

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 December 2011 (08.12.2011)

PCT

(10) International Publication Number
WO 2011/152877 A1

(51) International Patent Classification:
C09K 8/584 (2006.01) *E21B 49/08* (2006.01)
C09K 8/594 (2006.01)

(21) International Application Number:
PCT/US2011/001007

(22) International Filing Date:
3 June 2011 (03.06.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/351,603 4 June 2010 (04.06.2010) US

(71) Applicant (for all designated States except US): **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KRESCHOLLEK, Thomas, E.** [US/US]; 109 Hancock Street, Clute, TX 77531 (US). **CHAUDHARY, Sunil, K.** [CA/US]; 422 Fern Meadow Drive, Missouri City, TX 77459 (US). **SANDERS, Aaron, W.** [US/US]; 3503 Corbett Ct., Missouri City, TX 77459 (US). **CHRISTENSON, Christopher, P.** [US/US]; 1381 Old Colony Road, Seguin, TX 78155 (US). **CHAUVEL, Jean, P.** [US/US]; 31 Lake Road, Lake Jackson, TX 77566 (US).

(74) Agents: **HUEBSCH, Joseph, C.** et al.; 1221 Nicollet Avenue, Suite 500, Minneapolis, MN 55403 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: MONITORING EMULSION FORMATION

(57) Abstract: Embodiments of the present disclosure include an oil-field test kit and methods for monitoring emulsion formation in an oil well in an oil field. Oil-fields test kits of the present disclosure include (a) ammonium thiocyanate, (b) a metal nitrate, and (c) an organic solvent.



WO 2011/152877 A1

MONITORING EMULSION FORMATION

Field of the Disclosure

Embodiments of the present disclosure are directed toward monitoring emulsion
5 formation; more specifically, embodiments are directed toward methods and oil-field test
kits for monitoring emulsion formation in an oil containing reservoir.

Background

Enhanced oil recovery has been employed to increase the amount of oil recovered
10 from oil containing reservoirs. Enhanced oil recovery can include injecting fluids other
than water, such as steam, gas, surfactant solutions, and/or carbon dioxide, into the oil
containing reservoir.

To increase the enhanced oil recovery effectiveness, surfactants have been used to
promote emulsions between carbon dioxide and water in an oil containing reservoir. The
15 emulsions between carbon dioxide and water can help inhibit the flow of the carbon
dioxide into portions of the reservoir formation that have previously been swept. As such,
the emulsions of carbon dioxide and water including the surfactants can help direct the
carbon dioxide to the recoverable hydrocarbons in the less depleted portions of the oil
containing reservoir.

20 However, emulsions between oil and water can also form during enhanced oil
recovery. Emulsions between oil and water are undesirable from a production standpoint
since the emulsion of oil and water must be broken in order to recovery the oil.
Additionally, emulsions of oil and water can lead to plugging of the oil containing reservoir
and/or processing difficulties when the oil is sought to be extracted from the water in an oil
25 recovery process.

Monitoring emulsions formed between oil and water can be done by detecting the
presence of surfactants in water of the oil containing reservoir. However, detecting
surfactants, and in particular nonionic surfactants in the field can be difficult and can
require rigorous analytical techniques. For example, Liquid Chromatography Mass
30 Spectrometry (LCMS) has been used to detect nonionic surfactants. However, employing
LCMS can require other resources such as equipment located in laboratories not located on
the oil field and specially trained operators to perform the LCMS.

Summary

One or more embodiments of the present disclosure provide methods of monitoring emulsion formation in an oil containing reservoir during enhanced oil recovery with a nonionic surfactant. The methods include (a) obtaining a water sample from the oil
5 containing reservoir, (b) adding an effective amount of ammonium thiocyanate and an effective amount of a metal nitrate to the water sample to form a sample mixture, where the metal nitrate is selected from the group consisting of cobalt nitrate, iron nitrate, and combinations thereof, (c) adding an organic solvent to the sample mixture to form a sample-solvent mixture, (d) separating the sample-solvent mixture into an organic phase and an
10 aqueous phase, and (e) determining whether the organic phase has a predetermined color, where having the predetermined color indicates the water sample has a predetermined amount of the nonionic surfactant.

One or more embodiments of the present disclosure include oil-field test kits for monitoring emulsion formation in an oil containing reservoir in an oil field. The oil-field
15 test kits include (a) ammonium thiocyanate, (b) a metal nitrate, and (c) an organic solvent.

Additionally, one or more embodiments of the present disclosure include oil-field kits for enhanced oil recovery. The oil-field kits include (a) a container for a water sample that contains a nonionic surfactant, and (b) an oil-field test kit for monitoring emulsion formation in an oil containing reservoir in an oil field. The oil-field test kit includes (i)
20 ammonium thiocyanate, (ii) a metal nitrate, and (iii) an organic solvent.

The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which examples
25 can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

Definitions

Definitions

30 As used herein, the terms "a," "an," "the," "one or more," and "at least one" are used interchangeably and include plural referents unless the context clearly dictates otherwise.

Unless defined otherwise, all scientific and technical terms are understood to have the same meaning as commonly used in the art to which they pertain. For the purpose of the present disclosure, additional specific terms are defined throughout.

As used herein, the term "and/or" means one, more than one, or all of the listed elements.

Also herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.).

5 As used herein, a "surfactant" refers to a chemical compound that lowers the interfacial tension between two liquids.

As used herein, a "nonionic surfactant" refers to a surfactant where the molecules forming the surfactant are uncharged.

10 As used herein, the term "oil" refers to a naturally occurring liquid consisting of a complex mixture of hydrocarbons of various molecular weights and structures, and other organic compounds, which are found in geological formations beneath the earth's surface, referred to herein as an oil containing reservoir. "Oil" is also known, and may be referred to, as petroleum and/or crude oil.

15 As used herein, "water" refers to the water, water solution and/or brine that is located in the oil containing reservoir along with oil.

As used herein, "predetermined color" refers to the spectral property of having an absorption maximum at 316 ± 20 nanometers (nm) and an absorption maximum at 614 ± 20 nm. As used herein, a blue-purple color or red color are used as the predetermined color, i.e., the blue-purple color and the red color has an absorption maximum at 316 ± 20 nm and/or an absorption maximum at 614 ± 20 nm.

20 As used herein, the term "concentration" refers to a measure of an amount of a substance, such as a surfactant as discussed herein, contained per unit volume of solution. As used herein, parts-per-million (ppm) is used as one measure of concentration in which a given property exists at a relative proportion of one part per million parts examined, as would occur if a surfactant was present at a concentration of one-millionth of a gram per gram of water.

Detailed Description

30 The present disclosure provides methods for monitoring emulsion formation in an oil containing reservoir. Embodiments of the present disclosure also include oil-field test kits for monitoring emulsion formation in an oil containing reservoir. The methods and oil-field test kits of the present disclosure can be used to monitor emulsion formation in the oil containing reservoir during enhanced oil recovery. For one or more embodiments, monitoring emulsion formation can be performed by detecting surfactants, e.g. nonionic

surfactants, in water of the oil containing reservoir. Detecting the presence of nonionic surfactants in the water of the oil containing reservoir can help monitor emulsions formed and/or the potential formation of emulsions between oil and water.

As discussed herein, detecting nonionic surfactants can be difficult and employ
5 trained specialists to operate equipment not located on the oil field. For the methods and oil-field test kits of the present disclosure, emulsions formed and/or the potential formation of emulsions between oil and water can be monitored by detecting the presence of nonionic surfactants. For one or more embodiments, nonionic surfactants can be detected in the water of the oil containing reservoir at 10 ppm, as discussed herein.

10 One or more embodiments include monitoring emulsion formation in the oil containing reservoir during enhanced oil recovery with a nonionic surfactant. One or more embodiments include (a) obtaining a water sample from the oil containing reservoir, (b) adding an effective amount of ammonium thiocyanate and an effective amount of a metal nitrate to the water sample to form a sample mixture, where the metal nitrate is selected
15 from the group consisting of cobalt nitrate, iron nitrate, and combinations thereof, (c) adding an organic solvent to the sample mixture to form a sample-solvent mixture, (d) separating the sample-solvent mixture into an organic phase and an aqueous phase, and (e) determining whether the organic phase has a predetermined color, where having the predetermined color indicates the water sample has a predetermined amount of the nonionic
20 surfactant.

For one or more embodiments, obtaining the water sample can include obtaining the water sample from the oil containing reservoir. For example, the water sample can be obtained from a production well of the oil containing reservoir. Additionally, one or more embodiments include obtaining the water sample from a separator, e.g. a test separator.

25 Test separators can be vessels used to separate and meter quantities of oil, water, and gas to evaluate production performance of individual oil wells. Other methods for obtaining the water sample can be used as well.

For one or more embodiments, the water sample can be tested neat, i.e., the water sample is not diluted and/or altered before adding the ammonium thiocyanate, the metal
30 nitrate, and the organic solvent to test for the nonionic surfactant. In additional embodiments, the water sample can be diluted and/or altered prior to being tested for the nonionic surfactant. For embodiments where the water sample has been diluted, the methods and/or oil-field test kits of the present disclosure can determine an absolute weight of the nonionic surfactant present in the water sample, as discussed herein.

For one or more embodiments, after the water sample has been obtained, the water sample can be filtered. For example, the water sample can be filtered using a syringe filter to remove particulates before testing the water sample for the nonionic surfactant.

One or more embodiments include adding an effective amount of ammonium thiocyanate and an effective amount of the metal nitrate to the water sample to form a sample mixture. For one or more embodiments, adding the effective amount of ammonium thiocyanate to the water sample can include adding 1.0 part of ammonium thiocyanate by weight for 1.6 to 6.0 parts water sample by weight. In one embodiment, 1.0 part of ammonium thiocyanate by weight is added for 5.0 parts water sample by weight.

For one or more embodiments, adding the effective amount of the metal nitrate to the water sample can include adding 1.0 part metal nitrate by weight for 3.5 to 714.0 parts water sample by weight. In one embodiment, 1.0 part metal nitrate by weight is added for 20.0 parts water sample by weight. As discussed here, the metal nitrate can be selected from the group consisting of cobalt nitrate, iron nitrate, and combinations thereof. In one embodiment, the metal nitrate is cobalt nitrate.

For one or more embodiments the sample mixture can be mixed in a mixing container, e.g. shaken and/or stirred, using spatulas and stir rods, among other equipment. The sample mixture can be mixed for a period of time to sufficiently mix and/or dissolve the ammonium thiocyanate and cobalt nitrate with the water sample.

One or more embodiments include adding an organic solvent to the sample mixture to form a sample-solvent mixture. For one or more embodiments, the organic solvent can be organic solvents that are immiscible in water. One or more embodiments include using halogenated organic solvents, and in particular, chlorinated organic solvents that are immiscible in water. For example, the organic solvent can be selected from the group consisting of chloroform, dichloromethane, dichloroethane, benzene, and combinations thereof. Additionally, other immiscible solvents can be used. In one embodiment, the organic solvent is chloroform. For one or more embodiments, adding the organic solvent to the sample mixture includes adding 1.0 part organic solvent by weight for 2.0 to 6.0 parts water sample by weight. In one embodiment, 1.0 part organic solvent by weight is added for 4.0 parts water sample by weight. For one or more embodiments, the sample-solvent mixture can be mixed as described herein.

For the embodiments of the present disclosure, the order in which the ammonium thiocyanate, metal nitrate, and organic solvent are added to the water sample does not restrict the methods and oil-field test kits described herein. For example, the ammonium

thiocyanate, metal nitrate, and organic solvent can be added to the water sample separately, all together simultaneously, or in various combinations. The various combinations can include, but are not limited to, adding ammonium thiocyanate and the metal nitrate to the water sample first and then subsequently adding the organic solvent.

5 One or more embodiments include separating the sample-solvent mixture into an organic phase and an aqueous phase. For example, the sample-solvent mixture can be allowed to rest for a period of time sufficient to allow the organic phase and the aqueous phase to separate. One or more embodiments further include removing and retaining the organic phase for further analysis. For the methods and oil-field test kits of the present
10 disclosure, using halogenated organic solvents can assist in removing the organic phase. For example, halogenated organic solvents place the organic phase below the aqueous phase, i.e., on the bottom. Therefore, if a separatory funnel is used, the organic phase can be removed from a bottom tap of the separatory funnel. Additionally, the organic phase can be removed by pouring off the top layer, e.g. the aqueous phase, pipetting the organic phase
15 from the aqueous phase, or other methods known for separating two immiscible phases.

One or more embodiments include determining whether the organic phase has the predetermined color, where having the predetermined color indicates the water sample has a predetermined amount of the nonionic surfactant. Regardless of whether cobalt nitrate or iron nitrate is used, the predetermined color can have the spectral property of having an
20 absorption maximum at 316 ± 20 nm and/or an absorption maximum at 614 ± 20 nm. For example, if cobalt nitrate is used as the metal nitrate, the predetermined color of the organic phase can have a blue-purple color. Additionally, if iron nitrate is used as the metal nitrate, the predetermined color of the organic phase can have a red color. However, both the blue-purple color and red color have an absorption maximum at 316 ± 20 nm and/or an
25 absorption maximum at 614 ± 20 nm.

For one or more embodiments, the nonionic surfactant can complex with the cobalt and/or iron to form a colored complex that is more miscible in the organic phase. Since the colored complex is more miscible in the organic phase, the colored complex can partition into the organic solvent and can color the organic phase.

30 For one or more embodiments, the predetermined amount of the nonionic surfactant can be the amount of the nonionic surfactant that can form and/or promote emulsions between oil and water in the oil containing reservoir. Thus, when the organic phase has the predetermined color, the predetermined color can act as an indicator that the nonionic surfactant is present in an amount sufficient to potentially promote emulsions between oil

and water in the oil containing reservoir. It is understood that different nonionic surfactants can form emulsions between oil and water at different concentrations. Therefore, the predetermined amount of the nonionic surfactant can vary between applications and can depend on what type of nonionic surfactant is present the water sample. In one
5 embodiment, the predetermined amount of the nonionic surfactant can be at least 10 ppm.

For one or more embodiments, maintaining a nonionic surfactant concentration in the water below the predetermined amount of the nonionic surfactant can help minimize emulsions formed between oil and water within the oil containing reservoir. One or more
10 embodiments include remediating the contents of the oil containing reservoir when the organic phase has the predetermined color, e.g. a blue-purple color. Thus, the predetermined color can act as an indicator to remediate, e.g. reduce the concentration of the nonionic surfactant, the contents in the oil containing reservoir such that emulsions between oil and water can be minimized. As discussed herein, emulsions between oil and water are not desirable from a production standpoint. A water sample having the predetermined
15 amount of the nonionic surfactant can indicate that the nonionic surfactant is mixing with the water and oil, which can lead to emulsions between oil and the water in the oil containing reservoir. As discussed herein, forming emulsions that include oil, if not remediated, can decrease the amount of oil produced.

For one or more embodiments, the organic phase can be substantially colorless, i.e.,
20 substantially no color can be visually detected. When the organic phase is substantially colorless, this can indicate that the water sample does not contain the predetermined amount of the nonionic surfactant. Thus, when the organic phase is substantially colorless, this can indicate that the nonionic surfactant is not present in an amount sufficient to promote emulsions between oil and water in the oil containing reservoir. For example, if an organic
25 phase is substantially colorless, this can indicate that the organic phase has a nonionic surfactant concentration less than 10 ppm.

One or more embodiments of the present disclosure include an oil-field test kit for monitoring emulsion formation in an oil containing reservoir in an oil field.
Advantageously, the oil-field test kit can be used on the oil field during enhanced oil
30 recovery.

For one or more embodiments, the oil-field test kit includes predetermined amounts of (a) ammonium thiocyanate, (b) a metal nitrate, and (c) an organic solvent, each in a container. As discussed herein, the metal nitrate can be selected from the group consisting of cobalt nitrate, iron nitrate, and combinations thereof. For one or more embodiments, the

ammonium thiocyanate, metal nitrate, and organic solvent can each be packaged individually in separate containers. In additional embodiments, one or more of the ammonium thiocyanate, metal nitrate, and organic solvent can be packaged together. For example, the ammonium thiocyanate and the metal nitrate can be premixed and packaged in one container and the organic solvent can be packaged in a separate container. Additionally, the ammonium thiocyanate, metal nitrate, and organic solvent can all be premixed and packaged in a single container.

For one or more embodiments, the oil-field test kit can further include at least one of a mixing container to receive the predetermined amounts of the ammonium thiocyanate, metal nitrate, organic solvent, and water sample being tested. Additionally, the oil-field test kit can further include instructions on how to use the content of the oil-field test kit for monitoring emulsion formation in an oil containing reservoir during enhanced oil recovery, as discussed herein. In one or more embodiments, the mixing container can be optically transparent.

The oil-field test kit can be used with the methods described herein to monitor emulsion formation by detecting the presence of nonionic surfactants in the water of the oil containing reservoir. As discussed herein, once a water sample is obtained, 1.0 part ammonium thiocyanate by weight can be added for 5.0 parts water sample by weight and 1.0 part metal nitrate by weight can be added for 20.0 parts water sample by weight to form the sample mixture. For one embodiment, the metal nitrate is cobalt nitrate.

For one or more embodiments, the organic solvent of the oil-field test kit can be selected from the organic solvents as described herein. As discussed herein, 1.0 part organic solvent by weight can be added for 4.0 parts water sample to form the solvent-sample mixture. For one embodiment, the organic solvent is chloroform.

Determining whether the organic phase has the predetermined color can be determined visually or by using an ultraviolet-visible spectroscope. For one embodiment, the perception of the predetermined color of the organic phase can be used for qualitative determination of the predetermined amount of the nonionic surfactant in the water sample. Thus, an operator can visually determine if the organic phase has the predetermined color, e.g. a blue-purple color, to qualitatively determine whether the water sample has the predetermined amount of the nonionic surfactant. That is, the visual perception of the predetermined color of the organic phase by an operator can indicate that the water sample has at least 10 ppm of the nonionic surfactant.

One or more embodiments include an emulsion-formation color chart. For example, the emulsion-formation color chart can be used for quantification of the presence of the nonionic surfactant in the water sample. For one or more embodiments, the methods and oil-field test kits can have a visual detection limit within the range of from 10 ppm to 1000 ppm of a nonionic surfactant discussed herein.

For one or more embodiments, the emulsion-formation color chart can include the predetermined color at various intensities that correlate to concentrations of 10 ppm, 100 ppm, and 1,000 ppm of the nonionic surfactant. For example, when cobalt nitrate is used as the metal nitrate, the emulsion-formation color chart can include various levels of intensity of the blue-purple color, i.e., a pale blue-purple color to a dark blue-purple color, where each level of intensity correlates to a specific concentration, i.e., 10 ppm, 100 ppm, and 1,000 ppm. For one or more embodiments, the higher the intensity of the predetermined color, the higher the concentration of the nonionic surfactant in the water sample. If the intensity of the predetermined color can not be matched to the emulsion-formation color chart, it can be determined that the organic phase contains either less than the 10 ppm or greater than 1,000 ppm of the nonionic surfactant. For example, if the organic phase is substantially colorless or has an intensity of the predetermined color that is less intense than the intensity that correlates to the 10 ppm color, it can be determined that the organic phase contains less than 10 ppm of the nonionic surfactant.

For one or more embodiments, the operator can compare the organic phase to the emulsion-formation color chart to quantify the presence of the nonionic surfactant in the water sample. That is, the predetermined color, e.g. blue-purple, of the organic phase can be matched to the closest blue-purple color of the emulsion-formation color chart to quantify the concentration of the nonionic surfactant. As discussed herein, the emulsion-formation color chart can indicate the water sample has intensities of the predetermined color that correlate to nonionic surfactant concentrations of 10 ppm, 100 ppm, or 1,000 ppm.

Additionally, quantitative detection of the nonionic surfactant in the water sample can also include using ultraviolet-visible spectroscopy. For one or more embodiments, the organic phase can be removed and retained for testing with the ultraviolet-visible spectroscope. For one or more embodiments, the oil-field test kit has a spectroscopic detection limit of less than 10 ppm of the nonionic surfactant. In one embodiment, the oil-field test kit has a spectroscopic detection limit of less than 1 ppm of the nonionic surfactant.

As discussed herein, the methods and oil-field test kits can be used to determine whether the water sample contains the predetermined amount of the surfactant, where the predetermined amount can be a concentration of the nonionic surfactant. However, additional embodiments of the present disclosure include methods and oil-field test kits that can be used to determine an absolute weight of the nonionic surfactant in the water sample. For example, the water sample may be diluted and/or further altered after it has been obtained. In embodiments where the water sample has been diluted, the oil-field test kit can be used to determine the absolute weight of the nonionic surfactant in the water sample. Once the absolute weight of the nonionic surfactant is determined, the absolute weight of the surfactant can be converted back to a concentration of the nonionic surfactant based on the total volume of the water sample prior to dilution.

In one embodiment, the oil-field test kits of the present disclosure can visually detect an absolute weight of 1,000 micrograms (μg) of the nonionic surfactant in the water sample. Additionally, the oil-field test kits can detect an absolute weight of 100 μg of the nonionic surfactant using the ultraviolet-visible spectroscope. In one embodiment, the ultraviolet-visible spectroscope can detect 10 μg of the nonionic surfactant in the water sample.

An additional embodiment of the present disclosure includes an oil-field kit for enhanced oil recovery. The oil-field kit includes (a) a container for a water sample that contains a nonionic surfactant, and (b) an oil-field test kit for monitoring emulsion formation in an oil containing reservoir in an oil field. For one or more embodiments, the oil-field test kit includes: (i) ammonium thiocyanate, (ii) a metal nitrate; and (iii) an organic solvent. As discussed herein, ammonium thiocyanate, metal nitrate, and an organic solvent can be added to a water sample from the oil containing reservoir to monitor emulsion formation. For the embodiments, the metal nitrate and organic solvent of the oil-field test kit can be selected from the examples of each discussed herein.

The oil-field kit includes a container for a water sample that contains a nonionic surfactant. Examples of nonionic surfactants used in enhanced oil recovery can include, but are not limited to, ethoxylated aliphatic alcohols, polyoxyethylene, carboxylic esters, polyethylene glycol esters, anhydrosorbitol ester and ethoxylated derivatives, glycol esters of fatty acids, carboxylic amides, monoalkanolamine condensates, alkoxylates based on ammonia, primary amines or secondary amines, polyoxyethylene fatty acid amides, branched alkylphenol alkoxylates, linear alkylphenol alkoxylates, and branched alkyl alkoxylates.

For one or more embodiments, the oil-field kit can further include (c) a balance and (d) a separatory funnel. The separatory funnel, while not required, can assist in the separation of the organic phase and aqueous phase as disclosed herein.

For one or more embodiments, the oil-field test kit can further include a salt that can be added to the water sample to increase the extraction efficiency. Examples of salts include, but are not limited to, potassium chloride, sodium chloride, and combinations thereof. For one or more embodiments, the salt can be added to the water sample within a range of from 2 weight percent (wt%) to 15 wt%, based on a total weight of the water sample.

For the various embodiments, the visual detection limit and the spectroscopic detection limit of the nonionic surfactant are not affected by the presence of salt. For example, the presence of sodium chloride in the water sample does not affect the methods and/or oil-field test kits of the present disclosure. Additionally, varying the pH of the water sample does not affect the methods and/or oil-field test kits of the present disclosure.

It is to be understood that the above description has been made in an illustrative fashion, and not a restrictive one. Although specific embodiments have been illustrated and described herein, those of ordinary skill in the art will appreciate that other component arrangements can be substituted for the specific embodiments shown. The claims are intended to cover such adaptations or variations of various embodiments of the disclosure, except to the extent limited by the prior art.

In the foregoing Detailed Description, various features are grouped together in exemplary embodiments for the purpose of streamlining the disclosure. The methods of the disclosure are not to be interpreted as reflecting an intention that any claim requires more features than are expressly recited in the claim. Rather, as the following claims reflect, inventive subject matter lies in less than all features of a single disclosed embodiment. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment of the invention.

EXAMPLES

Materials

Experimental Surfactant 08-1015, Nonionic Enhanced Oil Recovery Surfactant, available from The Dow Chemical Company.

Deionized (DI) Water.

Ammonium thiocyanate, available from Fisher Scientific or equivalent (CAS # 1762-95-4).

Cobalt (II) nitrate, available from Fisher Scientific or equivalent (CAS # 10026-22-9).

5 Chloroform, available from Fisher Scientific or equivalent (CAS # 67-66-3)

Example 1

Dilute an appropriate amount of the nonionic enhanced oil recovery surfactant with DI water to form a solution mixture having a nonionic surfactant of at least 1,000 ppm. Add
10 100 grams (g) of the solution to a separatory funnel. Add 20 g of ammonium thiocyanate and 5 g of the cobalt (II) nitrate to the separatory funnel to form a sample mixture. Add an aliquot of 6 g of chloroform to the separatory funnel to form a sample-solvent mixture. Mix the sample-solvent mixture. Allow the organic phase to separate from the aqueous phase in the separatory funnel. Decant the organic phase and retain. Extract using 3 more aliquots
15 (a total of 4 aliquots or 24 g chloroform) using the same procedure. Determine the color of the organic phase.

Analysis

The organic phase of Example 1 was observed to have a blue-purple color, i.e., the
20 predetermined color. The blue-purple color indicates that there was at least 10 ppm of the nonionic surfactant in the solution.

CLAIMSWhat is claimed is:

1. A method of monitoring emulsion formation in an oil containing reservoir during enhanced oil recovery with a nonionic surfactant, the method comprising:
 - (a) obtaining a water sample from the oil containing reservoir;
 - (b) adding an effective amount of ammonium thiocyanate and an effective amount of a metal nitrate to the water sample to form a sample mixture, where the metal nitrate is selected from the group consisting of cobalt nitrate, iron nitrate, and combinations thereof;
 - (c) adding an organic solvent to the sample mixture to form a sample-solvent mixture,
 - (d) separating the sample-solvent mixture into an organic phase and an aqueous phase; and
 - (e) determining whether the organic phase has a predetermined color, where having the predetermined color indicates the water sample has a predetermined amount of the nonionic surfactant.
2. The method of claim 1, where obtaining the water sample includes obtaining the water sample from a production well of the oil containing reservoir.
3. The method of claim 1, wherein obtaining the water sample includes obtaining the water sample from a separator.
4. The method of claim 1, where adding an effective amount of ammonium thiocyanate to the water sample includes adding 1.0 part of ammonium thiocyanate by weight for 5.0 parts water sample by weight.
5. The method of claim 1, where adding an effective amount of the metal nitrate to the water sample includes adding 1 part metal nitrate by weight for 20.0 parts water sample by weight.
6. The method of claim 1, where adding organic solvent to the sample mixture includes 1.0 part organic solvent by weight for 4.0 parts water sample by weight.

7. The method of claim 1, where the predetermined amount of the nonionic surfactant is at least 10 parts-per-million.
8. The method of claim 1, where a substantially colorless organic phase indicates that the water sample does not have the predetermined amount of the nonionic surfactant.
9. The method of claim 1, where the predetermined color of the organic phase has an absorbance maximum wavelength at 316 ± 20 nanometers and an absorption maximum wavelength at 614 ± 20 nanometers.
10. An oil-field test kit for monitoring emulsion formation in an oil containing reservoir in an oil field, the oil-field test kit comprising:
 - (a) ammonium thiocyanate;
 - (b) a metal nitrate; and
 - (c) an organic solvent.
11. The oil-field test kit of claim 10, where the metal nitrate can be selected from the group consisting of cobalt nitrate, iron nitrate, and combination thereof.
12. The oil-field test kit of claim 11, where the metal nitrate is cobalt nitrate.
13. The oil-field test kit of claim 10, where the organic solvent is chloroform.
14. The oil-field test kit of claim 10, further comprising an emulsion-formation color chart.
15. The oil-field test kit of claim 14, where the emulsion-formation color chart has a visual detection limit within the range of from 10 ppm to 1,000 ppm of a nonionic surfactant.
16. The oil-field test kit of claim 10, where the oil-field test kit has a spectroscopic detection limit of 10 ppm of a nonionic surfactant.
17. An oil-field kit for enhanced oil recovery, the oil-field kit comprising:

- (a) a container for a water sample that contains a nonionic surfactant; and
 - (b) an oil-field test kit for monitoring emulsion formation in an oil containing reservoir in an oil field, wherein the kit comprises:
 - (i) ammonium thiocyanate;
 - (ii) a metal nitrate; and
 - (iii) an organic solvent.
18. The oil-field kit of claim 17, where the metal nitrate is cobalt nitrate.
19. The oil-field kit of claim 17, where the organic solvent is chloroform.
20. The oil-field kit of claim 17, where the oil-field test kit further includes:
- (c) a balance; and
 - (d) a separatory funnel.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/001007

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/584 C09K8/594 E21B49/08
ADD.

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)
C09K E21B

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)

EP0-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	EP 0 566 394 A1 (HALLIBURTON CO [US]) 20 October 1993 (1993-10-20) page 3, line 49 - line 52 page 4, line 7 - line 9 page 4, line 47 - page 5, line 1 page 19, line 34 - line 51; example II -----	1-12, 14-18,20
X	BROWN, HAYES: "The absorptiometric determination of polyethyleneglycol-monooleate", ANALYST, vol. 80, 1 October 1955 (1955-10-01), pages 755-767, XP009151808, page 756 - page 757 ----- -/--	10-13, 17-19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"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

7 September 2011

Date of mailing of the international search report

21/09/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Redecker, Michael

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/001007

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WEBER, DEGNER, BAHJAT: "Determination of nonionic ethylene oxide adduct in some commercial products", ANALYTICAL CHEMISTRY, vol. 36, 1 March 1964 (1964-03-01), pages 678-679, XP000002658306, page 678, column 3 - page 679, column 1 -----	10-12, 17,18
A	US 4 856 589 A (KUHLMAN MYRON I [US] ET AL) 15 August 1989 (1989-08-15) column 4, line 67 - column 5, line 58 column 8, line 30 - line 36 column 9, line 35 - line 49 column 12, line 54 - column 13, line 29 column 15, line 15 - line 16 -----	1-9
A	US 3 788 399 A (FEUERBACHER D ET AL) 29 January 1974 (1974-01-29) column 6, line 10 - line 42; claim 1 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/001007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0566394	A1	20-10-1993	AU 3691793 A 21-10-1993
			BR 9301570 A 19-10-1993
			CA 2094088 A1 18-10-1993
			DE 69303214 D1 25-07-1996
			DE 69303214 T2 14-11-1996
			US 5310002 A 10-05-1994

US 4856589	A	15-08-1989	NONE

US 3788399	A	29-01-1974	CA 963385 A1 25-02-1975
