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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
04 May 2023 (04.05.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/076014 A1

(51) International Patent Classification:
D04H 3/015 (2012.01) *C09K 8/40* (2006.01)
C09K 8/584 (2006.01)

(21) International Application Number:
PCT/US2022/045910

(22) International Filing Date:
06 October 2022 (06.10.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/272,772 28 October 2021 (28.10.2021) US

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(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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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, ME, 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).

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2023/076014 A1

(54) Title: SURFACTANT IMPREGNATED LOST CIRCULATION, SCRUBBING, AND SCOURING MATERIAL

(57) Abstract: A solid surfactant composition includes a water-wetting surfactant and a plant fiber carrying agent. A process includes forming a solid surfactant composition comprising a water-wetting surfactant and a plant fiber carrying agent and injecting the solid surfactant composition into a wellbore.

SURFACTANT IMPREGNATED LOST CIRCULATION, SCRUBBING, AND SCOURING MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a nonprovisional application which claims priority from U.S. provisional application number 63/272,772, filed October 28, 2021, which is incorporated by reference herein in its entirety.

FIELD

[0002] The disclosure relates generally to the use of lost circulation materials for well cleaning.

BACKGROUND ART

[0003] During drilling operations, loss of circulation, such as total or partial loss of drilling fluids or cement to high-permeability zones, cavernous formations and natural or induced fractures during drilling, may result in loss of drilling fluid and delay in the drilling of a well. In certain traditional drilling operations, lost circulation controllers added to the drilling fluid may form low-permeability bridges across openings in the formation that retard or prevent loss of circulation during drilling.

[0004] In a well cementing operation, casing and liners may be cemented in wellbores. For example, cement may be pumped into an annulus between the exterior surface of casing or liner and the walls of the wellbore or interior walls of casing. The cement may then harden in the annulus. The cement may act to prevent migration of fluids in the annulus. Preparation for the cementing operation is traditionally performed by pumping a fluid into the wellbore to clean solids and liquid, such as water and hydrocarbons. In certain traditional cementing operations, the fluid

may include a liquid surfactant to allow the fluid to be compatible with water- or oil-based drilling fluids. Inclusion of the liquid surfactant may allow cleaning of the wellbore by removal of any residual drilling fluid. Liquid surfactants may also water-wet surfaces in the wellbore, such as the wellbore wall and casing surfaces. Water wetting surfaces may allow for better cement bonding.

SUMMARY

[0005] In an embodiment, a solid surfactant composition is disclosed. The solid surfactant composition includes a water-wetting surfactant and a plant fiber carrying agent.

[0006] In another embodiment, a process is disclosed. The process includes forming a solid surfactant composition comprising a water-wetting surfactant and a plant fiber carrying agent and injecting the solid surfactant composition into a wellbore.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The present disclosure is best understood from the following detailed description when read with the accompanying figures. It is emphasized that, in accordance with the standard practice in the industry, various features are not drawn to scale. In fact, the dimensions of the various features may be arbitrarily reduced for clarity of discussion.

[0008] FIG. 1 is a pictorial representation of free flowing surfactant impregnated with a plant fiber carrier in accordance with Example 1.

[0009] FIG. 2 is a pictorial representation of free flowing surfactant impregnated with a plant fiber carrier in accordance with Example 1.

[00010] FIG. 3 is a graph of the results of a wettability test in accordance with Example 2.

[00011] FIG. 4 is a rotor wettability test in accordance with Example 3.

[00012] FIG. 5 is a rotor wettability test in accordance with Example 3.

[00013] FIG. 6 is a rotor wettability test in accordance with Example 3.

[00014] FIG. 7 is a rotor wettability test in accordance with Example 3.

[00015] FIG. 8 is a rotor wettability test in accordance with Example 3.

DETAILED DESCRIPTION

[00016] The following disclosure provides many different embodiments, or examples, for implementing different features of various embodiments. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. In addition, the present disclosure may repeat reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed.

[00017] This disclosure is not limited to the embodiments, versions, or examples described, which are included to enable a person having ordinary skill in the art to make and use the disclosed subject matter when the information contained herein is combined with existing information and technology.

[00018] Further, various ranges and/or numerical limitations may be expressly stated below. It should be recognized that unless stated otherwise, it is intended that endpoints are to be interchangeable. Further, any ranges include iterative ranges of like magnitude falling within the

expressly stated ranges or limitations. For example, if the detailed description recites a range of from 1 to 5, that range includes all iterative ranges within that range including, for instance, 1.3-2.7 or 4.9 – 4.95.

[00019] Certain embodiments of the present disclosure are to a solid surfactant composition including a water-wetting surfactant and a plant fiber carrying agent. The solid surfactant composition may be used with drilling fluids for control of lost circulation, or as a scrubbing or scouring material for such operations as preparation for a cementing operation or otherwise cleaning a wellbore. In certain embodiments, the solid surfactant composition may be used as a spacer fluid. Without being bound by theory, when used as a scrubbing or scouring agent, the solid surfactant composition may act chemically and mechanically to clean the wellbore.

[00020] In certain embodiments, the water-wetting surfactant may be an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, an olefin sulfonate, an alkyl betaine, a glycol ether, derivatives thereof, and combinations thereof. In some embodiments, the water-wetting surfactant may be non-hazardous, meeting US EPA Safer Product Standards.

[00021] In some embodiments, the plant fiber carrying agent may be of sustainable origin, such as corn cob hulls or fiber, walnut shells, peanut shells, coconut coir or shells, kenaf fiber and combinations thereof. The solid surfactant composition may include the water-wetting surfactant in an amount of 0.5-40% by weight of plant fiber carrying agent.

Examples

[00022] Example 1 – Sample Preparation

[00023] Several plant fiber carrying agents were chosen for review. These included Black Walnut Shell Fine LCM commercially available from Hammons with a 20/100 mesh size, English Walnut Shell, commercially available from Eco Shell with 35/60 and 70/200 mesh sizes respectively, Grit-O'Cobs, derived from the woody portion of corn cob, commercially available from Andersons Cob Products with a minus 80 and minus 40 granular mesh sizes respectively, and Coconut Coir, commercially available from Coco Absorb. The Coco Absorb was future sieved down to a 35/100 mesh size sample.

[00024] Each of the plant fiber carrying agents are spray dried with Tomadol 900, a [blend of C9-C11 ethoxylated alcohol and glycol ether], to determine maximum active concentrations, shown in Table 1, before the composite became visually clumped and remained in a flowable state, shown in FIG. 1 and FIG 2. Each solid composite was further labeled based on the carrier material and active surfactant concentration. For example, the Black Walnut Shell Fine LCM with a Tomadol 900 surfactant loading of 25.4% was labeled BW T25. Further example, the Grit-O'Cobs M80 with a Tomadol surfactant loading of 23% was labeled M80 T23.

Table 1: Maximum Surfactant Concentrations for Free Flowing Plant Fiber Carrier

Plant Fiber LCM Product	Max Surfactant A Conc. by Weight	Flowable (Yes/No)
Black Walnut Shell Fine LCM	25.4%	Yes
Eco Shell 35/60R	12%	Yes
Eco Shell 70/200	12%	Yes
Grit-O'Cobs M80	23%	Yes
Grit-O'Cobs M40G	30%	Yes
Coco Absorb	34.9%	Yes
Coco Absorb (35/100 Sieve)	30%	Yes

[00025] Example 2

[00026] Field originated oil-based mud (OBM), labeled Mount Everest OBM, was obtained for laboratory testing. Spacer formulations, shown in Table 2, were designed using the standalone

liquid surfactant, Tomadol 900, as well as the prepared surfactant impregnated lost circulation material samples. The standalone liquid surfactant loading of 0.438 gal per barrel (gpb) was determined to be the minimum concentration of Tomadol 900 to pass the Fann wettability spacer surfactant screening test (SSST), as shown in Figure 3. The loading for each solid composite was adjusted, based on surfactant activity level, to match a total surfactant loading of 0.438gpb.

Table 2: Spacer Formulations with Surfactant Impregnated Lost Circulation Material

Formula	I	II	III	IV	V
Barite (lb/bbl)	244.9	241.3	240.5	239.3	240.9
Diutan Gum (lb/bbl)	0.5	0.5	0.5	0.5	0.5
Tomadol 900 (gal/bbl)	0.438				
BW T25 (lb/bbl)		15.0			
35/100 Cocosorb T30 (lb/bbl)			12.13		
M80 T23 (lb/bbl)				15.83	
M40G T30 (lb/bbl)					12.14
Density (lb/gal)	12.8	12.8	12.8	12.8	12.8

[00027] Wettability, or SSST, tests were performed using a Fann Wettability Tester at 175°F and calibrated with the formulation spacer systems to 150 Hogans (Hn) prior to each test. Tests were run using the field originated OBM. Results for each spacer formulation wettability test are shown in Figure 3. As standardized in API RP 10B-2 Section 13.7 on Spacer Surfactant Screening Tests, a passing result is achieved if full conductivity, 150 Hn, is reached prior to the spacer equal to 75% of the OBM/spacer mixture added.

[00028] All surfactant impregnated lost circulation material composites effectively released the surfactant into the mixture and were able to flip the OBM to water wet. The results shown in Figure 3 illustrate an effective chemical wash method.

[00029] Example 3

[00030] A rotor wettability and wash test was performed on all spacer formulations using an OFITE Model 900 rheometer with all fluids conditioned to 175°F. Test procedure followed a 5, 5, 10, 5 test method; OBM for 5 minutes, water for 5 mins, spacer for 10 mins, followed by water for 5 mins. A final stage test rotor showing no beading will indicate water-wet results by the spacer.

[00031] Rotor wettability results for spacer formulation I from Table 2 are shown in Figure 4. Though the liquid surfactant was effective at water-wetting the OBM in the Fann wettability test, it failed to properly water-wet and wash during the rotor wettability test.

[00032] Improved results are shown in Figure 5 through Figure 8 for all surfactant impregnated lost circulation material spacer formulations. Notably both the M80 and M40G corn cob carrier products yielded the best rotor wettability and wash results.

[00033] Example 4

[00034] Well Integrity benefits of the surfactant formulations were tested on an OFITE HTHP (high temperature high pressure) Filter Press according to API RP 10B-2 test methods. Table 3 shows the surfactant impregnated lost circulation material improves fluid loss properties of the spacer formulation.

Table 3: HTHP Fluid Loss Results at 175°F

Formula	I	IV
Barite (lb/bbl)	244.9	239.3
Diutan Gum (lb/bbl)	0.5	0.5
Tomadol 900 (gal/bbl)	0.438	
M80 T23 (lb/bbl)		15.83
Fluid Loss (cc/30 mins)	237	166

CLAIMS:

1. A solid surfactant composition comprising a water-wetting surfactant and a plant fiber carrying agent.

2. The solid surfactant composition of claim 1, wherein the water-wetting surfactant comprises an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, an olefin sulfonate, an alkyl betaine, a glycol ether, derivatives thereof, and combinations thereof.

3. The solid surfactant composition of claim 2, wherein the plant fiber carrying agent comprises corn cob hulls or fiber, walnut shells, peanut shells, coconut coir or shells, kenaf fiber and combinations thereof.

4. The solid surfactant composition of claim 2, wherein the water-wetting surfactant is in an amount of 0.5-40% by weight of plant fiber carrying agent.

5. A process comprising:

   forming a solid surfactant composition comprising a water-wetting surfactant and a plant fiber carrying agent;

   injecting the solid surfactant composition into a wellbore.

6. The process of claim 5, wherein the water-wetting surfactant comprises an alcohol ethoxylate, an alcohol ethoxysulfate, an alkyl phenol ethoxylate, an olefin sulfonate, an alkyl betaine, a glycol ether, derivatives thereof, and combinations thereof.

7. The process of claim 6, wherein the plant fiber carrying agent comprises corn cob hulls or fiber, walnut shells, peanut shells, coconut coir or shells, kenaf fiber and combinations thereof.

8. The process of claim 6, wherein the water-wetting surfactant is in an amount of 0.5-40% by weight of plant fiber carrying agent.

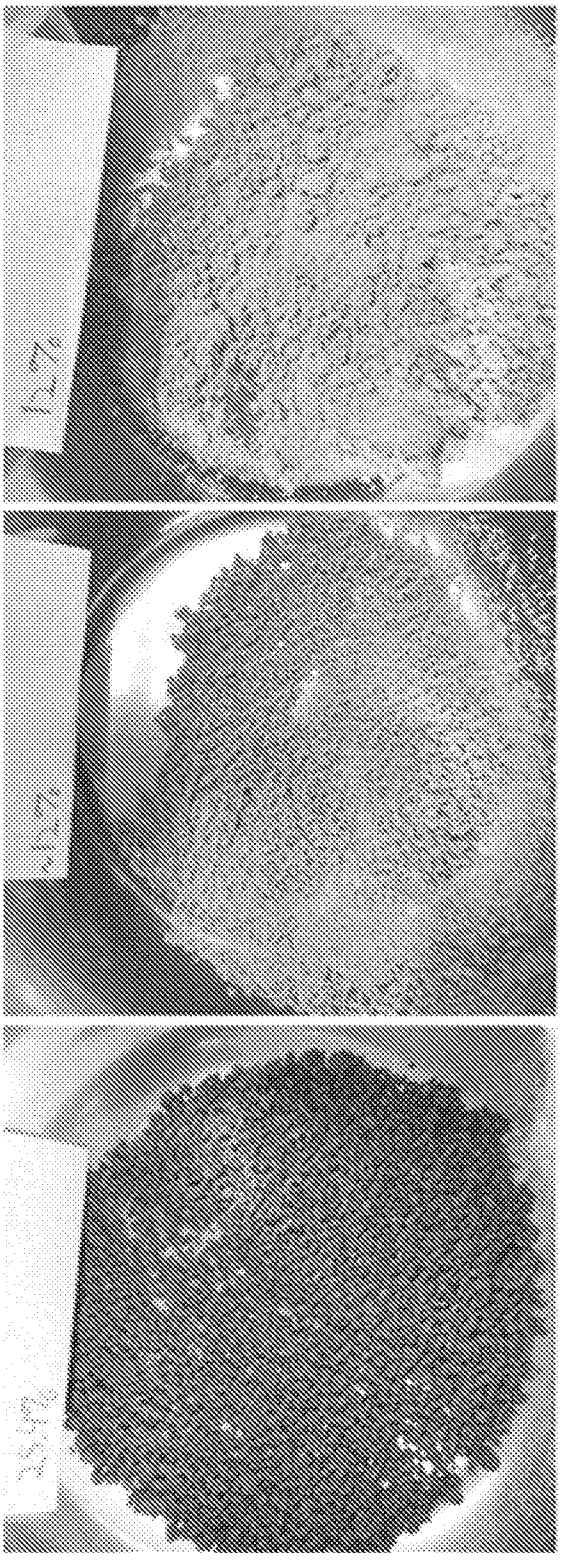


FIG. 1

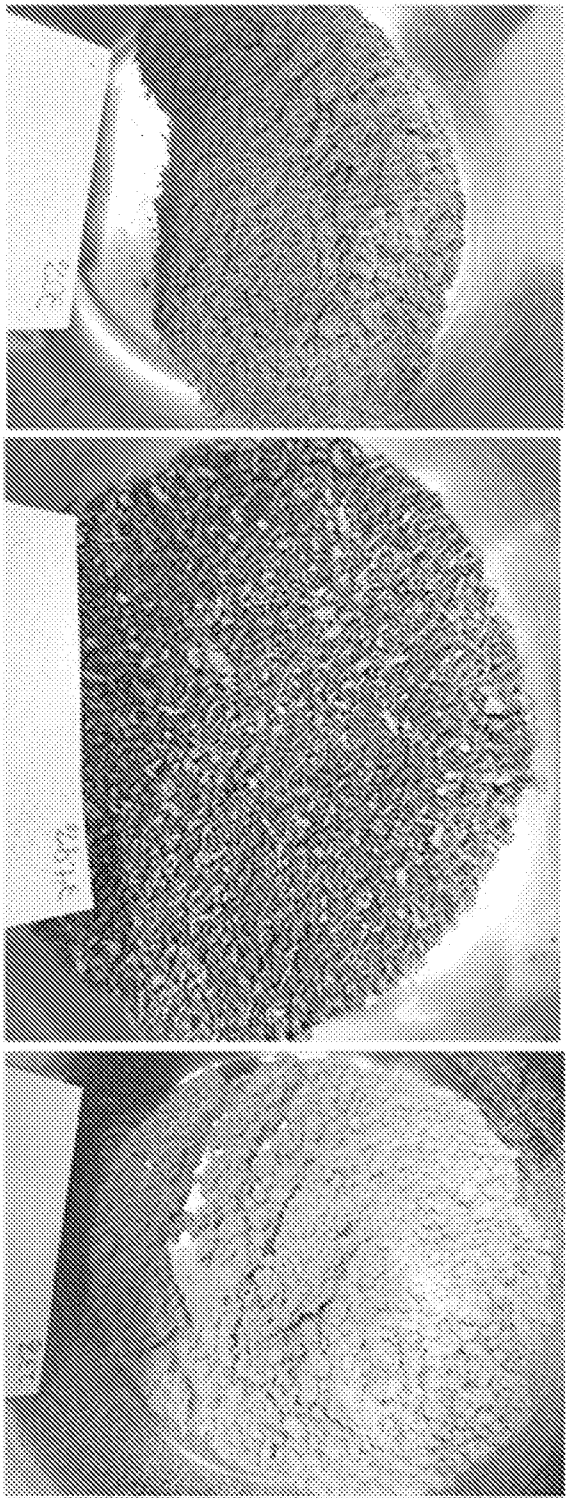


FIG. 2

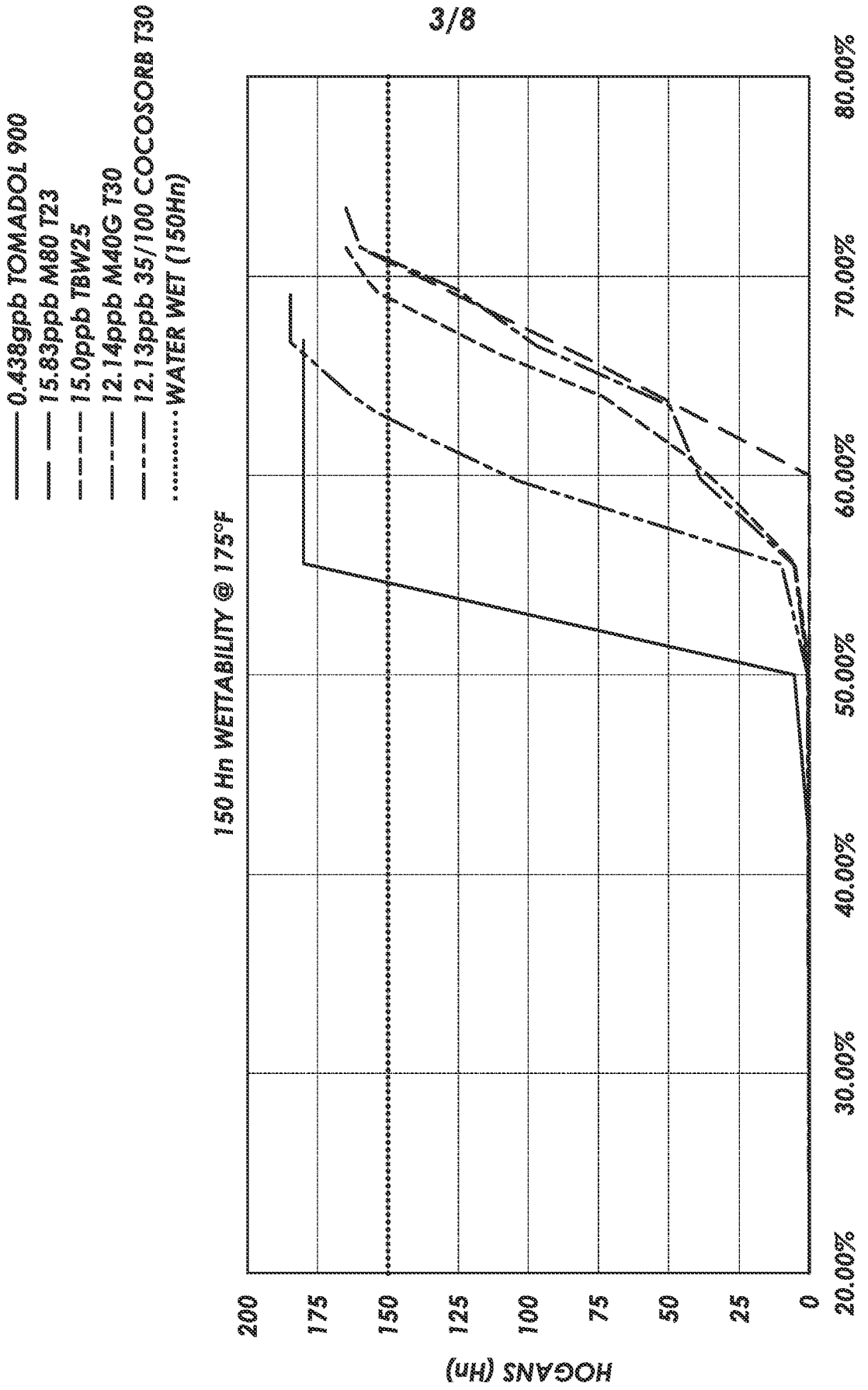

0.438gpb TOMADOL 900
15.83ppb M80 T23
15.0ppb TBW25
12.14ppb M40G T30
12.13ppb 35/100 COCOSORB T30
WATER WET (150Hn)
150 Hn WETTABILITY @ 175°F
HOGANS (Hn)
200
175
150
125
100
75
50
25
0
20.00%
30.00%
40.00%
50.00%
60.00%
70.00%
80.00%
% SPACER BY VOLUME

FIG. 3

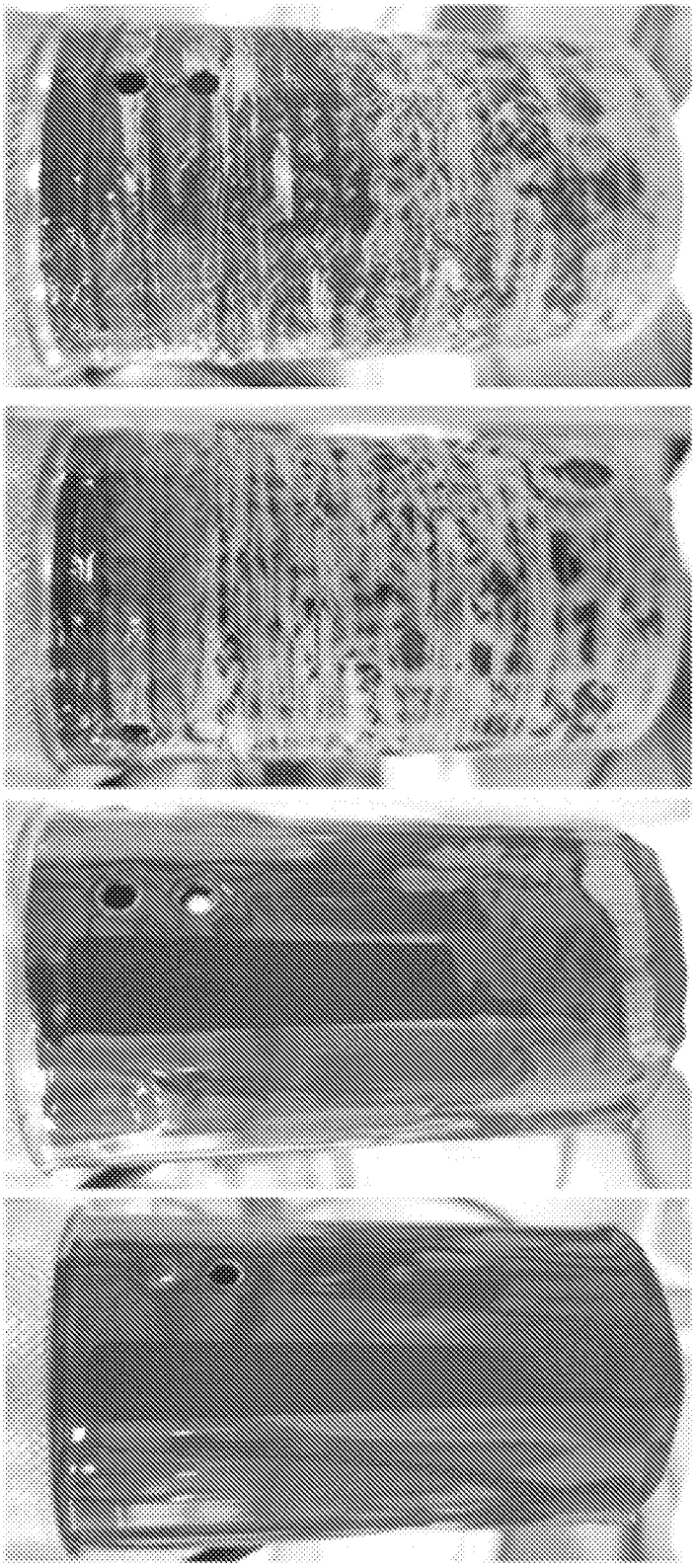

MOUNT EVEREST OBM
OBM - WATER
OBM - WATER - SPACER
OBM - WATER - SPACER - WATER
ROTOR WETTABILITY TEST WITH 0.438gpb TOMADOL 900 AT 175°F

FIG. 4

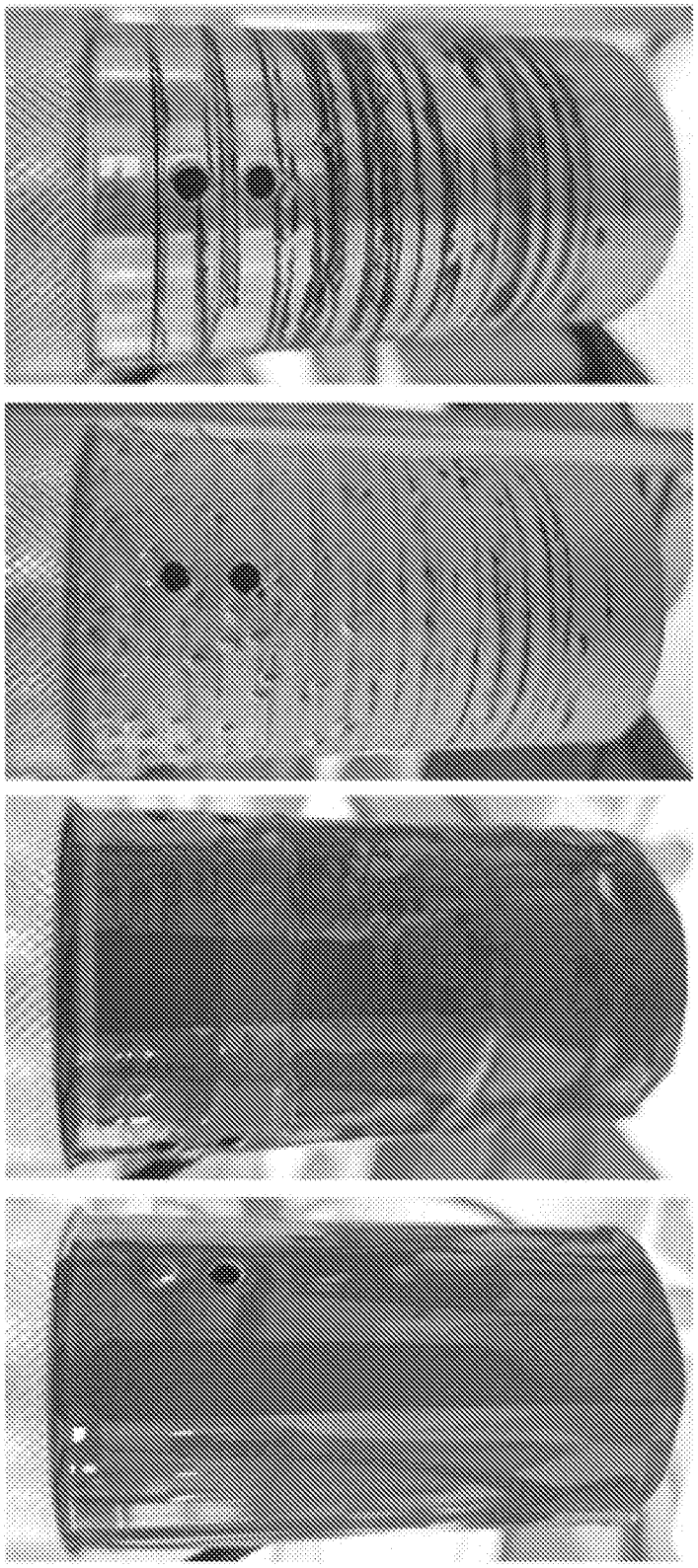

MOUNT EVEREST OBM
OBM - WATER
OBM - WATER - SPACER
OBM - WATER - SPACER - WATER
ROTOR WETTABILITY TEST WITH 15ppb TBW25 AT 175°F

FIG. 5

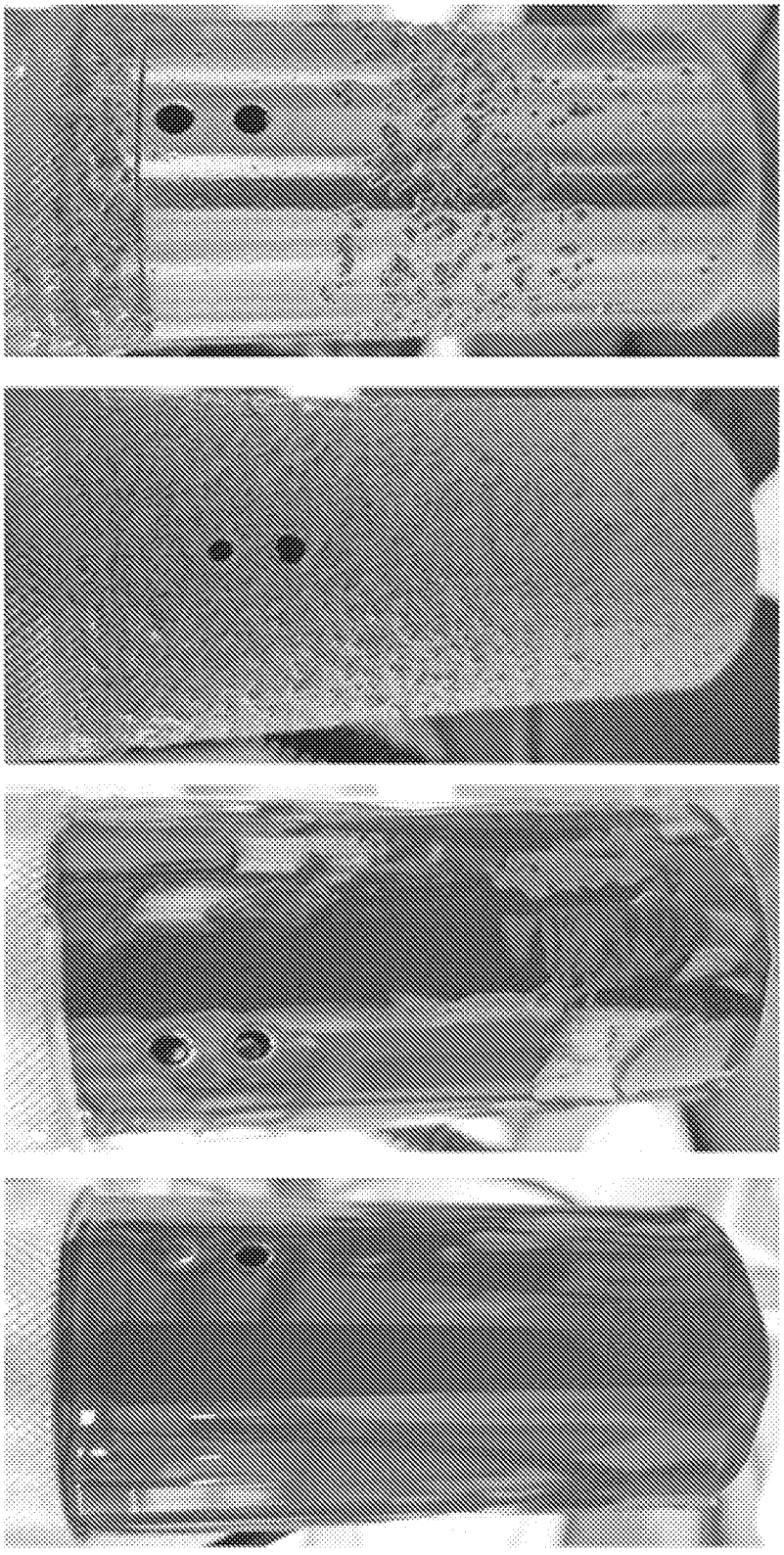

MOUNT EVEREST OBM
OBM - WATER
OBM - WATER - SPACER
OBM - WATER - SPACER - WATER
ROTOR WETTABILITY TEST WITH 12.13ppb 35/100 COCOSORB T30 AT 175°F

FIG. 6

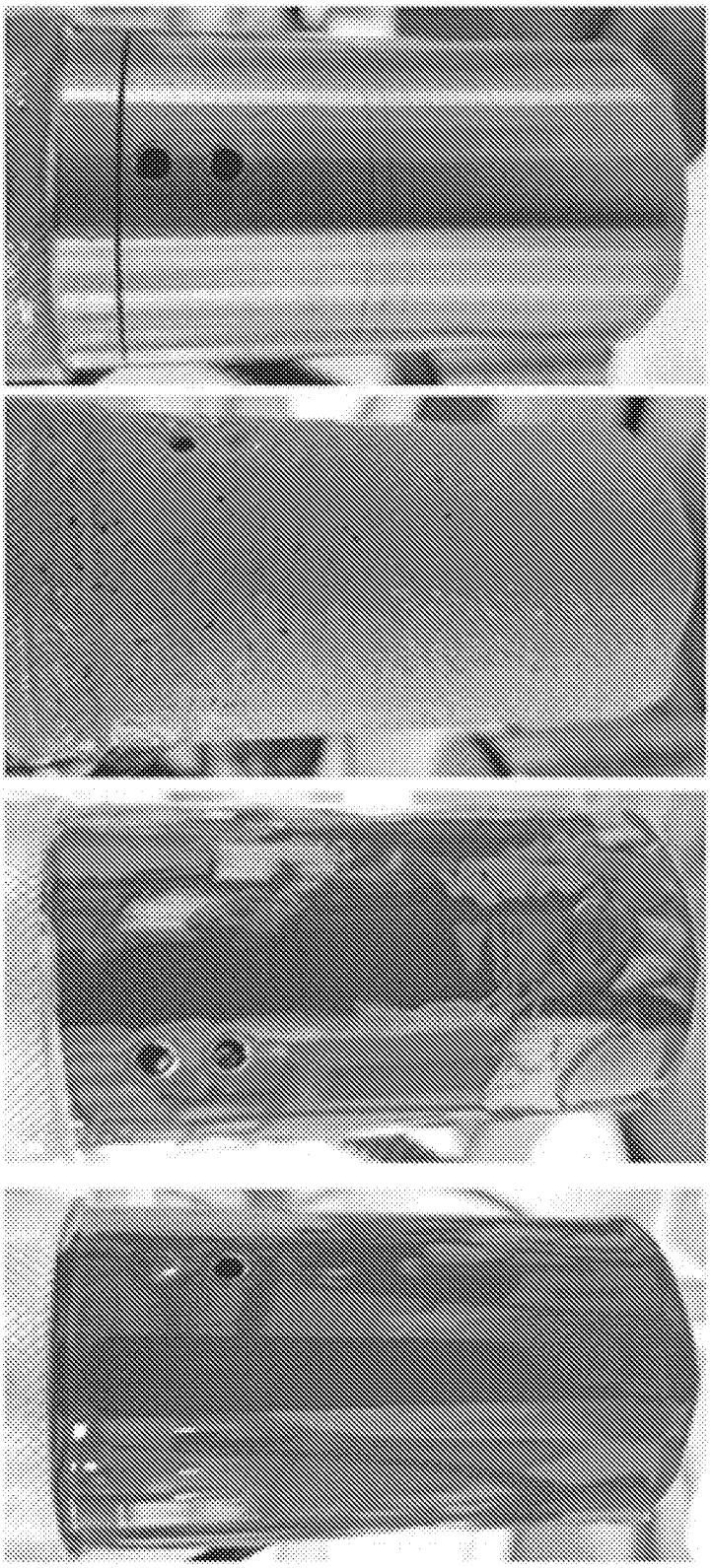
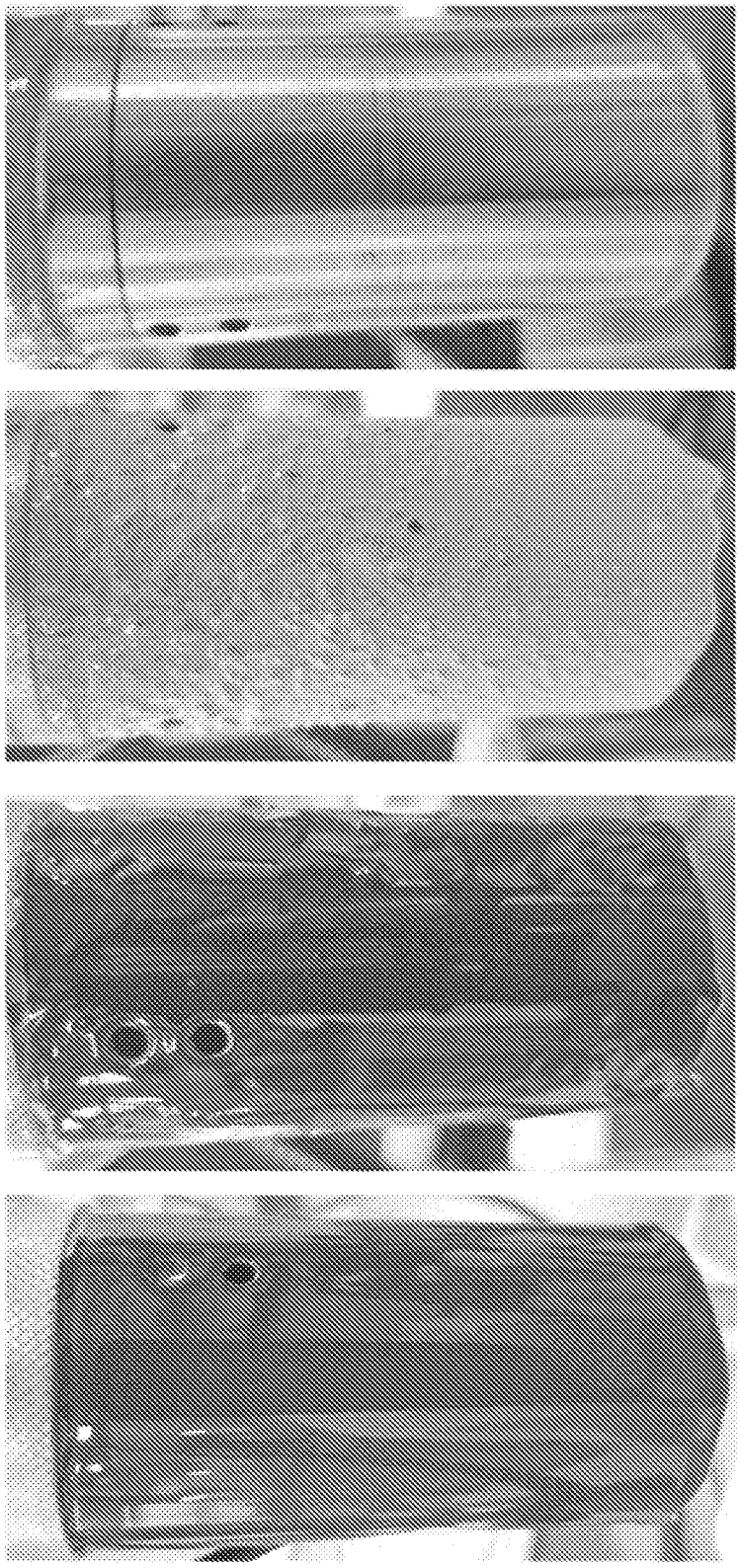

MOUNT EVEREST OBM
OBM - WATER
OBM - WATER - SPACER
OBM - WATER - SPACER - WATER
ROTOR WETTABILITY TEST WITH 15.83ppb M80 T23 AT 175°F

FIG. 7



ROTOR WETTABILITY TEST WITH 12.14ppb M40G T30 AT 175°F

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/45910

A. CLASSIFICATION OF SUBJECT MATTER
IPC - INV. D04H 3/015, C09K 8/584 (2022.01)
ADD. C09K 8/40 (2022.01)
CPC - INV. D04H 3/015, C09K 8/584
ADD. C09K 8/40
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)
See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/0104177 A1 (COSMETIC WARRIORS LIMITED) 19 April 2018 (19.04.2018); entire document, especially abstract, [0009], [0023]	1-2, 4
X	US 6,471,983 B1 (Veeger et al.) 29 October 2002 (29.10.2002); entire document, especially col 1 lines 38-41, col 2 lines 23-35	1-3
X	US 2016/0184203 A1 (The Dial Corporation) 30 June 2016 (30.06.2016); entire document, especially abstract, [0021], [0033], [0062], [0078]	1-4
A	US 2020/0140740 A1 (Halliburton Energy Services, Inc.) 07 May 2020 (07.05.2020); entire document	1-4
A	US 2020/0055777 A1 (PAREXGROUP SA) 20 February 2020 (20.02.2020); entire document	1-4
A	US 2011/0277261 A1 (Hasket et al.) 17 November 2011 (17.11.2011); entire document	1-4

☐ 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
"D" document cited by the applicant in the international application
"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
21 December 2022 (21.12.2022)	MAR 01 2023
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 22/45910

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:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-4, directed to a solid surfactant composition.

Group II: Claims 5-8, directed to a process of forming a composition and treating a wellbore.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

****See Supplemental Box****

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

2. ☐ As all searchable claims could be searched without effort justifying 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 report covers 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.:
1-4

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.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 22/45910

Continuation of Box III Observations where unity of invention is lacking

Special Technical Features:

Group II requires a process comprising: forming a solid surfactant composition and injecting the solid surfactant composition into a wellbore, not required by group I.

Common Technical Features:

Groups I and II share the technical feature of a solid surfactant composition comprising a water-wetting surfactant and a plant fiber carrying agent. However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being anticipated by US 2018/0104177 A1 to COSMETIC WARRIORS LIMITED (hereinafter "COSMETIC"). COSMETIC teaches a solid surfactant composition comprising a water-wetting surfactant and a plant fiber carrying agent (abstract, "A solid surfactant cosmetic composition includes (i) insoluble vegetable fibre, insoluble fruit fibre or mixture thereof; (ii) surfactant"; para [0009], "a vegetable pulp containing insoluble vegetable fibre, a fruit pulp containing insoluble fruit fibre or a mixture thereof, wherein the vegetable pulp, fruit pulp or mixture thereof is in an amount of 55 to 99 wt %; (ii) synthetic surfactant in an amount of 0.9 to 40 wt. %"; para [0023], "Whilst the primary role of the matrix is to maintain the structural integrity of the solid composition, it has a secondary purpose that allows for the synthetic surfactant to be dispersed throughout its structure. When water permeates the matrix the synthetic surfactant is actuated, allowing the composition to act in the desired manner").

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.