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(54) Title: PROCESSING MIXTURES OF HYDROCARBONS AND WATER

(57) Abstract: A method of facilitating separation of hydrocarbon from a mixture comprising 5 hydrocarbons and water is disclosed. The mixture is exposed to a composition comprising at least certain polymeric surfactants such that at least a portion of the hydrocarbons forms a separate layer from the remaining portion of the mixture. The disclosure further provides a use of certain polymeric surfactants to at least partially separate hydrocarbon from a mixture comprising hydrocarbons and water such that at least a portion of the 10 hydrocarbons forms a separate layer from the remaining portion of the mixture. The disclosure further provides a method of removing a sludge comprising a mixture of petroleum and water from a surface, the method comprising treating the sludge with an amount of a composition comprising certain polymeric surfactants effective to remove the sludge from the surface.

PROCESSING MIXTURES OF HYDROCARBONS AND WATER

Background

Mixtures of hydrocarbons and water are commonly found in industrial situations. Crude oil sludge contamination of oil tankers is one such occurrence. Such contamination is a problem, particularly where such oil tankers need to undergo repairs and other servicing activity usually involving high temperatures at ship yards. The presence of residual crude oil sludge can cause a number of problems during such cleaning (e.g., the presence of the cargo vapour, high disposal cost of the sludge and the difficulty in ensuring that the cleansing operation is fully effective). In another example, in tar sands processing plants spots of tar sand contaminate the equipment. Tar sands are mixtures of hydrocarbons, water, and typically sand or clay. Cleaning of such spots has proven to be difficult. In oil fields, above-ground equipment (e.g., vehicles and heavy equipment) also gets contaminated with crude oil which is difficult to remove. Use of strong acids such as hydrochloric and hydrofluoric acid is commonly necessary, which can cause corrosion of the equipment.

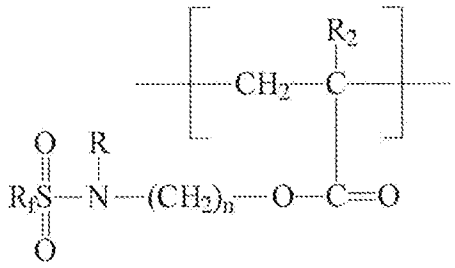
Another situation where mixtures of hydrocarbons and water exist are in emulsion form where it is desirable to recover as much of the oil as possible.

While there have been attempts to do so, methods of cleaning contaminated equipment and optionally recovery of the hydrocarbons still have drawbacks.

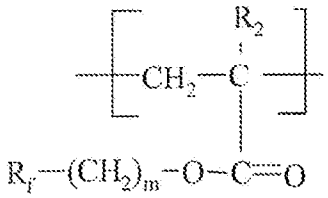
Summary

In one aspect, this disclosure provides a method of facilitating separation of hydrocarbon from a mixture comprising hydrocarbons and water, the method comprising: exposing the mixture to a composition comprising a first polymeric surfactant such that at least a portion of the hydrocarbons forms a separate layer from the remaining portion of the mixture, the first polymeric surfactant comprising

at least one first divalent unit selected from the group consisting of formulae:



(I); and



(II); and

a polyalkyleneoxy segment;

wherein

R_f represents a perfluoroalkyl group having from 1 to 6 carbon atoms;

R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

n is an integer from 2 to 10; and

m is an integer from 1 to 5.

In another aspect, this disclosure provides a use of a composition comprising a first polymeric surfactant as defined above to at least partially separate a mixture comprising hydrocarbons and water such that at least a portion of the hydrocarbons forms a separate layer from the remaining portion of the mixture.

In some embodiments of the foregoing aspects, at least 10%, 20%, 30%, 40%, 50%, 60%, 70%, or even at least 80% by volume of the hydrocarbons forms a separate layer from the remaining portion of the mixture.

In some embodiments of the foregoing aspects, the method and/or use further comprises removing at least a portion of the hydrocarbon from the separate hydrocarbon layer.

In some embodiments of the foregoing aspects, the mixture comprising hydrocarbons and water is a sludge comprising petroleum and water (e.g., a crude oil sludge). In other

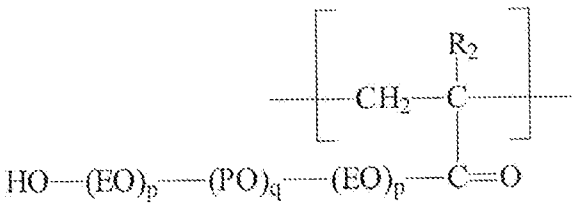
embodiments, the mixture is tar sand. In other embodiments, the mixture is an emulsion comprising at least the hydrocarbons and the water.

In another aspect, this disclosure provides a method of removing a sludge comprising a mixture of petroleum and water from a surface, the method comprising treating the sludge with an amount of a composition comprising a first polymeric surfactant as defined above effective to remove the sludge from the surface.

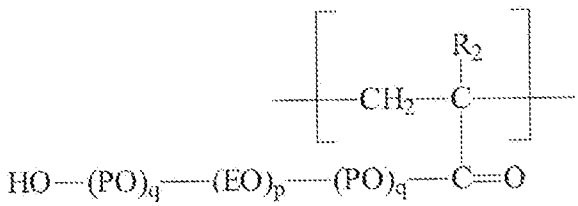
In another aspect, this disclosure provides a use of a composition comprising a first polymeric surfactant as defined above to remove a sludge comprising a mixture of petroleum and water from a surface.

In some embodiments of the foregoing aspects, the sludge is a contaminant in at least one of a crude oil storage container (e.g., an oil tanker) or a crude oil transport container.

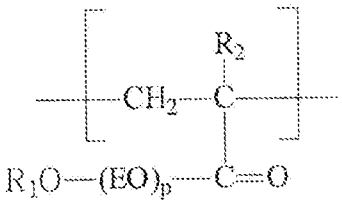
In some embodiments of the foregoing aspects and embodiments, the first polymeric surfactant comprises at least one second divalent unit selected from the group consisting of formulae:



(III);



(IV); and



(V);

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

EO represents $-CH_2CH_2O-$;

each PO independently represents $-CH(CH_3)CH_2O-$ or $-CH_2CH(CH_3)O-$;

each p is independently an integer of from 1 to about 128; and

each q is independently an integer of from 0 to about 55.

In some embodiments of the composition for use in the methods and/or uses disclosed herein, the composition comprises a mixture of at least two (e.g., two, three, four, five, or more) different polymeric surfactants, wherein each such surfactant comprises a first divalent unit selected from the group consisting of formulae (I) and (II) and a second divalent unit selected from the group consisting of formulae (III), (IV), and (V).

Methods and/or uses of the present disclosure typically allow easy cleaning of surfaces (e.g., on tankers and other equipment) contaminated with mixtures comprising hydrocarbons and water (e.g., sludge). In some embodiments, methods of the present disclosure allow recovery of at least some of the hydrocarbons (e.g., crude oil) present in these mixtures, which may provide economic and/or environmental advantages. In this application:

"Alkyl group" and the prefix "alk-" are inclusive of both straight chain and branched chain groups and of cyclic groups. Cyclic groups can be monocyclic or polycyclic and, in some embodiments, have from 3 to 10 ring carbon atoms.

The term "fluoroalkyl group" includes linear, branched, and/or cyclic alkyl groups in which all C-H bonds are replaced by C-F bonds as well as groups in which hydrogen or chlorine atoms are present instead of fluorine atoms provided that up to one atom of either hydrogen or chlorine is present for every two carbon atoms. In some embodiments of fluoroalkyl groups, when at least one hydrogen or chlorine is present, the fluoroalkyl group includes at least one trifluoromethyl group.

The term "hydrocarbon" refers to compounds consisting of carbon and hydrogen and includes linear, branched, and cyclic groups which may be saturated or unsaturated.

The term "sludge" refers to a viscous mixture comprising petroleum and water. A sludge may contain other components (e.g., mud, clay, sand, and other solids). The term "sludge" as used herein includes tar sand.

The term "crude oil" includes light, intermediate, and heavy crude oil.

The "mixtures of hydrocarbons and water" that are separated by the methods disclosed herein do not include materials where the hydrocarbons and water already exist in layers.

The terms "a", "an", and "the" are used interchangeably with "at least one".

All numerical ranges are inclusive of their endpoints unless otherwise stated.

Detailed description

In some embodiments, methods and/or uses according to the present disclosure can be used to process a sludge comprising petroleum and water (e.g., a crude oil sludge). The sludge may be present, for example, as a contaminant in a crude oil transport container (such as an oil tanker) or in a crude oil storage container. When servicing (e.g., cleaning and repairing) an oil tanker or other container of crude oil, for example, the sludge typically needs to be removed before the servicing work can be undertaken (e.g., at a ship yard). The sludge present in such containers is typically dense, viscous, and like cake dough in texture and usually contains paraffinic waxes, asphaltenes, salt water, mud and other residual solids, scale and organic acids.

In some embodiments, methods and/or uses of this disclosure can be used to process a crude oil contaminant spot (e.g., a spot of crude oil sludge) on above-ground equipment (e.g., vehicles, drilling equipment, oil rig components, pipelines, railroad tanker cars, storage silos, and other heavy equipment) in an oil field. Such crude oil contaminant spots

may result from normal use of the equipment or may result from an unexpected discharge (e.g., from a well or holding container).

In some embodiments, methods and/or uses according to the present disclosure can be used to process tar sand (i.e., oil sand). Spot contamination of tar sand may collect, for example, on above-ground equipment used in tar sands mines and processing plants.

The methods and/or uses of this disclosure, which use a composition comprising a first polymeric surfactant, are typically useful in removing sludge from the surfaces of containers (e.g., oil tankers and storage containers) and in removing spot contamination (e.g., crude oil or tar sand) from surfaces, for example, on above-ground equipment (e.g., in a field or processing plant). In some embodiments, the composition can be applied by wetting a cleaning cloth with the composition and manually rubbing the sludge or spot contamination. Where the sludge (e.g., in an oil tanker or storage container) is thick, a large amount of it may be removed by using a suitable implement such as a scraper, before resorting to manual cleaning with the cleaning cloth. In some embodiments, the composition can be applied to the container or equipment bearing the sludge or spot by spraying (e.g., with a high-pressure hose).

In some embodiments, methods and/or uses of the present disclosure are useful in enabling the recovery of at least some of the hydrocarbon (e.g., crude oil) present in mixtures of hydrocarbon and water (e.g., sludge and tar sand) to reduce the impact on the environment. Cleaning waste that is recovered, for example, after carrying out separation or surface treatment methods disclosed herein typically will segregate into layers in which at least a portion of the hydrocarbons forms a separate layer from the remaining portion of the mixture. Additionally, in embodiments wherein thick sludge is removed using an implement, the recovered sludge can be exposed to a composition comprising a first polymeric surfactant according to methods disclosed herein. In some embodiments, the recovered sludge can be converted into three readily separable layers, namely a first hydrocarbon containing upper layer; a second, middle phase of clear liquid, hydrocarbon-containing solids, and surfactant; and a third, lower phase which contains clear liquid, hydrocarbon-containing solids, and surfactant. In some of these embodiments,

hydrocarbon-containing solids are primarily located in the middle layer. In some embodiments, at least a portion of the hydrocarbon can be removed from the other layers using known techniques (e.g., decanting and draining). In some embodiments, the hydrocarbon-containing solids can be separated by known techniques (e.g., decanting and filtering).

In some embodiments, methods and/or uses of the present disclosure can be used when the mixture of hydrocarbons and water is an emulsion comprising at least the hydrocarbons and the water (e.g., an emulsion of at least the hydrocarbons in the water, an emulsion of least the water in the hydrocarbons, and a bicontinuous emulsion). The emulsion may be a naturally occurring form of crude oil as it is extracted from a well. The emulsion may be crude oil waste resulting, for example, from cleaning or other processing. When such emulsions are exposed to methods disclosed herein, at least of portion of the hydrocarbons form a separate layer from the remaining portion of the mixture (i.e., the emulsion is cracked). In some embodiments, methods disclosed herein can be used to recover useable crude oil effectively (e.g., in a recycling operation of crude oil waste) by separating at least of portion of the hydrocarbon from the hydrocarbon layer.

Methods and/or uses according to the present disclosure can typically be carried out at a temperature up to 60 °C (in some embodiments, up to 55, 50, 45, 40, 35, 30, or even up to 25 °C). Advantageously, methods and/or uses according to the present disclosure typically can be carried out at ambient temperature (e.g., external heating is typically not needed to facilitate separation of hydrocarbon from a mixture of hydrocarbons and water).

Compositions useful in practicing the methods and/or uses disclosed herein comprise a first polymeric surfactant, which comprises a compound having at least one first divalent unit selected from the group consisting of formulae (I) and (II); and at least one second divalent unit selected from the group consisting of formulae (III), (IV), and (V). In some embodiments of polymeric surfactants useful in practicing the methods disclosed herein, the first divalent unit is represented by formula (I). In other embodiments of polymeric surfactants useful in practicing the methods disclosed herein, the first divalent unit is represented by formula (II). In some embodiments of formula (I) or (II), the group R_f is

selected from the group consisting of perfluoromethyl, perfluoroethyl, perfluoropropyl, perfluorobutyl, (such as perfluoro-n-butyl or perfluoro-sec-butyl) perfluoropentyl, and perfluorohexyl. In some embodiments, R_f represents a fluoroalkyl group having from 2 to 5 (in some embodiments, 3 to 5) carbon atoms. In some embodiments, R_f is perfluorobutyl (such as perfluoro-n-butyl or perfluoro-sec-butyl).

Each of the groups R, R_1 and R_2 are independently hydrogen or alkyl of 1 to 4 carbon atoms, for example, methyl, ethyl, n-propyl, isopropyl, butyl, isobutyl, or t-butyl. In some embodiments, R is methyl or ethyl. In some embodiments, R_2 is hydrogen or methyl.

In some embodiments of polymeric surfactants useful in practicing the methods disclosed herein, n is 2 to 8 (in some embodiments, 2 to 6 or even 2 to 4). In formula (I), n may be 2, 3, 4, 5, 6, 7, 8, 9, or 10.

In some embodiments of polymeric surfactants useful in practicing the methods disclosed herein, m is 1 to 2. In formula (II), m may be 1, 2, 3, 4, or 5.

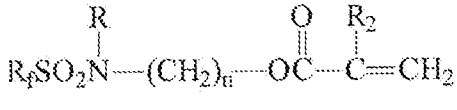
Each q can independently be an integer from 0 to about 55, generally in a range of 1 to 55.

In some embodiments, the ratio p/q is within a range from 0.15 to 5, in other embodiments, in a range from 0.3 to 5, 0.15 to 4, 0.15 to 3, 0.15 to 2.7, or even from 0.15 to 2.5. In some other embodiments the ratio p/q is within a range from 0.75 to 4, 0.75 to 3, 0.75 to 2.7, or even from 0.75 to 2.5. In some further embodiments the ratio p/q is within a range from 1 to 4, 1 to 3, 1 to 2.7, or even from 1 to 2.5. In some other embodiments the ratio p/q is within a range from 1.5 to 4, 1.5 to 3, 1.5 to 2.7 or even from 1.5 to 2.5.

In some embodiments of polymeric surfactants useful in practicing the present disclosure, the second divalent unit is represented by formula III, wherein p is an integer from 5 to 15 (in some embodiments, from 9 to 13 or even 11), and wherein q is an integer from 15 to 25 (in some embodiments, 19 to 23 or even 21).

In some embodiments, the polymeric surfactant useful in practicing the present disclosure is a reaction product formed by copolymerisation of:

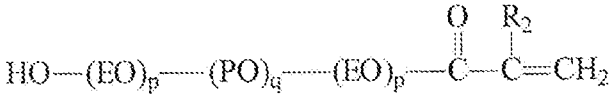
a first reactant which is at least one compound selected from the group consisting of:



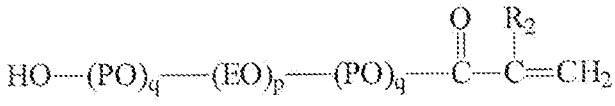
(VI); and

(VII); and

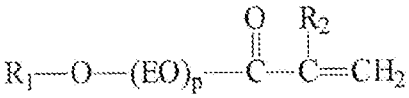
a second reactant which is at least one compound selected from the group consisting of compounds represented by formulae:



(VIII) ;



(IX) ; and



(X);

in which the groups R_f, R, R_1, R_2, m, n, EO, PO, p and q are as defined above.

The polymeric surfactants described above can be prepared, for example, by techniques known in the art (e.g., by free radical initiated copolymerization of a fluoroalkyl group-containing acrylate with a poly(alkyleneoxy) acrylate (e.g., monoacrylate or diacrylate or mixtures thereof). Adjusting the concentration and activity of the initiator, the concentration of monomers, the temperature, and the chain-transfer agents can control the molecular weight of the polyacrylate copolymer. The description of the preparation of such polyacrylates is described, for example, in U.S. Pat. No. 3,787,351 (Olson), the disclosure of which is incorporated herein by reference. Preparation of nonafluorobutanesulfonamido acrylate monomers are described, for example, in U.S. Pat. No. 2,803,615 (Ahlbrecht et al.), the disclosure of which is incorporated herein by reference. The methods described for making nonafluorobutylsulfonamido group-containing structures can be also used to make heptafluoropropylsulfonamido groups by

starting with heptafluoropropylsulfonyl fluoride, which can be made, for example, by the methods described in Examples 2 and 3 of U.S. Pat. No. 2,732,398 (Brice et al.), the disclosure of which is incorporated herein by reference. Examples of fluoroaliphatic polymeric esters and their preparation are described, for example, in U.S. Pat. No. 6,664,354 (Savu et al.), the disclosure of which is incorporated herein by reference.

Methods for making compounds of Formula VII are known; (see, e.g., EP1311637 B1, published April 5, 2006, and incorporated herein by reference for the disclosure of the preparation of 2,2,3,3,4,4,4-heptafluorobutyl 2-methylacrylate). Other compounds of Formula VII are available, for example, from commercial sources (e.g., 3,3,4,4,5,5,6,6,6-nonafluorohexyl acrylate from Daikin Chemical Sales, Osaka, Japan and 3,3,4,4,5,5,6,6,6-nonafluorohexyl 2-methylacrylate from Indofine Chemical Co., Hillsborough, NJ).

One polymeric surfactant suitable for practicing the present disclosure is the reaction product of N-methylperfluorobutanesulfonamidoethyl acrylate (MeFBSEA) and a second compound of the formula $HO(CH_2CH_2O)_{11}[CH(CH_3)CH_2O]_{21}(CH_2 CH_2O)_{11}C(=O)CH=CH_2$.

The weight ratio of the first and second reactants can be varied, for example, from 10:90 (in some embodiments from 15:85, 20:80, 25:75, 30:70, or even from 35:65) up to 50:50 (in some embodiments, 60:40, 65:35, 70:30, or even up to 75:25). In some embodiments, the weight ratio of the first reactant (in some embodiments, Formula (VI) to the second reactant (in some embodiments, Formula (VIII) is in a range from about 20:80 to about 50:50. In some embodiments wherein the first reactant is MeFBSEA and the second reactant is of formula $HO(CH_2CH_2O)_{11}[CH(CH_3)CH_2O]_{21}(CH_2 CH_2O)_{11}C(=O)CH=CH_2$, the ratio of MeFBSEA to the second reactant can be about 20:80, 23:77, 25:75, 28:72, 30:70, 33:67, 35:65, 38:62, 40:60, 43:57, 45:55, 48:52, or even about 50:50.

In some embodiments, polymeric surfactants useful in practicing the present disclosure include at least one anionic group. Useful anionic groups include sulfonates (e.g., $-SO_3M$), sulfates (e.g., $-OSO_3M$), and carboxylates (e.g., $-C(=O)OM$), wherein M is

hydrogen, a metal cation such as an alkali or alkaline earth metal cation (e.g., sodium, potassium, calcium or magnesium, and the like), or a nitrogen-based cation, such as ammonium or a protonated tertiary amine (e.g., $(HOCH_2CH_2)_2N^{\oplus}HCH_3$). The anionic groups can be incorporated into polymeric surfactants useful in practicing the methods disclosed herein, for example, by using appropriate monomers in the polymerization reaction. Useful monomers that contain anionic groups include acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, 2-carboxyethyl methacryate, and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS). Useful amounts of these monomers in the preparation of anionic polymeric surfactants are described, for example, in U.S. Pat. No. 6,664,354 (Savu et al.).

Polymeric surfactants useful in practicing the present disclosure typically have a number average molecular weight in a range of from 1000 to 100,000 (in some embodiments from 1000 to 50,000, 1000 to 40,000, 1000 to 30,000, 1000 to 20,000, or even 1000 to 10,000) grams/mole although higher and lower molecular weights may also be useful. In some embodiments, polymeric surfactants useful in practicing the present disclosure have a number average molecular weight of less than 100,000 grams/mole (in some embodiments, up to 100,000 grams/mole). In some embodiments, the polymeric surfactants have number average molecular weights of at least 1000 grams/mole. The polymeric surfactants typically have a distribution of molecular weights and compositions. Number average molecular weights can be measured, for example, by gel permeation chromatography (i.e., size exclusion chromatography) using techniques known in the art.

The polymeric surfactants useful in practicing the present disclosure can, in some embodiments, be free of hydrolyzable silane groups. This may be advantageous, for example, by prolonging the storage-life of the composition.

In some embodiments, compositions useful in practicing the present disclosure include the polymeric surfactant(s) in an amount sufficient to cause at least a portion of the hydrocarbon to form a separate layer from the remaining portion of the mixture. In some

embodiments, compositions useful in practicing the methods disclosed herein include the polymeric surfactant(s) in an amount effective to remove at least a portion of the sludge from the surface. Typically the amount of polymeric surfactant in the composition will be at least 0.1% (in some embodiments, at least 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5%, 4%, 4.5%, or even at least 5%) by weight, based on the total weight of the composition. In some embodiments, the polymeric surfactant(s) may be present in a range from 0.1% to 10% (in some embodiments, 0.5% to 10%, 1% to 10%, 1% to 6%, or even 0.1% to 6%) by weight, based on the total weight of the composition.

In some embodiments of compositions useful in practicing the present disclosure, the composition comprises at least one of water or an organic solvent (e.g., hydrocarbon liquid). In some embodiments wherein both water and organic solvent are present, the amount of water is greater than that of the organic solvent.

In some embodiments, the organic solvent is a hydrocarbon liquid such as C_6 to C_{10} alkane, in some embodiments, at least one of hexane or a C_9 or C_{10} alkane. In some embodiments, the organic solvent is an ether having up to 10 carbon atoms. Suitable ethers include glycol ethers available from Dow Chemical Co., Midland, Michigan under the trade designation "DOWANOL". In some embodiments, the organic solvent is 2-methoxymethylethoxypropanol. In some embodiments, the composition comprises both a hydrocarbon liquid and an ether having up to 10 carbon atoms.

In some embodiments of compositions useful in practicing the present disclosure, the amount of water is less than about 96% by weight and the amount of organic solvent is at least about 4% by weight, based on the total weight of the composition. The ratio of water to hydrocarbon liquid can be varied to achieve the most effective result.

Other materials can be added to the composition so long as they do not significantly adversely interfere with the activity of the polymeric surfactant(s). In some embodiments, compositions useful in practicing the present disclosure comprise 1-methyl-2-pyrrolidinone. In some embodiments, the other materials may have some useful function

as well. For example, in some embodiments, a second, different surfactant can be added. Useful second surfactants include silicone-based surfactants, polymeric surfactants, and surfactants available, for example, from Air Products and Chemicals, Inc., Allentown, PA, under the trade designation "SURFYNOL". Typically, and surprisingly, methods and uses disclosed herein can be carried out without using a second, different surfactant (e.g., a non-fluorinated surfactant).

Compositions useful in practicing the present disclosure can be prepared using conventional techniques such as stirring (e.g., by mechanical or magnetic methods), shaking, or homogenizing, for example, a mixture of polymeric surfactant(s), at least one of water or organic solvent, and optionally other materials (e.g., inert materials and a second, different surfactants). The components of the compositions can be combined in any order. In some embodiments wherein the composition comprises a hydrocarbon liquid and water, the hydrocarbon liquid is added to a mixture of polymeric surfactant(s) and water. In some other of these embodiments, the polymeric surfactant(s) is added to a mixture of hydrocarbon liquid and water.

Embodiments and advantages of this invention are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details should not be construed to unduly limit this invention.

Unless otherwise noted, all parts, percentages, ratios, etc. in the example and the rest of the specification are by weight.

Examples

Example 1

A polymeric surfactant was prepared as described in Example 4 of U. S. Pat. No. 6,664,354 (Savu et al.), the disclosure of which example is incorporated herein by reference, except using *N*-methylperfluorobutanesulfonamidoethyl acrylate (MeFBSEA) and the acrylate prepared from a block copolymer of ethylene oxide and propylene oxide obtained from BASF Corporation, Ludwigshafen, Germany, under the trade designation

"PLURONIC" in a weight ratio of 38:62 and using 15.6 grams (g) of 50/50 mineral spirits/organic peroxide initiator (*tert*-butyl peroxy-2-ethylhexanoate obtained from Akzo Nobel, Arnhem, The Netherlands under the trade designation "TRIGONOX-21-C50") in place of 2,2'-azobisisobutyronitrile, and with 9.9 g of 1-methyl-2-pyrrolidinone added to the charges.

A dense sludge from an oil tanker, weighing about 20 grams, viscous and like a cake dough in texture, was placed in a glass bottle to which was added a mixture of 100 milliliters (mL) n-decane, 200 mL water, and 5% by weight of the polymeric surfactant. The mixture was shaken for 30 seconds and left to settle for a further two minutes. The sludge after that time broke down into three layers. The layers were separated and placed in three glass jars (i.e., Jar 1, Jar 2, and Jar 3). The upper layer was a dark-colored liquid and was placed in Jar 1. The middle layer was a mixture of clear liquid and a large amount of black solid and was placed in Jar 2. The lower layer was a mixture of clear liquid and a small amount of black solid and was placed in Jar 3.

Sample 1 was prepared by dissolving a portion of the upper layer, contained in Jar 1, in acetone.

Sample 2:

Extraction Procedure: One mL of the clear liquid from Jar 2 was mixed with 1 mL dichloromethane, and the mixture was shaken overnight using a wrist-action shaker.

A portion of the dichloromethane layer was transferred to a glass autosampler vial to provide Sample 2 for analysis.

Sample 3 was prepared using the method described for Sample 2 except the extraction procedure used heptanes instead of dichloromethane.

Sample 4 was prepared using the method described for Sample 2 except the extraction procedure used 1 mL of the clear liquid from Jar 3 instead of from Jar 2.

Sample 5 was prepared using the method described for Sample 2 except the extraction procedure used 1 mL of the clear liquid from Jar 3 instead of from Jar 2, and the extraction procedure used heptanes instead of dichloromethane.

Sample 6 was prepared by dissolving a portion of the black solid from Jar 2 in acetone.

Sample 7 was prepared by dissolving a portion of the black solid from Jar 3 in acetone.

Samples 1 to 7 were analyzed using gas chromatography/mass spectroscopy (GC/MS). The GC/MS analysis was carried out using a mass selective detector (MSD) obtained from Agilent Technologies, Santa Clara, CA under the trade designation AGILENT, Model 5972, interfaced to a gas chromatograph obtained from Agilent Technologies under the trade designation AGILENT, Model 5890 Series II. The gas chromatograph was equipped with a 30 meter fused silica capillary column obtained from Agilent Technologies, Model DB 5, having an inside diameter of 0.25 mm and a film thickness of 1.0 micrometer. The analysis was carried out using a temperature program from 40 °C to 320 °C at a linear rate of 10 °C per minute. The final temperature was held for 17 minutes. Helium, at a flow velocity of approximately 40 cm/second, was used as the carrier gas, and the injector was maintained at a temperature of 250 °C. The MSD was operated in the electron impact ionization mode using 70 eV electrons for ionization. Data were collected by scanning the MSD over the mass range of 29-550 Daltons at a scan rate of approximately one scan per second.

The GC/MS analysis of Sample 1 showed that the upper layer contained primarily a mixture of saturated hydrocarbons ranging from $C_{13}H_{28}$ to $C_{32}H_{66}$. Several other hydrocarbons, either unsaturated or branched, were also detected.

The GC/MS analyses of Samples 2 through 5 did not show any of the hydrocarbons that were detected in Sample 1.

The GC/MS analyses of Samples 6 and 7 showed that the black solid contained the mixture of hydrocarbons detected in Sample 1.

Example 2

Surfactant Solution Preparation:

The polymeric surfactant prepared as described in Example 1 was diluted with 2-methoxymethylethoxypropanol to prepare a 25% by weight of the polymeric surfactant. The polymeric surfactant solution (2.4 mL) was mixed with 192 mL of de-ionized water and 8 mL of decane to provide a 0.3% by weight solution of surfactant.

Sample Preparation and Cleaning:

A sample of crude oil sludge was applied on a square, aluminum coupon (2 inches (5.1 cm) by 2 inches (5.1 cm)) in a thin layer. A 200-microliter portion of the prepared surfactant solution was used to clean the coupon using the following procedure. The time was noted, and two drops of the surfactant solution were placed onto the sludge-treated coupon and wiped off with a clean paper towel. This step was repeated three more times, at which point the full 200 microliters of surfactant solution were used.

Results:

Small streaks of sludge were visible on the coupon, and some clean streaks were observed in the vicinity of where the surfactant drops were placed.

Example 3

Surfactant Solution Preparation:

Example 3 was prepared according to the Surfactant Solution Preparation procedure described in Example 2, except 0.6 mL of a 100% active nonionic polymeric surfactant obtained from Mason Chemical, Arlington Heights, IL, under the trade designation "MASURF FS-2000" was used instead of the 25% by weight polymeric surfactant solution.

Sample Preparation and Cleaning:

A aluminium coupon was treated with a sample of crude oil sludge using the procedure of Example 2. The coupon of Example 3 was cleaned using the method of

Example 2 except that 200 microliters of the Illustrative Example surfactant solution were used for the test instead of 200 microliters of the 25% by weight polymeric surfactant solution.

Results:

Small streaks of sludge were visible on the coupon, and some hazy streaks were observed in the vicinity of where the surfactant drops were placed.

Comparative Example.

A aluminium coupon was treated with a sample of crude oil sludge using the procedure of Example 2. The coupon of the Comparative Example was cleaned using the method of Example 2 except that 200 microliters of water were used for the test instead of 200 microliters of the prepared surfactant solution.

Small streaks of sludge were visible on the coupon.

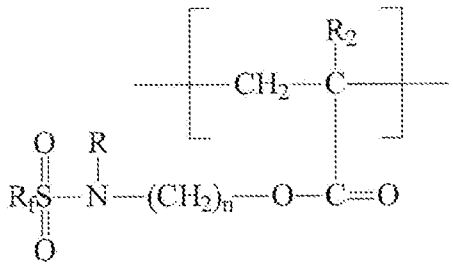
While the invention has been described with reference to preferred embodiments, it is to be understood that it is not to be limited thereto. Furthermore, where known materials and processing steps have been identified and equivalents are known to exist thereto, such equivalents are incorporated herein as if specifically set forth.

CLAIMS

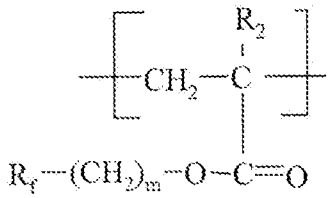
1. A method of facilitating separation of hydrocarbon from a mixture comprising hydrocarbons and water, the method comprising:

exposing the mixture to a composition comprising a first polymeric surfactant such that at least a portion of the hydrocarbons forms a separate layer from the remaining portion of the mixture, the first polymeric surfactant comprising:

at least one first divalent unit selected from the group consisting of formulae:



(I); and



(II); and

a polyalkyleneoxy segment;

wherein

R_f represents a fluoroalkyl group having from 1 to 6 carbon atoms;

R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

n is an integer from 2 to 10; and

m is an integer from 1 to 5.

2. A method as claimed as in claim 1 further comprising removing at least a portion of the hydrocarbons from the separate hydrocarbon layer.

3. A method as claimed in claim 1 or claim 2 in which the mixture is a crude oil sludge contaminant in at least one of a crude oil storage container or a crude oil transport container.

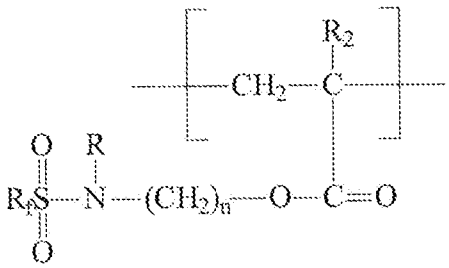
4. A method as claimed in claim 1 or claim 2 in which the mixture is a tar sand.

5. A method as claimed in claim 1 or claim 2 in which the mixture is an emulsion comprising at least the hydrocarbons and the water.

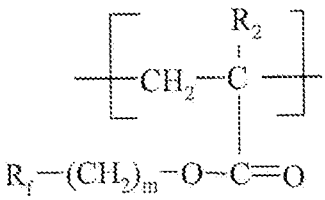
6. A method of removing a sludge comprising a mixture of petroleum and water from a surface, the method comprising:

treating the sludge with an amount of a composition comprising a first polymeric surfactant effective to remove the sludge from the surface, the first polymeric surfactant comprising:

at least one first divalent unit selected from the group consisting of formulae:



(I); and



(II); and

a polyalkyleneoxy segment;

wherein

R_f represents a fluoroalkyl group having from 1 to 6 carbon atoms;

R and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

n is an integer from 2 to 10; and

m is an integer from 1 to 5.

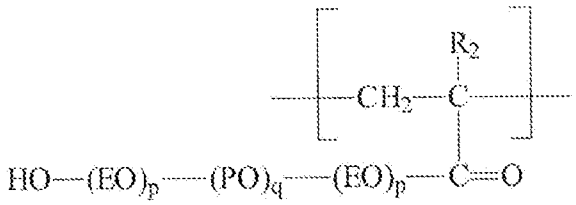
7. A method as claimed in claim 6 in which the sludge is a contaminant in at least one of a crude oil storage container or a crude oil transport container.

8. A method as claimed in claim 6 in which the sludge is a tar sand.

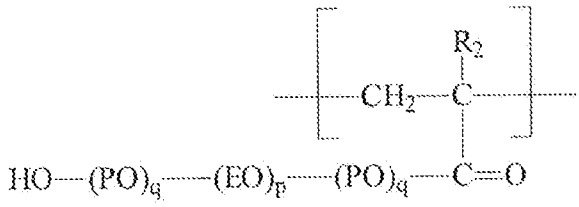
9. A method as claimed in claim 6 in which the sludge is a spot contaminant on above-ground equipment in an oil field.

10. A method as claimed in any one of the preceding claims, wherein the first polymeric surfactant comprises:

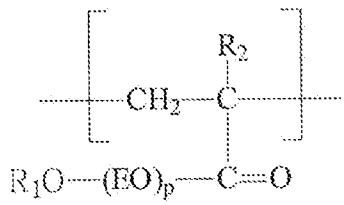
at least one second divalent unit selected from the group consisting of formulae:



(III);



(IV); and



(V);

wherein

R_1 and R_2 are each independently hydrogen or alkyl of 1 to 4 carbon atoms;

EO represents $-CH_2CH_2O-$;

each PO independently represents $-CH(CH_3)CH_2O-$ or $-CH_2CH(CH_3)O-$;

each p is independently an integer of from 1 to about 128; and

each q is independently an integer of from 0 to about 55.

11. A method as claimed in any one of the preceding claims, wherein R_f represents a fluoroalkyl group having from 2 to 5 carbon atoms.

12. The method as claimed in any one of the preceding claims, wherein the at least one first divalent unit is represented by formula I.

13. A method as claimed in any one of the preceding claims in which the composition further comprises an organic solvent.

14. A method as claimed in claim 12 in which the organic solvent comprises a C6 to C10 alkane.

15. A method as claimed in any one of claims 13 to 14 in which the organic solvent comprises an ether having up to 10 carbon atoms.

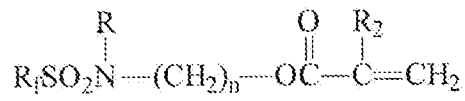
16. A method as claimed in any one of claims 13 to 15 in which the amount of organic solvent is at least about 4% by weight, based on the total weight of the composition.

17. A method as claimed in any one of the preceding claims in which the composition further comprises water.

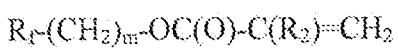
18. A method as claimed in any claim 17 in which the amount of water is less than about 96% by weight, based on the total weight of the composition.

19. A method as claimed in any one of the preceding claims in which the first polymeric surfactant is a reaction product formed by copolymerisation of:

a first reactant which is at least one compound selected from the group consisting of compounds represented by formulae:



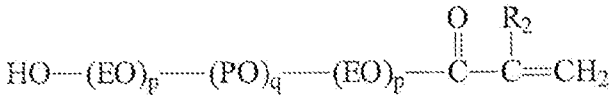
(VI); and



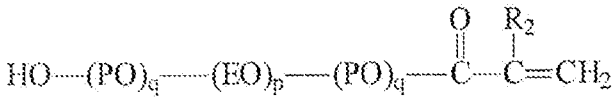
(VII); and

a second reactant which is a polyalkyleneoxy acrylate or diacrylate.

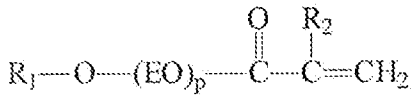
20. The method as claimed in claim 19, wherein the second reactant is selected from the group consisting of compounds represented by formulae:



(VIII) ;



(IX) ; and



(X).

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/071509

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D17/04 B08B9/08 C10G33/04 C11D1/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B08B C10G C11D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 54 065180 A (DAIKIN IND LTD) 25 May 1979 (1979-05-25) the whole document	1-5, 10-20
X	DATABASE WPI Week 197845 Thomson Scientific, London, GB; AN 1978-80638A XP002501782 & JP 53 111569 A (DAINIPPON INK & CHEM KK) 29 September 1978 (1978-09-29) the whole document	1-5, 10-20
A	US 2003/139550 A1 (SAVU PATRICIA M [US] ET AL) 24 July 2003 (2003-07-24) cited in the application	1-5, 10-20

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 October 2008	14/01/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Roider, Josef

4

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/071509

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 350 795 A (SMITH RICHARD S [US] ET AL) 27 September 1994 (1994-09-27) cited in the application	1-5, 10-20
A	US 3 787 351 A (OLSON M) 22 January 1974 (1974-01-22) cited in the application	1-5, 10-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/071509

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 5, 10 - 20 (partly)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5 and 10-20 as far as relating to a fluoroalkylsulfonamidalkyl acrylate compound in the polymeric surfactant according to claims 1-5

Group I is directed to a method for separating hydrocarbon from a mixture of hydrocarbons and water such that the at least a portion of the hydrocarbons forms a layer separate from the remaining portion of the mixture (demulsifying) by exposing the mixture to a first polymeric surfactant comprising a first divalent unit being a fluoroalkylsulfonamidalkyl acrylate.

---

2. claims: 1-5 and 10-20 as far as relating to a fluoroalkyl acrylate in the polymeric surfactant according to claims 1-5

Group II is directed to a method for separating hydrocarbon from a mixture of hydrocarbons and water such that the at least a portion of the hydrocarbons forms a layer separate from the remaining portion of the mixture (demulsifying) by exposing the mixture to a first polymeric surfactant comprising a first divalent unit being a fluoroalkyl acrylate.

---

3. claims: 1-5 and 10-20 as far as relating to a polyalkylenoxy segment in the polymeric surfactant according to claims 1-5

Group III is directed to a method for separating hydrocarbon from a mixture of hydrocarbons and water such that the at least a portion of the hydrocarbons forms a layer separate from the remaining portion of the mixture (demulsifying) by exposing the mixture to a first polymeric surfactant comprising a first divalent unit being a polyalkylenoxy segment.

---

4. claims: 6-9 and 10-20 as far as relating to a fluoroalkylsulfonamidalkyl acrylate compound in the polymeric surfactant according to claims 6-9

Group IV is directed to a method for removing sludge comprising a mixture of petroleum and water from a surface by treating the sludge (cleaning) with a first polymeric surfactant comprising a first divalent unit being a fluoroalkylsulfonamidalkyl acrylate.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

5. claims: 6-9 and 10-20 as far as relating to a fluoroalkyl acrylate in the polymeric surfactant according to claims 6-9

Group V is directed to a method for removing sludge comprising a mixture of petroleum and water from a surface by treating the sludge (cleaning) with a first polymeric surfactant comprising a first divalent unit being a fluoroalkyl acrylate.

---

6. claims: 6-9 and 10-20 as far as relating to a polyalkylenoxy segment in the polymeric surfactant according to claims 6-9

Group VI is directed to a method for removing sludge comprising a mixture of petroleum and water from a surface by treating the sludge (cleaning) with a first polymeric surfactant comprising a first divalent unit being a polyalkylenoxy segment.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2008/071509

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 54065180 A	25-05-1979	JP 1324586 C	27-06-1986
		JP 60051366 B	13-11-1985
JP 53111569 A	29-09-1978	JP 1268572 C	10-06-1985
		JP 59034404 B	22-08-1984
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US 3787351 A	22-01-1974	CA 1000888 A1	30-11-1976
		DE 2310357 A1	13-09-1973
		FR 2174071 A1	12-10-1973
		GB 1420031 A	07-01-1976
		JP 48100439 A	18-12-1973
		JP 57034300 B	22-07-1982