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(54) **Hydrocarbon wetting and separation agent**

(57) The invention relates to the provision of an oil wetting and removal agent which allows the effective and environmentally friendly removal and/or separation of oil and other petrochemical products from material such as oil drillings, rocks, plant and/or marine life. The

wetting agent is typically mixed to provide an emulsion which acts to attract the oil from the said materials and hence allow the cleaning of the same. The wetting agent includes a plant extract or extracts therein.

EP 1 380 630 A2

Description

[0001] This invention relates to an oil wetting agent for the separation of oil from oil containing matter.

[0002] Although the following description refers almost exclusively to an oil wetting agent for use in separating oil from drill cuttings, it will be appreciated by persons skilled in the art that the present invention can be used to separate oil from a range of oil containing matter. For example, the oil wetting agent of the present invention can be used for the cleaning of animals, such as marine wildlife and birds following an oil spill, cleaning plant matter, rocks or indeed any other material in which oil may be unwanted. Furthermore, reference to oil should be interpreted as including oil or other petrochemicals or hydrocarbons and/or the like.

[0003] There have been many incidents where oil spills and subsequent pollution have resulted in damage to wildlife and the environment. The public image of an oil company is greatly affected by the level of pollution the company produces. As such, a heavy burden is placed on oil companies by society to prevent or at least limit the damage and destruction caused by waste matter being released untreated into the environment and/or following accidental oil spills. For example, in the field of drilling for oil, disposal oil remains on the drill cuttings which are then dumped into the sea. Stricter legislation has recently been introduced to reduce the percentage of quantities of oil dumped into the sea along with the drill cuttings from 6% to less than 1%.

[0004] There is currently no method available for separating oil from drill cuttings to meet the required standards which are suitable for use in off shore operations. As such, many companies are currently forced to ship the drill cuttings back to shore for land based treatment prior to disposal. This is both expensive and time consuming.

[0005] It is therefore an aim of the present invention to provide an oil wetting agent, which allows oil to be separated from oil containing matter and which overcomes the abovementioned problems.

[0006] According to a first aspect of the present invention there is provided a hydrocarbon or oil wetting agent, hereinafter referred to in the description in a non specific manner as an oil wetting agent, suitable for separating oil from oil containing matter, said oil wetting agent including a plant extract which is buffered to an acidic pH level by one or more buffer agents.

[0007] When the oil wetting agent is added to a treatment solution of oil containing matter in an aqueous solution, a micro-emulsion is formed between the aqueous solution, oil wetting agent and the oil, thereby breaking the electro static attractions between the oil and the matter and facilitating subsequent separation of the matter from the oil and aqueous emulsion. The oil also dissolves in the lipophilic parts of the solution and the ionic concentration of the solution promotes the attraction of the oil to the solution rather than attachment to the matter to which it was originally attached. Typically the oil containing matter is an oil containing solid such as rock, drill cuttings or the like.

[0008] The advantage of using a plant extract is that it produces efficient separation of the oil from the solid matter whilst being biodegradable, thereby preventing or at least limiting harm to the environment.

[0009] In one preferred embodiment the plant extract used is Glycyrrhiza glabra, also known as liquorice, which can be provided in a liquid or powdered form.

[0010] Preferably the plant extract is provided in a hydro alcoholic solution. The solution typically includes liquorice extract and contains glycyrrhizin acid.

[0011] Preferably the buffer agents buffer the oil wetting agent to a pH level of 5.5.

[0012] Preferably the buffer agents include biodegradable material such as any or any combination of fruit acids and/or sodium salts suspended in a saline solution.

[0013] Further preferably, the buffer agents contain the ions of salts as well as sugars (both simple and complex), proteins, amino acids, saponins, fatty acids, lipids, starches, plant acids and carbohydrates.

[0014] Preferably the alcohol is removed from the wetting agent and preservation is by potassium sorbate at 0.2%.

[0015] Reference to "oil" encompasses any type of oil, crude oil, refined oil, hydrocarbon or petrochemical.

[0016] Preferably the emulsion mixture is separated from the solid matter using a form of density separation. For example, a separation technique such as I-SEP (Caltec) can be used.

[0017] In one embodiment the oil containing matter comprises mainly drill cuttings. However, the matter can be any mineral (i.e. crushed or broken rock, soil or dirt contaminated with oil), animal (i.e., marine animals, birds, land animals or people), plant matter contaminated with oil and/or the like.

[0018] In accordance with a further aspect of the invention, there is provided a wetting agent, said wetting agent provided for application to oil containing material to allow the separation of at least some of said oil from the material, wherein said wetting agent includes a plant extract.

[0019] In a preferred embodiment, the wetting agent includes propylene glycol, citric acid, liquorice extract, potassium sorbate and water.

[0020] In one embodiment, the wetting agent includes the plant extract in the form of liquorice extract in the percentage of between 1 and 20% of the composition. prior to addition to water. In a further embodiment, the composition is between 10% and 20%.

[0021] In a further embodiment, the composition of the wetting agent includes sodium chloride, disodium hydrogen

phosphate, citric acid, liquorice extract, potassium sorbate (also referred to as Nipaguard) and water.

[0022] In a further embodiment, the liquorice extract is substituted by a further plant extract or alternatively, further plant extract is used in conjunction with the liquorice extract.

[0023] According to a further aspect of the present invention there is provided a method of separating oil from an oil containing matter, said method including the steps of mixing the oil containing matter with an aqueous solution and a hydrocarbon wetting agent, said oil wetting agent including a plant extract which is buffered to an acidic pH level by one or more buffer agents, stirring the mixture for a pre-determined period of time until said oil, oil wetting agent and aqueous solution form a micro-emulsion, with oil having being released from the said solid matter.

[0024] The present invention has the advantage that the process utilising the oil wetting agent can be performed in relatively inclement conditions such as, for example, using off shore facilities, thereby overcoming the need for transporting the material such as shipping drill cuttings back to shore for processing. In addition, the process of the present invention is safer and more ecologically acceptable than conventional processes.

[0025] Although the invention is of use in separating any hydrocarbon material from material as is shown, the wetting agent is found to be particularly effective with oil.

[0026] Embodiments of the present invention will now be described with reference to the following examples and figures, wherein:

[0027] Figure 1 illustrates apparatus in one embodiment for use in the process of separating the oil from the oil containing matter.

[0028] In accordance with this embodiment of the present invention, a hydrocarbon wetting agent is provided which is formed from the plant extract *Glycyrrhiza glabra*, otherwise known as liquorice. The wetting agent has been shown to easily remove oil from oil containing solid matter when added to an aqueous solution, such as water, thereby having many potential uses.

[0029] One important use of the oil wetting agent of the present invention is for de-oiling drill cuttings using off shore facilities. Once the wetting agent of the present invention has wetted or been added to water, it has been shown to easily remove the oil from the drill cuttings as the resulting emulsion formed between the oil, water and oil wetting agent can subsequently be separated from the slurry of drill cuttings using separation techniques. The oil in the emulsion is preferentially separated with the aqueous solution rather than with the slurry.

[0030] An example of a separation technique used to remove the slurry from the oil and water emulsion mixture is the I-SEP compact separation technique (Caltec). This separation technique relies on the constituents of the mixture being separated having different densities.

[0031] An example of typical separation apparatus 2 used in the method of the present invention is shown in figure 1. The apparatus 2 comprises a collecting tank 4 for the containment of the oil containing material which are transferred via an auger 6 to a pump 8. From the pump 8 the material passes , with the addition of the wetting agent 10 in accordance with the invention and perhaps some returned partially separated material 12, to three separator phases, a first phase liquid/solids separator 14, an oil and water liquid phase 16 and an I-sep type oil water separator 18. On entry into the I-sep separator 18, the mixture is subjected to high 'g' forces which separate the light phases from the dense phases in the mixture (i.e., the water from the oil mixture). From the separator 18 water and some oil 12 passes largely to a membrane filter 20 which allows final removal of oil so that the water less than typically 0.1% of oil 22 is discharged. The separated oil 24 can be passed for disposal or recycling as required.

[0032] The solids 26 which are removed after the first phase separation can be discharged to sea as they typically only contain less than 0.1% of oil.

[0033] In one specific example of the invention, tests were performed on two samples 1, 2. Sample 1 comprised a portion of oiled drill cuttings tested prior to treatment and Sample 2 comprised 30kg oiled drill cuttings with 100kg water, and 10kg of the wetting agent in accordance with the invention added and the separation treatment performed.

[0034] Various measurements were performed on the two samples with the following results.

Sample No.	1	2
Mass of empty receptacle	573.11	573.15
Mass Full receptacle	647.93	630.34
Mass of cuttings	74.82	57.19
Mass of cylinder (empty)	85.03	85.04
Mass of cylinder + liquid	108.5	106.91
Volume of water	11	20.5
Mass of liquid	23.47	21.87
Mass of dry cuttings	51.35	35.32
Mass of oil	12.47	1.37

(continued)

Sample No.	1	2
Oil on Cuttings	24.28	3.88
Sample 1 comprises the cuttings before treatment Sample 2 comprises 100KG water, 10 kg wetting agent 30 kg cuttings		

[0035] These results clearly show how the quantity of oil retained in the drill cuttings is significantly reduced after treatment with the wetting agent in accordance with the invention and as indicated by the value of "Oil on cuttings" of 3.88 for the treated Sample 2 compared to the value of 24.28 for the untreated Sample 1.

[0036] In one example of the wetting agent and, it should be appreciated a non limiting example, the composition of the wetting agent can be:

Product	Qty/kg in GM
Sodium Chloride	67.5
Disodium Hydrogen Phosphate	48.75
Citric Acid	30
Liquorice Ext	30
Potassium Sorbate	20
Water	1000

[0037] Wherein it is shown that in addition to the plant extract and acid, potassium sorbate, disodium hydrogen phosphate and sodium chloride are added.

[0038] Further examples of the invention are set out below:

[0039] A wetting agent is prepared so that 5mm of the wetting agent diluted in 1,000mm of water can be used to wet 1kgm of cuttings, i.e. the oil containing material. For this purpose, the following composition can be used:-

Product	Spec	Qty/kg	in GM
Sodium Chloride	99.98	1.8	90
Disodium Hydrogen Phosphate	99.98	1.3	65
Citric Acid	99.98	0.8	80
Liquorice extract	10.01	0.8	80
Potassium Sorbate (Nipaguard)	99.98	1.5	20
Water	-	-	1,000

[0040] In this case, the procedure for 10 tonnes wetting agent is to weigh out the ingredients and sheer into 1,500 litres of hot water. This is then diluted to 10,000 litres and mixed thoroughly with bottom, top and middle samples taken to test for weight per millilitre, solids and HPLC values.

[0041] An alternative form to make the wetting agent so that 5ml is diluted into 1,000ml of water to wet 1 kg of oil containing material, has the following specification:-

Product	Spec	Qty/kg	in GM
Propylene Glycol	99.98	1.8	400
Citric Acid	99.98	0.8	40
Liquorice Extract	10.01	0.8	40
Potassium Sorbate	99.98	2.0	2
Water	-	-	600

[0042] The same procedure as the previous example is used to prepare the constituents.

[0043] The invention therefore provides a product and method of particular advantage in reducing and allowing removal of oil or hydrocarbon content from matter, typically solid matter. This reduces the pollution which may occur conventionally and allows the safe disposal of the oil. The method also lends itself to being performed in situ rather

than requiring transport of the material prior to treatment.

Claims

1. A hydrocarbon wetting agent suitable for separating a hydrocarbon from hydrocarbon containing matter, said wetting agent including a plant extract which is buffered to an acidic pH level by one or more buffer agents.
2. A hydrocarbon wetting agent according to claim 1 wherein when the wetting agent is added to a treatment solution of a hydrocarbon containing material in an aqueous solution, a micro emulsion is formed between the aqueous solution, wetting agent and hydrocarbon.
3. A hydrocarbon wetting agent according to claim 2 wherein the micro emulsion breaks the electrostatic attractions between the hydrocarbon and the hydrocarbon containing material and facilitates subsequent separation of the hydrocarbon from the material.
4. A hydrocarbon wetting agent according to claim 2 wherein the hydrocarbon dissolves in the lipophilic parts of the solution.
5. A hydrocarbon wetting agent according to claim 2 wherein the ionic concentration of the solution attracts the hydrocarbon to the solution rather than the material to which it was originally attached.
6. A hydrocarbon wetting agent according to claim 1 wherein the hydrocarbon containing matter is an oil containing solid.
7. A hydrocarbon wetting agent according to claim 1 wherein the plant extract used is glycyrrhiza glabra.
8. A hydrocarbon wetting agent according to claim 7 wherein the plant extract is used in a liquid form.
9. A hydrocarbon wetting agent according to claim 7 wherein the plant extract is used in a powder form.
10. A hydrocarbon wetting agent according to claim 1 wherein the plant extract is provided in a hydro-alcoholic solution including liquorice extract and glycyrrhizin acid.
11. A hydrocarbon wetting agent according to any of the preceding claims wherein the hydrocarbon is oil.
12. A hydrocarbon wetting agent according to claim 1 wherein the buffer agents include biodegradable material.
13. A hydrocarbon wetting agent according to claim 12 wherein the biodegradable material includes any or any combination of fruit acids and/or sodium salts suspended in a saline solution.
14. A hydrocarbon wetting agent according to claim 1 wherein the buffer agents contain any, or any combination, of ions or salts, sugars, proteins, amino acids, saponins, fatty acids, lipids, starches, plant acids and carbohydrates.
15. A hydrocarbon wetting agent according to claim 1 wherein alcohol is removed from the wetting agent and potassium sorbate added.
16. A hydrocarbon wetting agent according to any of the preceding claims wherein the emulsion mixture is separated from the solid matter using density separation.
17. A wetting agent, said wetting agent provided for application to oil containing material to allow the separation of at least some of said hydrocarbon from the material, wherein said wetting agent includes a plant extract.
18. A wetting agent according to claim 17 wherein the wetting agent includes propylene glycol, citric acid, liquorice extract, potassium sorbate and water.
19. A wetting agent according to claim 17 wherein the wetting agent includes the plant extract in the form of liquorice extract in the percentage of between 1 and 20% of the composition prior to addition to water.

20. A wetting agent according to claim 19 wherein the liquorice extract is included in the percentage 10% and 20%.

21. A wetting agent according to claim 17 wherein the composition of the wetting agent includes sodium chloride, disodium hydrogen phosphate, citric acid, liquorice extract, potassium sorbate (also referred to as Nipaguard) and water.

22. A wetting agent according to claim 17 wherein more than one type of plant extract is used.

23. A method of separating oil from oil containing matter, said method including the steps of mixing oil containing matter with an aqueous solution including a hydrocarbon wetting agent, said oil wetting agent including a plant extract which is buffered to an acidic pH level by one or more buffer agents; stirring the mixture for a predetermined period of time until the said oil, oil wetting agent and aqueous solution form a micro emulsion, with the oil released from the said solid matter.

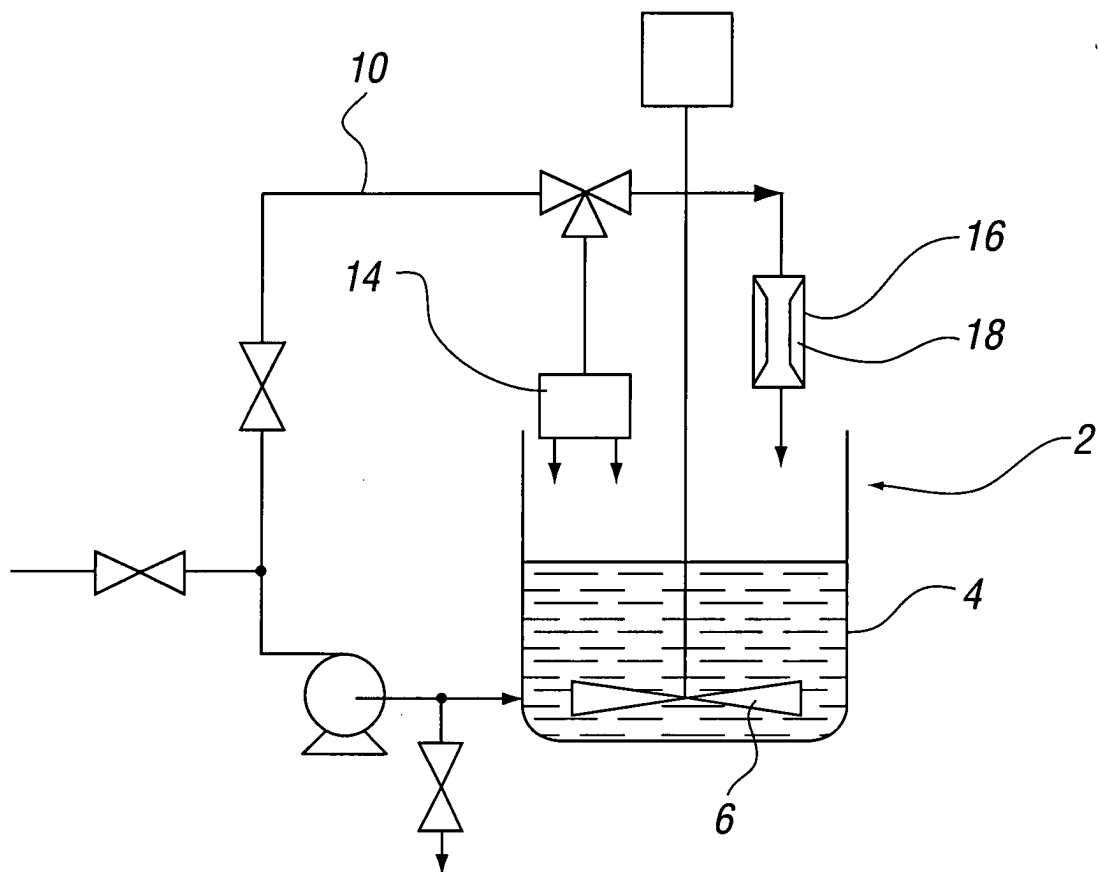


FIG. 1