as well a step of vaporizing the remained light hydrocarbon off the solid phase. This can be attained with heating or under an environment with reduced pressure. More preferably, the removing step is vaporizing the remained light hydrocarbon off the solid phase through 25 heating the solid phase at a temperature below the flash point of the light hydrocarbon.

To enhance efficiency of the disclosed method, the emulsified composition preferably further comprises a chelating agent selected from the group consisting of ethylenediamine tetraacetic acid, hydroxyethylenediamine triacetic acid, nitriolotriacetic acid, citric acid, 30 acetylacetone, porphyrin, catechol, dithiolene phosphonic acids and their salts, polyphosphates, phosphate esters, nonpolymeric phosphonates, aminophosphonates,

polyphosphonates phosphino polymers, polyphosphinates, polycarboxylates, polysulfonates or any combination derived thereof in another embodiment of the disclosed invention.

In another embodiment, the disclosed method of cleaning oily solid particles entrapping heavy crude oil comprises the steps of reacting the oily solid particles with an emulsified composition containing light hydrocarbon in the presence of a basic solution to displace the entrapped oil from the surface of the oily solid particles using the light hydrocarbon; separating the reacted oily solid particles into a liquid phase and a solid phase; and removing residues of the emulsified composition from solid phase, wherein the emulsified composition comprises a surfactant in 2 to 40% by weight of total composition selected from alkyl polyglycosides, glyceryl-based surfactant, polyglyceryl-based surfactant, sucrose-based surfactant, sorbitol fatty acid esters, sulfofatty acid methyl esters, acylated aminoacids, acyl glutamates, acyl glycines, acyl alanines, lauroyl sarcosinate, nopol alkoxylates; a co-surfactant in 1 to 30% by weight of total composition selected from the group consisting of C3 to C18 alcohols, C3 to C18 alkyl lactates, lecithins, C3 to C18 fatty acids, amino acids, diols, and any mixtures thereof; an oil phase in 15 to 90% by weight of total composition; and an aqueous phase in 0.5 to 20% by weight of total composition.

Brief Description Of The Drawings

Figure 1 is flowchart showing one embodiment of the invented method.

Detailed Description Of The Invention

It is to be understood that the present invention may be embodied in other specific forms and is not limited to the sole embodiment described herein. However modification and equivalents of the disclosed concepts such as those which readily occur to one skilled in the art are intended to be included within the scope of the claims which are appended thereto.

It is important to be noted herein that the term “oily mass” used herein throughout the specification refers to mixture of solid particles and heavy oil such as oil sludge, sludge from oil production well, drilling fluids containing barite and/or bentonite and/or clay, or hydrocarbon contaminated-soil, sand, clay and inorganic minerals from oil & gas production except mentioned otherwise.

The term "heavy oil" used herein shall refer to residual fuel oil or heavy crude oil which has density and/or specific gravity higher than light crude oil.

5 The present invention involves a method of cleaning oily mass having heavy oil adsorbed onto solid particles comprising the steps of creating electrostatic repulsion in between the surfaces of the solid particles and the adsorbed heavy oil using a basic solution; reacting the oily mass with an emulsified composition containing light hydrocarbon in the presence of the basic solution to displace the adsorbed heavy oil from the surface of the solid particles
10 using the light hydrocarbon; separating the reacted oily mass into a liquid phase and a solid phase; and removing residues of the emulsified composition from solid phase, wherein the emulsified composition comprises a surfactant in 2 to 40% by weight of total composition selected from alkyl polyglycosides, glyceryl-based surfactant, polyglyceryl-based surfactant, sucrose-based surfactant, sorbitol fatty acid esters, sulfofatty acid methyl esters,
15 acylated aminoacids, acyl glutamates, acyl glycinates, acyl alaninates, lauroyl sarcosinate, nopol alkoxylates; a co-surfactant in 1 to 30% by weight of total composition selected from the group consisting of C3 to C18 alcohols, C3 to C18 alkyl lactates, lecithins, C3 to C18 fatty acids, diols, amino acids and any mixtures thereof; an oil phase in 15 to 90% by weight of total composition; and an aqueous phase in 0.5 to 20% by weight of total
20 composition. Preferably, the surfactant is biodegradable and substantially low in toxicity.

Preferably, in one embodiment, the reacting step further comprises the steps of dispersing the oily mass in the basic solution. The dispersion can be carried out using any known apparatus in the art to stir or apply physical force to break the oily mass into smaller
25 portions to increase overall surface area of the oily mass to be reacted with the basic solution and the emulsified composition. In the dispersion process, portion of the oil or heavy crude oil is dissociated from the solid particles in the form of small droplets distributed in the basic solution due to the brute force applied. With hydrophobic heavy crude oil coated the surface of the solid particles, these small droplets may again dissolve
30 and accumulate onto oil-coating surface of the solid particles. Nevertheless, it was found by the inventors of the present invention that presence of the basic solution changes the surface charge of the solid particles and the dissociated small oil droplets to be negative or stronger

negative forming strong electrostatic forming a charge barrier thereof to prevent clumping (re-deposition) of these small droplets onto the hydrophobic surface of the solid particles again. Further, the basic solution also builds up negative charges on surfaces of the solid particles and the adsorbed heavy oil that an electrostatic repulsive force is generated therebetween to assist the dissociation of the adsorbed heavy oil from the solid particles. To effectively change the surface charges of the heavy oil and the solid particles into negative charges, the basic solution preferably has a pH value ranged in between 8 to 12. Preferably, the basic solution is prepared from water soluble alkaline salts of hydroxide, carbonate, phosphate or any combination derived thereof.

In the case where the electrostatic repulsive force is insufficient to repel off the adsorbed crude oil, the disclosed method further enhance the dissociation using the emulsified composition which infiltrates gaps existing in between the surface of the solid particles and the adsorbed heavy oil to subsequently repel the adsorbed heavy oil off. More specifically, the coated negative charges reduce the interfacial tension between the solid-oil interface allowing subsequent infiltration of aqueous phase or emulsified composition thereof. In conjunction with the basic pH in the reaction environment, the emulsified composition of the disclosed method is developed to deliver the contained surfactant to adsorb onto the solid surface thus squeezing off the adsorbed heavy oil. Through adsolubilizing of the surfactant, the adsorbed surfactant promotes adsorption of the light hydrocarbon to displace the heavy oil from the surface of the solid particles and avoid re-adsorption of the displaced heavy oil. In a more preferable embodiment, the light hydrocarbon is any one or combination of paraffin, kerosene, arene, mineral oil, triglycerides, esters, ethers, ketones, fatty alcohols, and light crude oil.

As in setting forth, the emulsified composition preferably comprises a surfactant in 2 to 40% by weight of total composition selected from alkyl polyglycosides, glyceryl-based surfactant, polyglyceryl-based surfactant, sucrose-based surfactant, sorbitol fatty acid esters, sulfofatty acid methyl esters, acylated aminoacids, acyl glutamates, acyl glycinate, acyl alaninates, lauroyl sarcosinate, nopol alkoxylates, a co-surfactant in 1 to 30% by weight of total composition selected from the group consisting of C3 to C18 alcohols, C3 to C18 alkyl lactates, lecithins, C3 to C18 fatty acids, diols, amino acids and any mixtures

thereof; an oil phase in 15 to 90% by weight of total composition; and an aqueous phase in 0.5 to 20% by weight of total composition. Chelating agents such as ethylenediamine tetraacetic acid, hydroxyethylenediamine triacetic acid, nitrilotriacetic acid, citric acid, acetylacetone, porphyrin, catechol, dithiolene phosphonic acids and their salts, polyphosphates, phosphate esters, nonpolymeric phosphonates, aminophosphonates, polyphosphonates phosphino polymers, polyphosphinates, polycarboxylates, polysulfonates or any combination thereof can be incorporated into emulsified composition used in the disclosed method. The chelating agent preferably has a concentration of 1 to 10% by weight of total composition to remove metal ion such as calcium, magnesium, barium, strontium, ferum, vanadium, nickel and cuprum suspended in the sludge and oil residue. According to the preferred embodiment, the oil phase of the emulsified composition is any one or combination of terpenes, aromatic hydrocarbons, mineral oil, paraffin oil, glycols, esters, fatty acid ester, fatty ester, glycol ethers, palm oil and other oil from plant source, diesel, and petroleum distillates. To impart better biodegradability and to be ecological friendly, oil from plant source, terpene from plant extraction or chemically synthesized, glycol, esters, fatty acid ester, or fatty ester is preferably used to constitute the oil phase of the present invention. Relying upon the types and the heavy oil content of oily mass, the emulsified composition is of 0.01 to 15% wt of the basic solution.

As in foregoing, the disclosed method further separates the reacted oily mass into the liquid phase and the solid phase. The separation of the liquid phase and the solid phase can be conducted through decantation with or without centrifugation. Upon complete of the decantation, the disclosed method has the liquid phase channel for a de-oiling process and the solid phase subjected to washing to further reduce oil content and remove residues of the emulsified composition in the solid phase. Specifically, the disclosed method has additional step of recovering the heavy oil from the liquid phase. In the oil recovery step, deoiler of a concentration of 20 to 200ppm is mixed into the liquid phase to promote the aqueous-oil separation. Preferably, the deoiler can be any one or combination of highly valent metal salt or polymeric flocculants. Highly valent metal salt is selected from but not limit to Iron(III) salts, Zinc(II) salts, and Aluminum(III) salts and mixtures thereof. Polymeric flocculants includes but not limit diallyldimethylammonium chloride polymers, acrylamide-based polymers, acrylate-based polymers, polyalkyleneimines,

polyalkanoamines, polyvinylammonium chloride, polyallylammonium chloride, branched polyvinylimidazoline acid salts, polysaccharides, chitosan, condensed tannins, dithiocarbamates, hydrolyzed polyacrylamide-grafted xanthan gum, poly- γ -glutamic acid, polyaspartic acid and mixtures thereof. The liquid phase substantially free of oil is then
5 discharged or being recycled to reuse in the disclosed method again.

Pursuant to another preferred embodiment, the steps of removing the residues of emulsified composition and the remaining heavy oil in the solid phase is washing or flushing the solid phase with an aqueous solution at least one time followed by separating the washed solid
10 phase from the solution. The aqueous phase can be water or water mixed with co-solvent such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, methanol, ethanol, propanols, butanols, butoxyethanol or any combination derived thereof. The aqueous phase dissolves most of the remaining residues of the emulsified composition including the surfactant adsorbed onto the surface of the solid particles in the
15 solid phase and small amount of the adsorbed heavy oil as well as light hydrocarbon. Upon finishing the washing or flushing, the solid phase is separated from the solution which is subsequently subjected to decantation to remove the heavy oil and the light hydrocarbon.

Accordingly, in another embodiment, the removing step is washing or flushing the solid
20 phase with a solvent mixture of an aqueous solution mixed with a co-solvent at least one time followed by separating the washed solid phase from the solution that the co-solvent is ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, methanol, ethanol, propanols, butanols, 2-butoxyethanol or any combination derived thereof. Particularly, the use of co-solvent in this embodiment improves efficiency to
25 extract the remaining hydrophobic compounds on the solid phase especially the heavy oil and light hydrocarbon while the aqueous phase dissolves most of the remaining hydrophilic residues of the emulsified composition. As in the foregoing, the washed or flushed solid phase is separated from the solvent mixture which is subsequently subjected to decantation to remove the heavy oil and the light hydrocarbon dissolved.

30 Similarly, the decantation of the solution or solvent mixture may include as well recovery of the oil in the solution using deoiler of a concentration of 20 to 200 ppm mixed into the

used solution or solvent mixture to promote the aqueous-oil separation. Likewise, the deoiler can be any one or combination of highly valent metal salt or polymeric flocculants. Highly valent metal salt is selected from but not limit to Iron(III) salts, Zinc(II) salts, and Aluminum(III) salts and mixtures thereof. Polymeric flocculants includes but not limit
5 diallyldimethylammonium chloride polymers, acrylamide-based polymers, acrylate-based polymers, polyalkyleneimines, polyalkanoamines, polyvinylammonium chloride, polyallylammonium chloride, branched polyvinylimidazoline acid salts, polysaccharides, chitosan, condensed tannins, dithiocarbamates, hydrolyzed polyacrylamide-grafted xanthan gum, poly- γ -glutamic acid, polyaspartic acid and mixtures thereof. The solution or solvent
10 mixture substantially free of oil is then discharged or being recycled to reuse in the disclosed method again.

In the preferred embodiment, the removing step involves also vaporizing the remained light hydrocarbon off the solid phase. It is important to be noted herein that the vaporizing step
15 can be conducted with or without having the washing step performed beforehand though it is more preferred to have the residue of emulsified composition to be washed off first. The evaporation of the light hydrocarbon is conducted in a pressure reduced environment or through heating or combination of both. To vaporize the light hydrocarbon off the solid phase, it is important to control the temperature of the heating below the flash point to avoid
20 ignition of the light hydrocarbon. Specifically, the removing step is vaporizing the remained light hydrocarbon off the solid phase through heating the solid phase at a temperature below the flash point of the light hydrocarbon.

Figure 1 shows an example of process flow related to the present invention involving
25 different steps as listed below.

Process I: Dispersion and oil removal; breaking down the oily solid cluster, dispersing the solid and oil removing/degreasing simultaneously. The invented emulsified composition and/or alkaline salt are added into this process to treat the oily solid.

Process II: Decantation to separate liquid (water with emulsified/removed oil) from solid.

30 Process III: Washing with water or mixed co-solvent with water. This washing step aims to remove the remaining composition of the cleaning chemical solution and also eliminate the

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effect of adsolubilization (oil solubilized by surfactant admicelles on solid surface) by dilution and surfactant desorption.

Process IV: Decantation to separate liquid (water with emulsified/removed oil) from clean solid;

5 Process V: Disposal treatment

Process V_a: Drying; at the temperature around 80-100 °C aiming to remove moisture and remaining light oil replacing the heavy oil in the sample during the cleaning process; and

Process V_b: De-Oiling water; water treatment with de-oiler (< 1000 ppm).

10 One skilled in the art will readily appreciate that the present invention is well adapted to carry out the objects and obtain the ends and advantages mentioned, as well as those inherent therein. The embodiment describes above is not intended as limitations on the scope of the invention.

15 EXAMPLE 1

The invented emulsified composition presented in following examples are water-in-oil nanoemulsion with oil-water interfacial tension lower than 0.01 mN/m (measured at 25 °C by KRUSS spinning drop tensiometer; model SITE100). The mean particle size of the nanoemulsion is smaller than 100 nm (measured at 25 °C by particle size analyzer; Malvern Zetasizer Nano ZS). The oily solid samples listed in TABLE 1 are the samples used in testing various embodiments of the present invention. The properties of each oily solid sample were determined by using the retort analysis. All samples are actual specimens from Oil & Gas industrial processes. Treatment on these oily solid samples aims to reduce the oil content in the disposed solid to < 1 w/w%. The evaluation of the effectiveness of the invented emulsified composition, treatment process and other related cleaning chemicals are demonstrated in the next EXAMPLES.

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TABLE 1: Composition of oily solid samples from retort analysis

Sample No.	General name	Form	% Total hydrocarbon that can be extracted up to 950 °F (w/w%)	% Light oil that can be extracted up to 950 °F (w/w%)	% Wax (heavy oil) that can be extracted up to 950 °F (w/w%)	% Water (w/w%)	Solids (w/w%)
A	Drill cuttings	Solid	13	4	9	0.3	86.7
B	Sand produced from production well	Solid	12	5	7	7	81
C	Solid sediment from the used oil-based drilling fluid	Solid	13	5	8	8	79
D	Crude oil sludge solid sediment	Paste	29	12	17	6	65

Note: Weight of wax and light oil were calculated based on an assumed density of 0.82 g/mL.

EXAMPLE 2

- 5 The efficiency of the invented oily solid treatment method and cleaning chemical composition was evaluated with different process steps and cleaning chemicals used. The efficiency of the process was referred to the total oil content in the solid after final treatment. Oil content was determined by the retort analysis and/or Soxhlet solvent extraction (if the oil content was expected to be < 1 w/w%). The typical target of the oil content in the solid after treatment is < 1 w/w%. Sample A, which is drill cuttings had been used for the experiment in this EXAMPLE. Sodium carbonate, sodium tripolyphosphate and potassium hydroxide had been used as the alkaline salt to adjust the pH of the cleaning solution to 8-12. The cleaning solution/sample ratio is 1/1 by weight. The washing solvent was water or water mixed with co-solvent (ethylene glycol, isopropanol, or butoxyethanol).
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- 15 Water was the solvent of cleaning solution for the first process step. The % concentration of cleaning solution is the % compared with the treated sample weight otherwise stated. Cleaning solution/sample ratio was 1/1 by weight. This experiment also compares the efficiency between the invented method and cleaning composition (Experiment A4-A15) and the conventional surfactant cleaning method (Experiment A1-A3). All cleaning methods were conducted at room temperature, except the drying process in the final treatment step.
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Conventional surfactant cleaning method

- 25 For the conventional surfactant cleaning method using surfactant aqueous solution to wash out the oil from the solid samples (A1-A3), according to TABLE 1, conventional non-ionic

surfactant, which is insensitive to ions, has been used for this process. Conventional anionic surfactants were avoided to be used in treating these samples as precipitation of surfactants occurs in the presence of hard ions such as Ca^{2+} in the samples.

- 5 The oil content was reduced from 13 w/w% to 10 w/w% although the used surfactant concentration was very high (20 w/w%). No significant improvement of the cleaning efficiency of the surfactant solution to extract the oil from the solid was observed when the surfactant concentration was increased from 5 to 20 w/w%. This implies that the surfactant cleaning power has limitation, potentially because the surface tension (which directly refers
10 to wettability and emulsification efficiency) of the surfactant solution become constant after its critical micelle concentration.

In addition, this conventional surfactant was not effective possibly because of another two reasons (1) oil/water interfacial tension induced by this surfactant might not be sufficiently
15 low and (2) the wax or heavy oil strongly adsorb on the solid surface, as well as, the heavy oil molecularly blended with the trapped light oil helping light oil to be trapped together with heavy oil and difficult to be emulsified.

Invented treatment method and cleaning chemical compositions

- 20 The invented emulsified composition with and without sodium carbonate (alkaline salt) were mixed in water to produce treating solution to clean the solid Sample A (drill cuttings) with the original oil content of 13 w/w% (Experiment A4-A15).

The treatment without sodium carbonate was shown in experiment A4 and A5. Experiment
25 A4 indicated that the 1 w/w% invented emulsified composition was not sufficient to reduce the oil content in the solid from 13 w/w% to < 1 w/w% even though the drying process in the final process was applied. Increasing concentration of the invented emulsified composition to 15 w/w% was showing the significantly increased oil removal efficiency; reducing oil content of the solid to < 1 w/w%. Improving cleaning efficiency using sodium
30 carbonate was demonstrated in the next experiments.

Experiment A6 shows that if Sample A was treated with cleaning solution consisting of 1 w/w% of the invented emulsified composition and 5 w/w% sodium carbonate and subsequently washed with water without drying process in the last process step, the oil content in the solid after treatment was about 3.6 w/w% without drying process in the final process step, possibly because the emulsified oil and wax were still trapped in the void space between the solid particles, which was promoted by adsolubilization phenomena (oil solubilized by surfactant admicelles on solid surface). The oil removal efficiency of this process was slightly improved when the concentration of the invented emulsified composition was increased from 1 to 5 w/w% without drying process in the final step. However, with the drying process as the final cleaning process step, the oil content was reduced to 0.6 w/w% (< 1 w/w%). This efficiency is comparable with the treatment with 15 w/w% invented emulsified composition without sodium carbonate in experiment A5.

Experiment A9 indicated that increasing concentration of sodium carbonate higher than 5 w/w% was not effective way to improve the cleaning efficiency of the whole cleaning process for this sample, since the surface charge density on the solid surface might be already reach the maximum and dispersion of the solid particles were maximized. Sodium carbonate is the key component for improving particle dispersion and degreasing effect.

The different kinds of alkaline salts for the invented cleaning method were tested in experiment A10 for sodium tripolyphosphate and A11 for potassium hydroxide. The results showed that these phosphate and hydroxide forms of alkaline salts also worked very well to improve oily solid cleaning efficiency as good as the carbonate form. The oil contents in the solid after treatment were below 1 w/w% for both cases.

Impact of the co-solvent was investigated in the experiment A12-15, which used water mixed with ethylene glycol, isopropanol or butoxyethanol as the mixed solvent respectively, for the washing process step. The water/co-solvent ratio is 9/1 by volume. The results shows that the co-solvent assists in reducing the oil content in the solid after drying process in final cleaning process step to < 0.5 w/w%, consistently.

However, using co-solvent without drying process in the final process step did not provide acceptable cleaning efficiency of the invented oily solid cleaning method as observed the oil content in the solid after final treatment > 2 w/w%. (target is < 1 w/w%).

5 TABLE 2: Efficiency of the invented oily solid treatment method and chemical cleaning compositions

Experiment No.	Process I Cleaning solution	Process III Cleaning solution	Process V Thermal treatment (Vaporization)	Total oil content in original oily solid sample (before treatment)	Total oil content in solid after treatment
Sample A					
A1	5% Surfactant aqueous solution	Water	No	13%	11%
A2	20% Surfactant aqueous solution	Water	No	13%	10%
A3	20% Surfactant aqueous solution	Water	Yes (90°C)	13%	9%
A4	1% Invented emulsified composition	Water	Yes	13%	6%
A5	15% Invented emulsified composition	Water	Yes	13%	0.8%
A6	1% Invented emulsified composition + 5% sodium carbonate	Water	No	13%	3.6%
A7	5% Invented emulsified composition + 5% sodium carbonate	Water	No	13%	3%
A8	1% Invented emulsified composition + 5% sodium carbonate	Water	Yes	13%	0.6%
A9	1% Invented emulsified composition + 10% sodium carbonate	Water	Yes	13%	0.6%
A10	1% Invented emulsified composition + 10% sodium tripolyphosphate	Water	Yes	13%	0.8%
A11	1% Invented emulsified composition + 10% potassium hydroxide	Water	Yes	13%	0.7%
A12	1% Invented emulsified composition + 10% sodium carbonate	Water/Ethylene glycol (9/1 v/v)	Yes	13%	0.2%
A13	1% Invented emulsified composition + 10% sodium carbonate	Water/Isopropanol (9/1 v/v)	Yes	13%	0.1%
A14	1% Invented emulsified composition + 10% sodium carbonate	Water/Butoxyethanol (9/1 v/v)	Yes	13%	0.1%
A15	1% Invented emulsified composition + 10% sodium carbonate	Water/Butoxyethanol (9/1 v/v)	No	13%	2.7%

Note: % Concentration of cleaning solution is the % compared with the treated sample.

10 EXAMPLE 3

The treatment of different kinds of oily solid samples was evaluated in this example. There are 4 kinds of samples shown in TABLE 1 which are drill cuttings (experiment A8), sand produced from oil production well (experiment B1), solid sediment from the used oil-based drilling fluid (experiment C1), and crude oil sludge solid sediment (experiment D1, D2 & D3). The cleaning solution in the first process step contains 1 w/w% of the invented emulsified composition and 5 w/w% sodium carbonate in water. Water was used as the washing agent in the washing step. All experiments used drying process as the final treatment step. It was indicated that the oil could be efficiently removed from the solid for

sample A, B and C (experiment A6, B1 and C1, respectively) effectively, reducing the oil content in the solid samples from 12-13 w/w% to < 1 w/w%.

However, the same cleaning solution composition used to treat these 3 samples was not very effective for sample D (experiment D1) since the oil content is possibly too high. The invented emulsified composition might not be sufficient to emulsify, disperse and replace the oil on the solid surface (in the sample). Once this issue occurs, sodium carbonate would not be able to change the surface charge of the solid surface in the sample easily, since the thick adsorbed oil layer on solid surface was blocking.

Another experiment using higher dosage of the invented emulsified composition and sodium carbonate was conducted in experiment D2 to improve the cleaning efficiency. However, the oil content in the solid after final process step was still higher than 1 w/w%.

Improvement by using water/co-solvent (butoxyethanol) mixture for washing step was exhibited in experiment D3. The oil content in the solid after final treatment could be successfully reduced to < 1 w/w%.

TABLE 3: Effectiveness of the invented oily solid cleaning method on different kinds of oily solids

Experiment No.	Process I Cleaning solution	Process III Cleaning solution	Process V Thermal treatment (Vaporization)	Total oil content in original oily solid sample (before treatment)	Total oil content in solid after treatment
A8	1% Invented emulsified composition + 5% sodium carbonate	Water	Yes	13%	< 1%
B1	1% Invented emulsified composition + 5% sodium carbonate	Water	Yes	12%	< 1%
C1	1% Invented emulsified composition + 5% sodium carbonate	Water	Yes	13%	< 1%
D1	1% Invented emulsified composition + 5% sodium carbonate	Water	Yes	29%	9.0%
D2	5% Invented emulsified composition + 10% sodium carbonate	Water	Yes	29%	3.3%
D3	5% Invented emulsified composition + 10% sodium carbonate	Water/Butoxyethanol (9/1 v/v)	Yes	29%	< 1%

Note: % Concentration of cleaning solution is the % compared with the treated sample.

Claims

1. A method of cleaning oily mass having heavy oil adsorbed onto solid particles
5 comprising the steps of
creating electrostatic repulsion in between the surface of the solid particles and the adsorbed
heavy oil using a basic solution;
reacting the oily mass with an emulsified composition containing light hydrocarbon in the
presence of the basic solution to displace the adsorbed heavy oil from the surface of the
10 solid particles using the light hydrocarbon;
separating the reacted oily mass into a liquid phase and a solid phase; and
removing residues of the emulsified composition from solid phase, wherein the emulsified
composition comprises a surfactant in 2 to 40% by weight of total composition selected
from alkyl polyglycosides, glyceryl-based surfactant, polyglyceryl-based surfactant,
15 sucrose-based surfactant, sorbitol fatty acid esters, sulfofatty acid methyl esters, acylated
aminoacids, acyl glutamates, acyl glycines, acyl alanines, lauroyl sarcosinate, nopol
alkoxylates; a co-surfactant in 1 to 30% by weight of total composition selected from the
group consisting of C3 to C18 alcohols, C3 to C18 alkyl lactates, lecithins, C3 to C18 fatty
acids, diols, amino acids and any mixtures thereof; an oil phase in 15 to 90% by weight of
20 total composition; and an aqueous phase in 0.5 to 20% by weight of total composition.
2. A method of claim 1 further comprising the step of recovering oil from the liquid
phase.
- 25 3. A method of claim 1 or 2, wherein the emulsified composition is of 0.01 to 15% wt of
the basic solution.
4. A method of claim 1 or 2, wherein the removing step is washing the solid phase with
an aqueous solution at least one time followed by separating the washed solid phase from
30 the solution.

5. A method of claim 1 or 2, wherein the removing step is washing the solid phase with a solvent mixture of an aqueous solution mixed and a co-solvent at least one time followed by separating the washed solid phase from the solution that the co-solvent is ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, diprolylene glycol, methanol, ethanol, propanols, butanols, butoxyethanol or any combination derived thereof.
6. A method of claim 1 or 2, wherein the removing step is vaporizing the remained light hydrocarbon off the solid phase.
7. A method of claim 1 or 2, wherein the removing step is vaporizing the remained light hydrocarbon off the solid phase through heating the solid phase at a temperature below the flash point of the light hydrocarbon.
8. A method of claim 1 or 2, wherein the reacting step further comprises dispersing the oily mass in the basic solution.
9. A method of claim 1 or 2, wherein the basic solution is prepared from alkaline salts of hydroxides, carbonates, , phosphates or any combination derived thereof.
10. A method of claim 1 or 2, wherein the emulsified composition further comprises a chelating agent selected from the group consisting of ethylenediamine tetraacetic acid, hydroxyethylenediamine triacetic acid, nitriolotriacetic acid, citric acid, acetylacetone, porphyrin, catechol , dithiolene phosphonic acids and their salts, polyphosphates, phosphate esters, nonpolymeric phosphonates, aminophosphonates, polyphosphonates phosphino polymers, polyphosphinates, polycarboxylates, polysulfonates or any combination derived thereof.