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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 October 2016 (27.10.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/171653 A1

(51) International Patent Classification:
C23G 1/06 (2006.01)

(21) International Application Number:
PCT/US2015/026673

(22) International Filing Date:
20 April 2015 (20.04.2015)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **HALLIBURTON ENERGY SERVICES, INC.** [US/US]; 3000 N. Sam Houston Parkway E., Houston, Texas 77032-3219 (US).

(72) Inventors: **PENG, Yang**; 6118 Aspen Pass Dr., Kingwood, Texas 77345 (US). **ZHAO, Funian**; 17203 Elverson Oaks Dr., Tomball, Texas 77377 (US). **YUE, Zhiwei**; 2019 Cypress Bend Ln., Sugar Land, Texas 77478 (US). **SHI, Liu**; 17630 Amber Mist, Houston, Texas 77095 (US). **QU, Liangwei**; 7 N Plum Crest Circle, Spring, Texas 77382 (US). **FAN, Chunfang**; 12502 Queensbury Ln., Houston, Texas 77024 (US).

(74) Agent: **LECOINTE, Michelle M.**; Baker Botts L.L.P., 98 San Jacinto Blvd., Suite 1500, Austin, Texas 78701 (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, BN, 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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

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

(54) Title: COMPOSITIONS, SYSTEMS, AND METHODS FOR REMOVING IRON SULFIDE SCALE FROM OILFIELD COMPONENTS

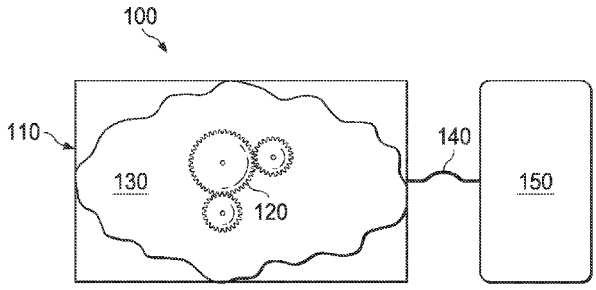


FIG. 1

(57) Abstract: The present disclosure relates to compositions, systems and methods for removing iron sulfide scale from a solid object, such as an oilfield component. The compositions include a carbon-carbon (C-C) double bond with an electron withdrawing group bonded to at least one of the double-bonded carbons.

WO 2016/171653 A1

COMPOSITIONS, SYSTEMS, AND METHODS FOR REMOVING IRON SULFIDE SCALE FROM OILFIELD COMPONENTS

TECHNICAL FIELD

The present disclosure relates to compositions, systems, and methods for removing iron sulfide scale from a solid object, such as an oilfield component.

BACKGROUND

Iron sulfide scale commonly forms in the oilfield environment, particularly if there is water in the formation being drilled or used for production. Scale can cause equipment to break or perform sub-optimally and may also reduce production from a well. Iron sulfide scale is difficult to remove because of its low water solubility and its complex composition and structure. Conventional methods for removing scale in the oilfield setting involve chemicals with limited effectiveness, such as tetrakishhydroxymethylphosphonium salt (THPS) or chelate sequestrants. More effective chemicals, such as strong inorganic or organic acids or acrolein (2-propenal) are dangerous. For instance, acrolein has a very high acute toxicity, necessitating extremely careful handling.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention and its features and advantages, reference is now made to the following description, taken in conjunction with the accompanying drawings, which are not drawn to scale, and in which:

FIGURE 1 presents a schematic diagram of a closed system for iron sulfide removal;

FIGURE 2 presents a schematic diagram of a system for iron sulfide removal from a tubular in an oil or gas well;

FIGURE 3 presents results from an iron sulfide removal test immediately upon addition of a removal material (FIGURE 3A), and after ten minutes (FIGURE 3B);

FIGURE 4 presents results from an iron sulfide removal test immediately upon addition of another removal material (FIGURE 4A), and after ten minutes (FIGURE 4B); and

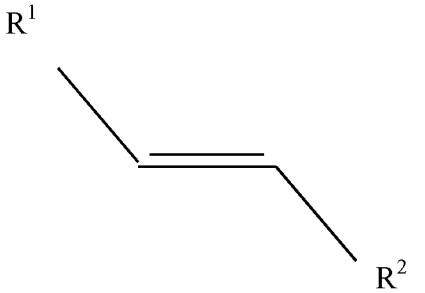
FIGURE 5 presents results from an iron sulfide removal test immediately upon addition of yet another removal material (FIGURE 5A), and after thirty minutes (FIGURE 5B).

DETAILED DESCRIPTION

The present disclosure relates to compositions, systems, and methods for removing iron sulfide scale from a solid object. Specifically, the object may be an oilfield component.

Compositions of the present disclosure generally include a carbon-carbon (C-C) double bond with an R^1 group bonded to at least one of the double-bonded carbons. The R^1 group includes an electron withdrawing group. Both of the double-bonded carbons may be bonded to an R^1 group, or one of the double-bonded carbons may be bonded to hydrogen (H) instead. Typically, compositions in which both double-bonded carbons are bonded to an R^1 group may be more effective at removing iron sulfide scale than compositions with only one R^1 group and with H on the other double-bonded C.

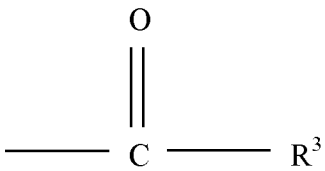
Compositions of the present disclosure may thus have the following general structural formula:



(I),

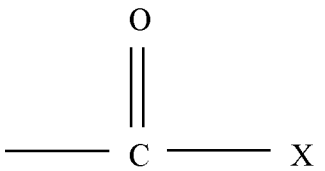
wherein R^1 is an electron withdrawing group and R^2 is R^1 or H.

R^1 may, for instance, include an acetate ($C_2H_3O_2^-$) group; a nitrile (C≡N) group; a ketone group:



(A),

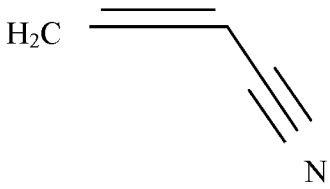
wherein R^3 is a carbon-containing group, such as an alkyl group, particularly a methyl (CH_3) group or a methyl-terminated group; or a acyl halide group:



(B),

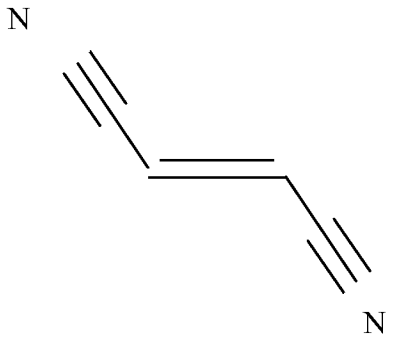
wherein X is a halide, such as chlorine (Cl), bromine (Br), or fluorine (F). R^1 may further be selected so that the composition has a lower corrosion rate and/or lower toxicity than acrolein or a strong inorganic or organic acid.

For example, when R^1 includes a nitrile group and R^2 is H, the composition may have the following general structural formula:



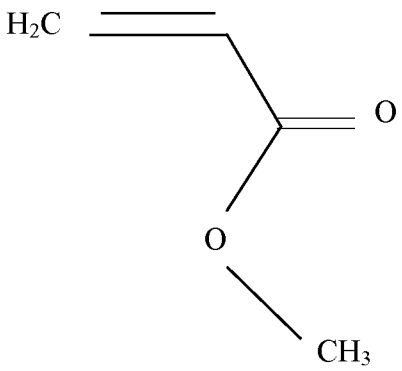
(II).

In another example, when R^1 includes a nitrile group and R^2 is the same as R^1, the composition may have the following general structural formula:



(III).

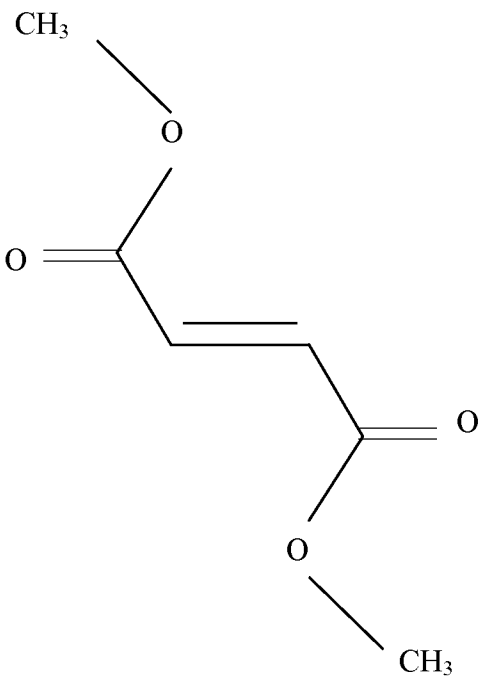
In another example, when R^1 includes an acetate group and R^2 is H, the composition may be methyl acrylate and may have the following general structural formula:



(IV),

or it may be a methyl-acrylate-containing composition, such as a composition with more than

one acrylate group and, for example, the following general structural formula:



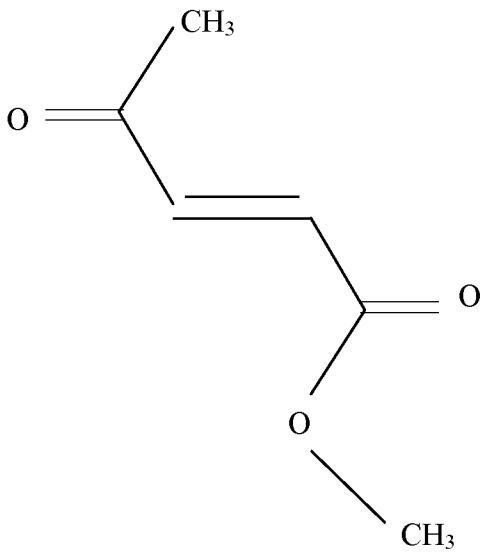
(V).

Although in these examples the electron withdrawing group is directly bonded to one of the double-bonded carbon atoms, spacer moieties, such as carbon chains, may also be present. These may allow the attachment of multiple electron withdrawing groups in the same R^1 group.

Although, for ease of synthesis, all electron withdrawing groups in an R^1 group will typically be the same, it is possible to have different electron withdrawing groups in an R^1 group. In addition, although, if R^2 is not H, it will typically be the same as R^1 also for ease of synthesis, it may differ from R^1, for instance by having different electron withdrawing groups. One of ordinary skill in the art may achieve the substitution of different electron withdrawing groups or different R^1 and R^2 groups

on the carbon-carbon double bond backbone molecule by using blocking groups or other chemical synthesis techniques.

For instance, when R^1 contains an acetate group and R^2 is not H and is not the same as R^1, but is another electron withdrawing group, the composition may have the following general structural formula:



(VI).

Although typically synthesis conditions will yield primarily one type of molecule, it is possible to obtain a mixture of different molecules at times. For instance, synthesis conditions may yield a mixture of a) molecules in which R^1 and R^2 are the same and b) molecules in which R^1 is an electron withdrawing group and R^2 is H.

Ferric sulfide scale may be removed from a solid object, such as an oilfield component, using any composition described above or any combination of any compositions described above in the form of a removal material. The removal material may contain a composition or compositions of the present disclosure in an aqueous solvent or another polar solvent able to dissolve both the composition or compositions of this disclosure and iron and sulfide or any iron or sulfide-containing

compounds produced by reaction of iron sulfide with the composition or compositions of this disclosure.

Ferric sulfide scale may have the general formula Fe_xS_y. The value of x and y may vary primarily due to the redox state of Fe, which may be 2+ or 3+. The ferric sulfide scale typically includes a mixture of molecules. For instance, iron sulfide commonly contains one or more of the following: pyrrhotite, ($Fe_{1-x}S$), troilite (FeS), mackinawite ($Fe_{1+x}S$), pyrite or marcasite (FeS_2), or greigite (Fe_3S_4).

Removal may be accomplished by breaking the iron sulfide into component ions, which are then dissolved in the removal mixture or by forming a compound containing a component of a composition or compositions of this disclosure and iron or sulfide. The amount of scale removed from solid object may be at least 80%, at least 90%, at least 95%, or substantially all of the iron sulfide scale.

The solid object may include any oilfield component on which iron sulfide scale accumulates. For instance, it may include a component with movable parts whose movement is hampered by the iron sulfide scale or a component with a fluid passageway that is blocked by iron sulfide scale. Specific oilfield components from which iron sulfide scale may be removed include perforations, casing, production tubulars, valves, pumps, such as electric submersible pumps, and downhole completion equipment, such as safety equipment and gas lift mandrels.

Iron sulfide scale may be removed from a solid object by exposing the object to a removal material for a length of time sufficient to remove all or a pre-determined amount of iron sulfide scale. A pre-determined amount may be the amount sufficient to allow the solid object to fulfill its intended function for a selected period of time. The length of time may vary depending upon the composition of the removal material,

the concentration of the compound or compounds according to this disclosure in the removal material, the amount of iron sulfide scale to be removed, and the removal material and iron sulfide scale temperature, among other factors. Removal may take place at atmospheric pressure, or at an elevated pressure resulting from removal material being stored in a pressurized container.

Appropriate removal material composition and length of time for the removal process may be determined by conducting tests such as those described in the following examples designed to mimic the iron sulfide scale to be removed and removal conditions.

Although compositions of the present disclosure are generally safer than conventional iron sulfide removal materials, protective measures and equipment may still be put in place during the removal process in order to protect personnel and/or the environment and/or to recover removal materials and removed scale.

For instance, the removal process may be conducted in a closed system 100, such as that depicted in FIGURE 1. Sealed container 110 may solid object 120 and removal material 130 to avoid release of removal material 130, which may be a liquid or a gas. Removal material 130 may be provided to sealed container 110 via a connector 140. Removal material 130 may be stored in a pressurized container 150 or in another suitable vessel. Connector 140 may also further contain various pressurized manifolds, hoses, and/or fittings (not shown) to transfer removal material 130 to sealed container 140. Sealed container 110 may contain applicators (not shown) that direct removal material 130 to particular areas of solid object 120. Closed system 100 may further contain leak-proof chemical pumps, metering equipment, and a purge subsystem to remove removal material 130 from sealed

container 110 (all not shown) as suitable for use with a particular solid object 120 and removal material 130.

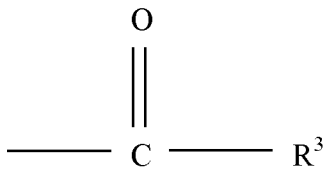
The present disclosure also provides a system and method for improving production from an oil and gas well by removing iron sulfide scale from a tubular located in the well using a removal material, thereby improving oil or gas flow through the tubular. For example, as shown in FIGURE 2, system 200 may contain removal material 210 in a sealed container 220, which may be a pressurized container. Connector 230 allows the removal material to flow from container 220 to tubular 240, where it removed iron sulfide scale. Connector 230 may contain applicators (not shown) that direct removal material 210 to particular areas of tubular 240. Closed system 200 may further contain leak-proof chemical pumps, metering equipment, and a recapture subsystem to capture removal material 210 from tubular 240.

In an embodiment A, the disclosure provides a method of removing iron sulfide scale from an oilfield component with iron sulfide scale, by applying to the oilfield component a removal material comprising a composition with the general structural formula (I). R^1 is an electron withdrawing group and R^2 is R^1, hydrogen (H) or a carbon (C)-containing group. The removal material is applied in an amount and for a time sufficient to remove iron sulfide scale from the oilfield component.

In an embodiment B, the disclosure provides a system for removing iron sulfide scale, the system containing the removal material from embodiment A and a system for applying the removal material to the oilfield component in an amount and for a time sufficient to remove iron sulfide scale from the oilfield component.

Embodiments A and B may be combined with one another or with any of the following additional elements, which may also be combined with one another: 1) the

removal material may include at least two distinct compositions with the general structural formula I, 2) R^1 may include an acetate group, 3) R^1 may include a nitrile group; The method of claim 1, wherein R^1 comprises a ketone group with the following general structural formula:

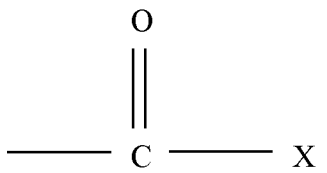


(A),

wherein R^3 is a carbon-containing group.

6. The method of claim 5, wherein R^3 is an alkyl group.

7. The method of claim 1, wherein R^1 comprises an acyl halide group having the following general structural formula:



(B),

wherein X is a halide.

4) the removal material may further include a polar solvent; 5) the polar solvent may include water; 6) at least 80% of the iron sulfide scale may be removed from the oilfield component; 7) applying may occur in a sealed container; 8) the removal material may be recovered; 9) the oilfield component may include a perforation, a casing, a production tubular, a valve, a pump, or downhole completion equipment with iron sulfide scale; 10) the composition may have the general structural formula II; 11) the composition may have the general structural formula III; 12) the composition may be methyl acrylate or a methyl acrylate-containing composition; 13) the composition may have the general structural formula IV; 14) the composition may

have the general structural formula V; 15) the composition may have the general structural formula VI; 16) the removal material may include an additional composition able to remove iron sulfide scale from the oilfield component; 17) the system for applying the removal material may include a sealed container; 18) the system for applying the removal material may further include a subsystem for recovering the removal material; 19) the oilfield component may include a tubular and the system for applying the removal material to the oilfield component may include a container to house the removal material and a connector to supply the removal material to the tubular; 20) the container may be a pressurized container; 21) the oilfield component may be placeable in a container and the system for applying the removal material to the oilfield component may include a sealed container in which the oilfield component is placed, a container housing the removal material, and a connector to supply the removal material to the sealed container; 22) the container housing the removal material may be a pressurized container.

EXAMPLES

The following examples further illustrate embodiments of the disclosure and ways to determine appropriate systems and methods of removing iron sulfide scale with a removal material. They are not intended to and should not be interpreted to encompass the entire scope of the invention.

Example 1

A removal material containing a composition of formula II was prepared and added to water containing 10 ppm iron and 100 ppm sulfide, which mimics iron sulfide scale. At the time the removal material was added, the water was black due to the presence of iron sulfide as shown in FIGURE 3A. After 10 minutes at 50 °C,

atmospheric pressure, and a pH of 7-8, the sample to which the removal material was added was white, as shown in the right bottle in FIGURE 3B, while the untreated water remained black, as shown in the left bottle in FIGURE 3B. This shows that the removal material containing a composition with formula II is able to react with iron sulfide in a manner that would result in its removal from a solid object.

Example 2

A removal material containing a composition of formula III was prepared and added to water containing 10 ppm iron and 100 ppm sulfide, which mimics iron sulfide scale. At the time the removal material was added, the water was black due to the presence of iron sulfide as shown in FIGURE 4A. After 10 minutes at 50 °C, atmospheric pressure, and a pH of 7-8, the sample to which the removal material was added was white, as shown in the right bottle in FIGURE 4B, while the untreated water remained black, as shown in the left bottle in FIGURE 4B. This shows that the removal material containing a composition with formula III is able to react with iron sulfide in a manner that would result in its removal from a solid object.

Example 3

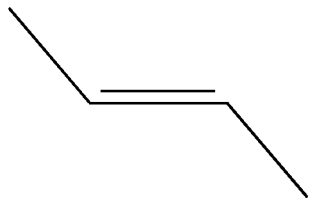
A removal material containing a composition of formula IV was prepared and added to water containing 50 ppm iron and 200 ppm sulfide, which mimics iron sulfide scale. At the time the removal material was added, the water was black due to the presence of iron sulfide as shown in FIGURE 5A. After 30 minutes at 50 °C, atmospheric pressure, and a pH of 7-8, the sample to which the removal material was added was white, as shown in the right bottle in FIGURE 5B, while the untreated water remained black, as shown in the left bottle in FIGURE 5B. This shows that the

removal material containing a composition with formula IV is able to react with iron sulfide in a manner that would result in its removal from a solid object.

The above disclosed subject matter is to be considered illustrative, and not restrictive, and the appended claims are intended to cover all such modifications, enhancements, and other embodiments which fall within the true spirit and scope of the present disclosure. Thus, to the maximum extent allowed by law, the scope of the present disclosure is to be determined by the broadest permissible interpretation of the following claims and their equivalents, and shall not be restricted or limited by the foregoing detailed description. For instance, although the compositions and mixtures of compositions described herein are adequate to remove iron sulfide scale on their own, they may also be mixed with conventional materials.

CLAIMS

1. A method of removing iron sulfide scale from an oilfield component with iron sulfide scale, the method comprising applying to the oilfield component in an amount and for a time sufficient to remove iron sulfide scale from the oilfield component a removal material comprising a composition with the general structural formula:



(I),

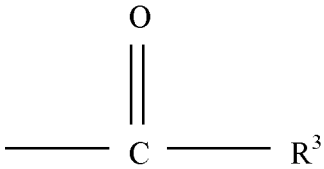
wherein R^1 is an electron withdrawing group and R^2 is R^1, hydrogen (H), or a moiety comprising another electron withdrawing group.

2. The method of claim 1, wherein the removal material comprises at least two distinct compositions with the general structural formula (I).

3. The method of claim 1, wherein R^1 comprises an acetate group.

4. The method of claim 1, wherein R^1 comprises a nitrile group.

5. The method of claim 1, wherein R^1 comprises a ketone group with the following general structural formula:



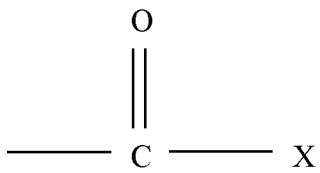
(A),

wherein R^3 is a carbon-containing group.

6. The method of claim 5, wherein R^3 is an alkyl group.

7. The method of claim 1, wherein R^1 comprises an acyl halide group

having the following general structural formula:



(B),

wherein X is a halide.

8. The method of claim 1, wherein the removal material further comprises a polar solvent.

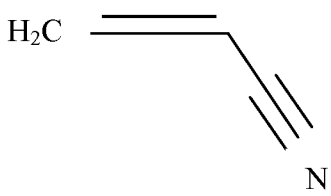
9. The method of claim 1, wherein at least 80% of the iron sulfide scale is removed from the oilfield component.

10. The method of claim 1, wherein applying occurs in a sealed container.

11. The method of claim 1, further comprising recovering the removal material.

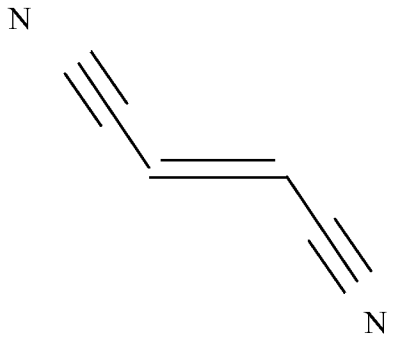
12. The method of claim 1, wherein the oilfield component comprises a perforation, a casing, a production tubular, a valve, a pump, or downhole completion equipment with iron sulfide scale.

13. The method of claim 1, wherein the composition has the general structural formula:



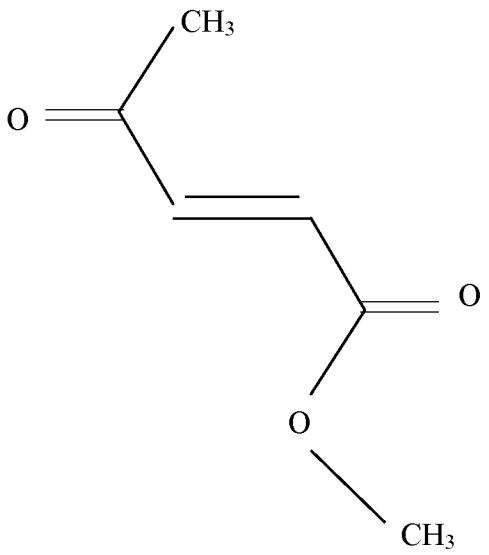
(II).

14. The method of claim 1, wherein the composition has the general structural formula:



(III).

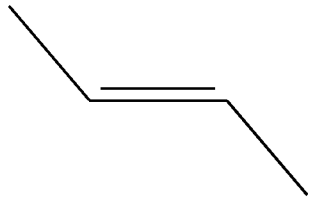
15. The method of claim 1, wherein the composition has the general structural formula:



(VI).

16. A system for removing iron sulfide scale from an oilfield component with iron sulfide scale, the system comprising:

a removal material comprising a composition with the general structural formula:



(I),

wherein R^1 is an electron withdrawing group and R^2 is R^1, hydrogen (H), or a moiety comprising another electron withdrawing group; and

a system for applying the removal material to the oilfield component in an amount and for a time sufficient to remove iron sulfide scale from the oilfield component.

17. The system of claim 16, wherein the system for applying the removal material comprises a sealed container.

18. The system of claim 16, wherein the system for applying the removal material further comprises a subsystem for recovering the removal material.

19. The system of claim 16, wherein the oilfield component comprises a perforation, a casing, a production tubular, a valve, a pump, or downhole completion equipment with iron sulfide scale.

20. The system of claim 16, wherein the system for applying the removal material comprises a pressurized container.

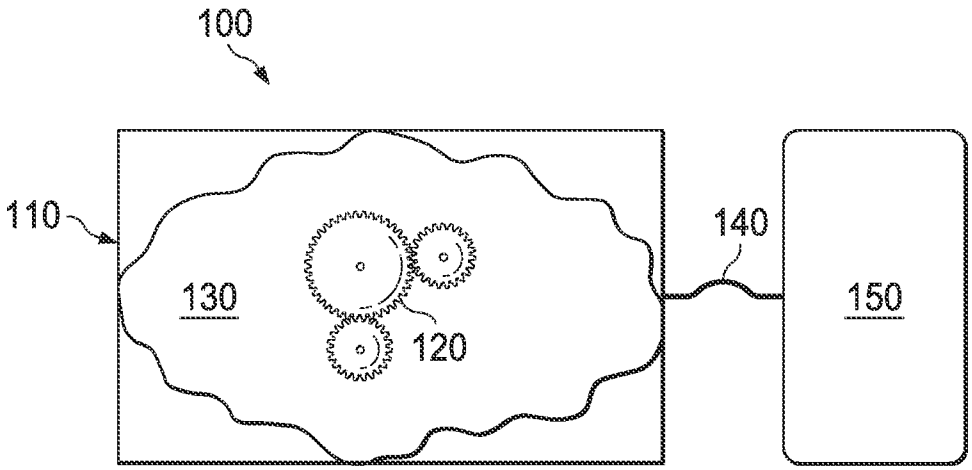


FIG. 1

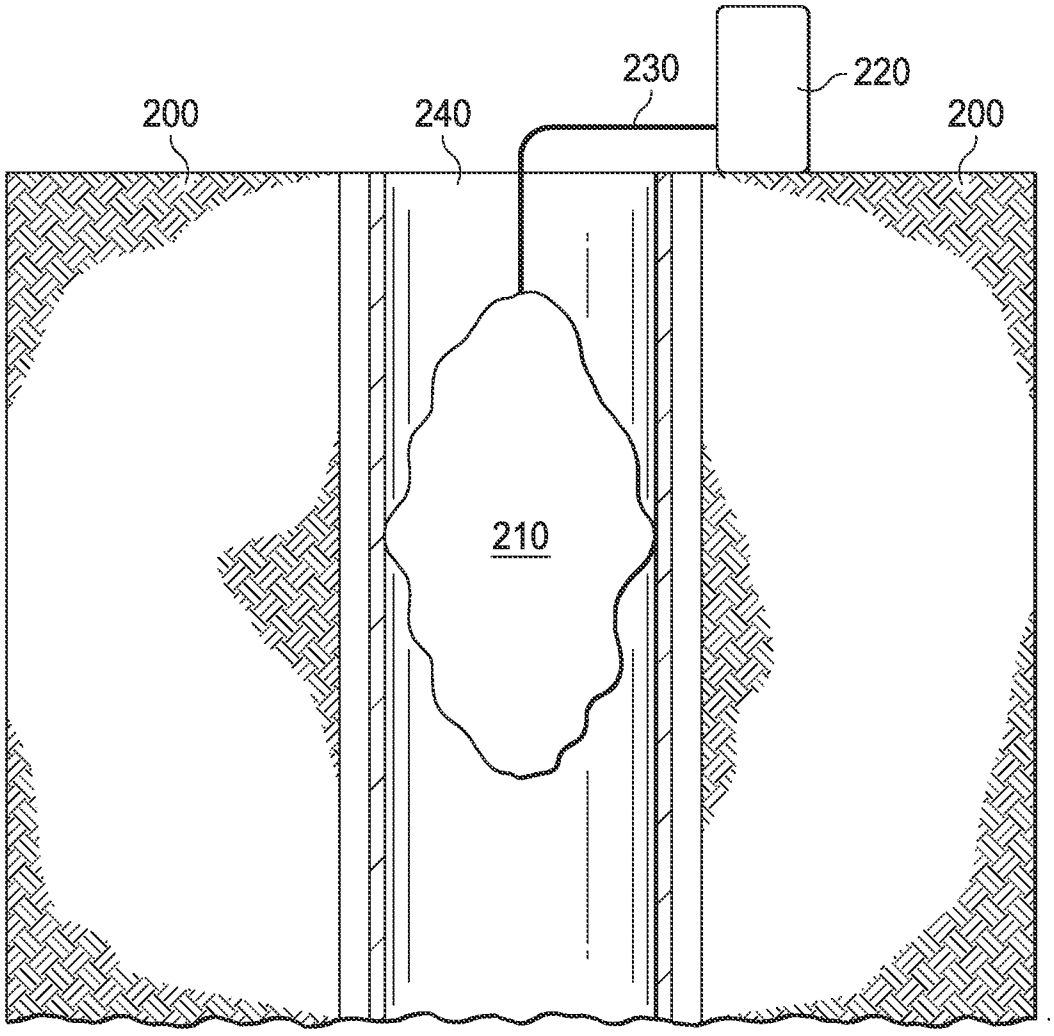


FIG. 2

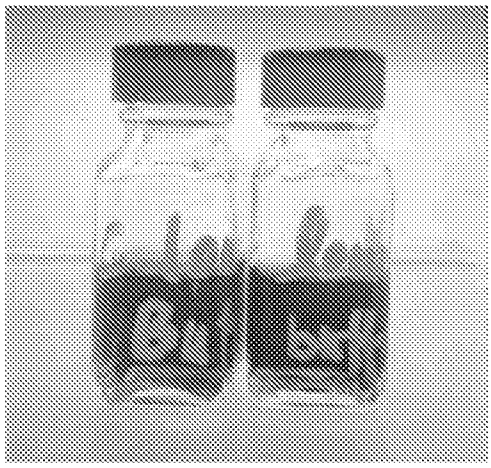


FIG. 3A

FIG. 3B

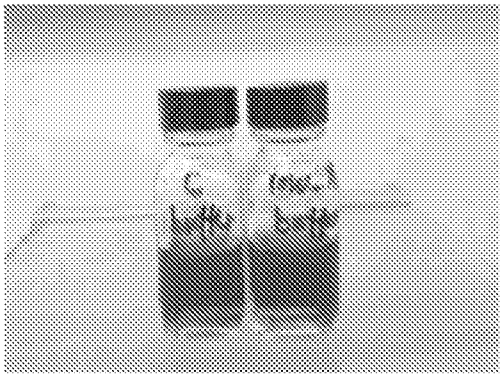


FIG. 4A

FIG. 4B

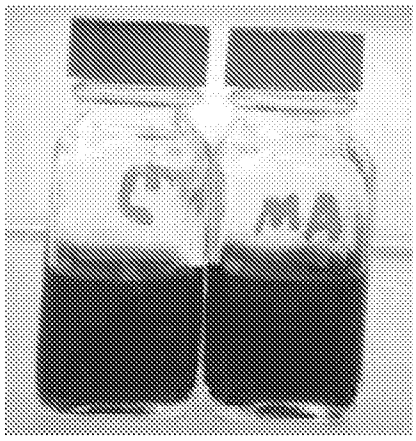


FIG. 5A

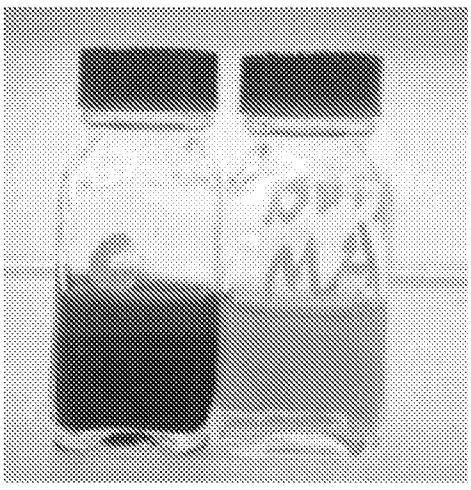


FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/026673

A. CLASSIFICATION OF SUBJECT MATTER

C23G 1/06(2006.01)i

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)
C23G 1/06; C11D 1/00; C01B 17/16; B08B 9/00; C11D 3/60; B08B 3/08; C01B 17/00; C02F 5/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: removal, iron sulfide, oilfield, composition, double bonded carbon, and electron withdrawing group

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012-0080641 A1 (RELENYI, ATTILA G.) 05 April 2012 See abstract; paragraphs [0072]-[0082]; and claims 1-5.	1-20
A	US 2010-0099596 A1 (TRAHAN, DAVID O.) 22 April 2010 See abstract; paragraphs [0042]-[0048]; claims 1-3; and figures 1-3.	1-20
A	US 2003-0133827 A1 (MATTOX, MARK ANDREW) 17 July 2003 See abstract; paragraphs [0008]-[0012]; and claims 1-8.	1-20
A	US 4032360 A (SHARP, THOMAS L.) 28 June 1977 See abstract; column 2, line 25 - column 3, line 47; and claim 1.	1-20
A	US 5104630 A (HOLMES, ERVINE S. et al.) 14 April 1992 See abstract; and claim 1.	1-20

☐ 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 application or patent 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
07 January 2016 (07.01.2016)	**07 January 2016 (07.01.2016)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 35208, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
CHO, Han Sol
Telephone No. +82-42-481-5580

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2015/026673

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0080641 A1	05/04/2012	AU 2010-361425 A1	21/02/2013
		AU 2010-361425 B2	14/08/2014
		JP 2012-533432 A	27/12/2012
		JP 557649 B2	20/08/2014
		MX 2011001237 A	18/12/2012
		NZ 591490 A	31/10/2014
		SG 178819 A1	30/05/2012
		WO 2012-044274 A1	05/04/2012
US 2010-0099596 A1	22/04/2010	US 2011-0152153 A1	23/06/2011
		US 7855171 B2	21/12/2010
		US 8673834 B2	18/03/2014
US 2003-0133827 A1	17/07/2003	US 6866048 B2	15/03/2005
US 4032360 A	28/06/1977	US 4003856 A	18/01/1977
		US 4123220 A	31/10/1978
US 5104630 A	14/04/1992	None	