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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 June 2020 (25.06.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/131092 A1

(51) International Patent Classification:
*G01N 27/02* (2006.01) *G01N 15/02* (2006.01)
*E21B 47/10* (2012.01) *G01N 33/28* (2006.01)

(21) International Application Number:
PCT/US2018/067000

(22) International Filing Date:
21 December 2018 (21.12.2018)

(25) Filing Language: English

(26) Publication Language: English

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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, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, 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).

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

(54) Title: METHOD AND SENSOR SYSTEM FOR MONITORING ASPHALTENE STABILITY IN CRUDE OIL

(57) Abstract: A method for in-situ detection of asphaltene aggregation, the method comprises providing a sensor; deploying the sensor within a multiphase stream comprising asphaltenes, wherein the sensor and the asphaltenes interact to generate an asphaltene signal; and monitoring the asphaltene signal changes to detect asphaltene aggregation.

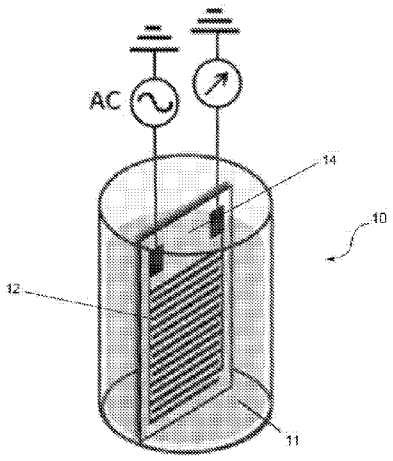


FIG. 1

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# METHOD AND SENSOR SYSTEM FOR MONITORING ASPHALTENE STABILITY IN CRUDE OIL

## FIELD OF INVENTION

**[0001]** The disclosed technology generally described hereinafter provides for monitoring of the aggregation state of asphaltenes in crude oils and multiphase streams, and more specifically, to a method and a sensor that allows real-time *in-situ* monitoring of the aggregation state of asphaltenes in crude oils and multiphase streams.

## BACKGROUND OF THE INVENTION

**[0002]** Asphaltene stability is one of the major factors that impacts oil flow in boreholes, transport pipelines, and other production facility components. Changes in operational conditions and certain practices may destabilize asphaltenes in crude oil and lead to catastrophic flow failures due to asphaltene deposition. This in turn leads to decreased productivity and costly treatments to remove deposits.

**[0003]** In upstream oil and gas production, the typical destabilizing factors include pressure and temperature changes, practices involving $CO_2$ injection into oil reservoir to enhance oil recovery (also known as $CO_2$ flooding), blending heavy and light (paraphinic) oils to reduce viscosity. Flow assurance necessitates the implementation of special metering control systems that detect flow interruptions and instruct injection of specially designed chemistries (*i.e.* stabilizers) to mitigate the formation of asphaltene and other solid deposits. Specifically, the existing flow assurance monitoring approaches detect abnormalities in oil properties (*e.g.*, flow patterns, acoustic or optical properties) caused by deposition of solids (typically asphaltene, wax, hydrates or scale) and then appropriate chemical treatment intervention is devised.

**[0004]** The fundamental limitation of these approaches is that they lack the capability for detection of early signs of asphaltene precipitation when the chemical intervention is most effective. Thus, the industry-standard optical methods assess asphaltenes at the stage when they are already unstable and start precipitating from the oil. Other techniques, such as based on gravimetric method, filtration and microscopy, are suitable primarily for off-line measurements.

**[0005]** In upstream oil and gas applications, specifically down-hole, stringent requirements are imposed to a sensing element exposed to the hostile high-pressure and high-temperature environment. Furthermore, scaling and fouling of sensing elements may compromise the sensor performance. These challenges require careful consideration and disqualify many existing sensing technologies for upstream monitoring applications.

**[0006]** Thus, what is needed in the art is method and a sensor system to overcome these limitations and that allows for real-time *in-situ* monitoring of the aggregation state of asphaltenes in crude oils and multiphase streams.

## SUMMARY OF THE INVENTION

**[0007]** The disclosed technology generally described hereinafter provides for a method for *in-situ* detection of asphaltene aggregation. In one aspect of the present technology, the method comprises providing a sensor; deploying the sensor within a multiphase stream comprising asphaltenes, wherein the sensor and the asphaltenes interact to generate an asphaltene signal; and monitoring the asphaltene signal changes to detect asphaltene aggregation.

**[0008]** In some embodiments, the sensor comprises an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate. In some embodiments, the interdigitated electrode comprises tungsten, copper, gold, or other conductive metal. In some embodiments, the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards (e.g. polyvynal acetate coated F4). In some embodiments, the sensor is deployed in either a down-hole or in surface production facility. In some embodiments, the multiphase stream is an oil, water, and/or gas stream. In some embodiments, the multiphase stream is a crude oil stream.

**[0009]** In some embodiments, the asphaltene aggregation is monitored using broad-range dielectric spectroscopy. In some embodiments, the asphaltene aggregation is determined by monitoring signal changes at a single frequency. In some embodiments, the asphaltene aggregation state is detectable in a multiphase stream with an asphaltene content of at least 0.1 wt.%.

**[0010]** In yet another aspect of the present technology, a sensor is provided. The sensor comprises an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate, wherein the sensor is configured to detect an asphaltene aggregation state in a multiphase stream with an asphaltene content of at least 0.1 wt.%.

**[0011]** In some embodiments, the interdigitated electrode comprises tungsten, copper, gold, or other conductive metal. In some embodiments, the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards (e.g. polyvynal acetate coated F4). In some embodiments, the interdigitated electrode has an electrode finger width ($W$) of at least 150μm. In some embodiments, the interdigitated electrode has an interelectrode spacing ($G$) of at least 150μm. In some embodiments, the interdigitated electrode has a periodicity ($\lambda$) value of at least 63.5μm. In some embodiments, the sensor allows for real-time *in-situ* monitoring of the asphaltene aggregation state.

**[0012]** In yet another aspect of the present technology, a sensor system for monitoring asphaltene stability is provided. The sensor system comprises a sensor maintained in fluid communication within a multiphase stream comprising asphaltenes, wherein the sensor is configured to determine dielectric signal changes at a single frequency; and an impedance analyzer.

**[0013]** In some embodiments, the sensor comprises an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate. In some embodiments, the interdigitated electrode comprises tungsten, copper, gold, or other conductive metal. In some embodiments, the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards (e.g. polyvynal acetate coated F4). In some embodiments, the sensor is configured to detect an asphaltene aggregation state in the multiphase stream having an asphaltene content of at least 0.1 wt.%. In some embodiments, the sensor is deployed in either a down-hole or in surface production facility.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0014]** These and other features of the disclosed technology, and the advantages, are illustrated specifically in embodiments now to be described, by way of example, with reference to the accompanying diagrammatic drawings, in which:

**[0015]** FIG. 1 is an illustrative embodiment of the disclosed technology;

**[0016]** FIG. 2 is a schematic of an illustrative embodiment of the disclosed technology;

**[0017]** FIGS. 3A-3B are graphical representations of an illustrative embodiment of the disclosed technology; and

**[0018]** FIGS. 4A-4B are graphical representations of an illustrative embodiment of the disclosed technology.

## DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

**[0019]** The disclosed technology generally discloses a method and a sensor that allows real-time *in-situ* monitoring of the aggregation state of asphaltenes in crude oils and multiphase streams. Asphaltenes are present as colloidal particles in crude oils and exhibit characteristic spectral signatures in the complex impedance spectra arising from their behavior as colloidal particles (interfacial polarization) and mobile charge carriers. The conductive nature of asphaltenes is used for assessing the asphaltene aggregation state. The present technology provides *in-situ* monitoring of the aggregation state of asphaltenes in crude oils and multiphase streams through the use of broad-spectral range dielectric spectroscopy (DS) and a specially designed robust electrode structure to be deployed both down-hole and in surface production facilities.

**[0020]** In an exemplary embodiment, the disclosed technology provides a method for *in-situ* detection of asphaltene aggregation. The method comprises providing a sensor, deploying the sensor within a multiphase stream comprising asphaltenes, and monitoring the asphaltene signal changes in order to detect the aggregation state of asphaltenes.

**[0021]** As shown in FIG. 1, a sensor 10 is provided. The sensor 10 allows for real-time *in-situ* monitoring of the asphaltene aggregation state of asphaltenes within a multiphase stream 11. For example, the sensor 10 is shown immersed within a multiphase

stream 11, as shown in FIG. 1. The robust sensing electrode structure of the sensor 10 is specifically designed for the use in harsh conditions, such as, but not limited to, high temperature and high pressure environments.

**[0022]** In some embodiments, the sensor 10 comprises an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers 12 provided on a ceramic substrate 14. In some embodiments, the oppositely charged electrode fingers 12 do not physically touch one another. For example, the positively charged electrode fingers do not physically touch the negatively charged electrode fingers, and visa versa.

**[0023]** FIG. 2 provides a general schematic depicting how each pair of oppositely charged electrode fingers 12 of the IDE produces a local electric field that probes the multiphase fluid in contact with the IDE. In dielectric spectroscopy (DS), (*i.e.* impedance spectroscopy), a sensing material is positioned between electrodes and is "probed" with an alternating electric field over a desired frequency range. DS is generally applied to characterize fundamental aspects of materials performance related to dispersion (dielectric constant) and dielectric losses (due to conductivity and other mechanisms).

**[0024]** In some embodiments, for example, when AC voltage is applied to the IDE, each pair of oppositely charged electrode fingers 12 creates a local electric field that probes the multiphase fluid in the electrode vicinity. It should be understood by a person of ordinary skill in the art that the term "probe" is a general term used to mean send out an electrical signal, read the reflected signal, and record the pertubation in that signal. Changes in the dielectric properties of the material affect the impedance of the sensing element and are measured as a function of frequency. As shown in FIG. 2, the fluid dielectric properties (Eps'($\omega$) and Eps"($\omega$)) can be deduced from the measured impedance values. $P_d$ is the depth of penetration of the electric field generated by the electrode perpendicular to the IDE.

**[0025]** The IDE and substrate materials of the present technology possess high thermal and chemical resistance, as well as high compressive strength for pressure resistance and hardness for wear resistance. In some embodiments, the IDE comprises tungsten, copper, gold, or other conductive metal that is suitable for the sensing environment. In some embodiments, the substrate comprises aluminum oxide, other

ceramics, teflon, or coated printed circuit boards (*e.g.* polyvynal acetate coated F4). In some embodiments, other ceramics may include any dielectric material that is suitable for the sensing environment. The conductive and dielectric materials that used for a specific sensor should be relatively easy to manufacture and have thermal expansion coefficents as close to one another as possible to decrease temperature dependance.

**[0026]** The IDE geometry of the present technology provides a high sensor sensitivity due to a large electrode area and a small interelectrode spacing, and at the same time, provides an overall compact size of the sensing structure, which is important in applications where the space is constrained (for example, inside a borehole). In some embodiments, the IDE has an electrode finger width (W) of at least 150μm, an interelectrode spacing (*G*) of at least 150μm, and a periodicity (λ) value of at least 63.5μm.

**[0027]** The method of the present technology further provides for deploying the sensor within a multiphase stream comprising asphaltenes. It should be understood by one skilled in the art that the step of deploying the sensor can be carried out by any means suitable or known for multiphase stream applications. In some embodiments, the multiphase stream is an oil, water, and/or gas stream. In other embodiments, the multiphase stream is a crude oil stream. In some embodiments, the sensor is deployed in either a down a bore hole or in surface production facility to determine if mitigation of asphaltene formation is required. In some embodiments, such mitigations include, but are not limited to, addition of solvent (such as xylene to coax precipitating asphaltenes back into solution), addition of stabilizing chemicals, or manipulations of environmental or physical aspects of the operation (such as changes in temperature, pressure, or flow). In some embodiments, mitigations can be applied manually or in a closed loop control scenario.

**[0028]** As previously discussed, asphaltenes are present as colloidal particles in multiphase streams, such as crude oils, and exhibit characteristic spectral signatures in the complex impedance spectra arising from their behavior as colloidal particles (interfacial polarization). In some embodiments, an asphaltene signal reveals itself at low frequencies in both real (dielectric constant) and imaginary (dielectric loss) parts of the

spectra, where the asphaltene signal undergoes considerable decline as the asphaltene colloids aggregate. This can be understood as a decrease in the charge density and mobility of growing asphaltene aggregates. As such, analysis of the spectra shows that the imaginary part (*i.e.* dielectric loss) is more suitable for monitoring of the aggregation state of asphaltene colloids. Therefore, in an exemplary embodiment, the asphaltene aggregation or aggregation state of asphaltenes can be deduced by monitoring the asphaltene signal changes at a single frequency, rather than examining an entire spectrum, and as such, the present technology allows for simplification of the signal acquisition and processing.

**[0029]** In some embodiments, the asphaltene aggregation is monitored using broad-range dielectric spectroscopy. In some embodiments, the asphaltene aggregation state is detectable in a multiphase stream with an asphaltene content of at least 0.1 wt.%, where wt. % is defined as the proportional weight of asphaltene content in the total solution of the multiphase fluid (*e.g.* raw crude oil).

**[0030]** In yet another exemplary embodiment, a sensor system for monitoring asphaltene stability is provided. The sensor system comprises a sensor, wherein the sensor provides an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate. In some embodiments, the interdigitated electrode comprises tungsten, copper, gold, or other conductive metal. In some embodiments, the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards (*e.g.* polyvynal acetate coated F4).

**[0031]** In some embodiments, the sensor is configured to detect an asphaltene aggregation state in the multiphase stream having an asphaltene content of at least 0.1 wt.%.

## EXAMPLES

**[0032]** The present technology will be further described in the following examples, which should be viewed as being illustrative and should not be construed to narrow the scope of the invention or limit the scope to any particular invention embodiments.

EXAMPLE 1. Performance of the disclosed sensor vs. the benchmark optical method.

**[0033]** The performance of the disclosed dielectric spectroscopy (DS) sensor was compared to the benchmark optical method (Turbiscan™) with respect its ability to detect asphaltene aggregation. A titration experiment was performed, in which the solubility of asphaltenes was gradually decreased by stepwise addition of flocculant (*e.g.* heptane) to oil to the point when asphaltenes became unstable and began to precipitate. The experimental results for both methods are presented in FIGS. 3A-3B. The optical method reveals the scattering plot with the typical 'hockey-stick' shape, or the point where the backscatter intensity begins to rise is typically regarded as the onset of precipitation (~50% heptane, as shown Fig. 3A). At this point, growing asphaltene aggregates reach the critical particle size, and the probing light begins to be effectively scattered by the aggregates. In contrast, the DS sensor system of the present technology starts detecting changes in the aggregation state of asphaltenes at ~20% heptane (Fig. 3B), *i.e.* well before the aggregates reach the critical size needed for detection with the optical method. In other words, the presently disclosed method allows for early detection of aggregation of the asphaltenes at the stage when they are still colloidally stable and show no precipitation from the medium. The rate of a sensor signal change (change in Eps" at 100 Hz was monitored) increases as the aggregation progresses according to a power law curve.

EXAMPLE 2. Monitoring of asphaltene precipitation caused by $CO_2$ injection into oil.

**[0034]** It is known that the $CO_2$ flooding (*i.e.* upstream technology aimed at enhanced oil recovery) may cause asphaltene precipitation in crude oils. This was simulated in process in a Parr reactor filled with oil that was pressurized by $CO_2$. The asphaltene state was monitored during pressure cycles with the sensor mounted inside the reactor. It was found that the crude oils tested showed different behavior in response to $CO_2$ injection. Some oils showed no asphaltene signal change up to a certain $CO_2$ pressure point, above which the signal rapidly declined with pressure, indicating progressive asphaltene aggregation. These oils demonstrated excellent stability (*i.e.* no precipitation) when stored. Other crudes demonstrated a gradual signal decline as the reactor was pressurized by $CO_2$. FIG. 4A shows the example of the latter behavior for three crudes

with different asphaltene content. The magnitude of the asphaltene signal correlated with the asphaltene concentration in the crudes and the aggregation state of asphaltenes. The signal change due to $CO_2$-induced asphaltene aggregation was the strongest for the heavy oil containing ~5 wt% asphaltenes (labeled as Oil #1 in FIG. 4A). The asphaltene aggregation was still detectable for the oil with the asphaltene content of ~0.1 wt% (labeled as Oil #2), and no asphaltene signal was detected for the extra-light oil containing a trace amount of asphaltenes (labeled as Oil #3). The asphaltenes in the Oils #1 and #2 were found to be unstable. The asphaltene signal for these oils declined upon long storage, indicating gradual asphaltene precipitation, which was confirmed by visual observation of the precipitate.

EXAMPLE 3. Monitoring of asphaltenes in oil treated with stabilizer chemistry.

**[0035]** Specially formulated chemistries, known as stabilizers, have been used to mitigate the asphaltene precipitation issues. The DS sensor was used for *in-situ* monitoring of the efficiency of a proprietary Suez stabilizer at controlling asphaltene aggregation in the Oil #1, (see Example 2 above). FIG. 4B illustrates the response of the oil containing different amounts of the stabilizer to $CO_2$ injection. The asphaltenes underwent rapid precipitation as the oil was pressurized when no stabilizer was present. In contrast, the oils with small amounts of the stabilizer showed drastically improved resistance to asphaltene precipitation. No asphaltene precipitation was observed when the stabilizer concentration reached 1000 ppm. The experiment shows that the sensor can be deployed in a closed-loop control system for monitoring of the asphaltene state and dispensing an appropriate dosage of stabilizer chemistry in real-time to prevent the asphaltene precipitation issues.

**[0036]** While embodiments of the disclosed technology have been described, it should be understood that the present disclosure is not so limited and modifications may be made without departing from the disclosed technology. The scope of the disclosed technology is defined by the appended claims, and all devices, processes, and methods that come within the meaning of the claims, either literally or by equivalence, are intended to be embraced therein.

# CLAIMS

1. A method for *in-situ* detection of asphaltene aggregation, the method comprising:

providing a sensor;

deploying the sensor within a multiphase stream comprising asphaltenes, wherein the sensor and the asphaltenes interact to generate an asphaltene signal; and

monitoring the asphaltene signal changes to detect asphaltene aggregation.

2. The method as recited in claim 1, wherein the sensor comprises an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate.

3. The method as recited in claim 2, wherein the interdigitated electrode comprises tungsten, copper, or gold.

4. The method as recited in claim 2, wherein the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards.

5. The method as recited in claim 1, wherein the sensor is deployed in either a down-hole or in surface production facility.

6. The method as recited in claim 1, wherein the multiphase stream is an oil, water, and/or gas stream.

7. The method as recited in claim 6, wherein the multiphase stream is a crude oil stream.

8. The sensor as recited in claim 1, wherein the asphaltene aggregation is monitored using broad-range dielectric spectroscopy.

9. The method as recited as in claim 1, wherein the asphaltene aggregation is determined by monitoring signal changes at a single frequency.

10. The method as recited in claim 1, wherein the asphaltene aggregation state is detectable in a multiphase stream with an asphaltene content of at least 0.1 wt.%.

11. A sensor, comprising:

an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate,

wherein the sensor is configured to detect an asphaltene aggregation state in a multiphase stream with an asphaltene content of at least 0.1 wt.%.

12. The sensor as recited in claim 11, wherein the interdigitated electrode comprises tungsten, copper, or gold.

13. The sensor as recited in claim 11, wherein the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards.

14. The sensor as recited in claim 11, wherein the interdigitated electrode has an electrode finger width ($W$) of at least 150μm.

15. The sensor as recited in claim 11, wherein the interdigitated electrode has an interelectrode spacing ($G$) of at least 150μm.

16. The sensor as recited in claim 11, wherein the interdigitated electrode has a periodicity ($\lambda$) value of at least 63.5μm.

17. The sensor as recited in claim 11, wherein the sensor allows for real-time *in-situ* monitoring of the asphaltene aggregation state.

18. A sensor system for monitoring asphaltene stability, the sensor system comprising:

a sensor maintained in fluid communication within a multiphase stream comprising asphaltenes, wherein the sensor is configured to determine dielectric signal changes at a single frequency; and

an impedance analyzer.

19. The system as recited in claim 18, wherein the sensor comprises an interdigitated electrode (IDE) having a pair of oppositely charged electrode fingers provided on a ceramic substrate.

20. The system as recited in claim 19, wherein the interdigitated electrode comprises tungsten, copper, or gold.

21. The sensor as recited in claim 19, wherein the substrate comprises aluminum oxide, other ceramics, teflon, or coated printed circuit boards.

22. The system as recited in claim 18, wherein the sensor is configured to detect an asphaltene aggregation state in the multiphase stream having an asphaltene content of at least 0.1 wt.%.

23. The system as recited in claim 18, wherein the sensor is deployed in either a down-hole or in surface production facility.

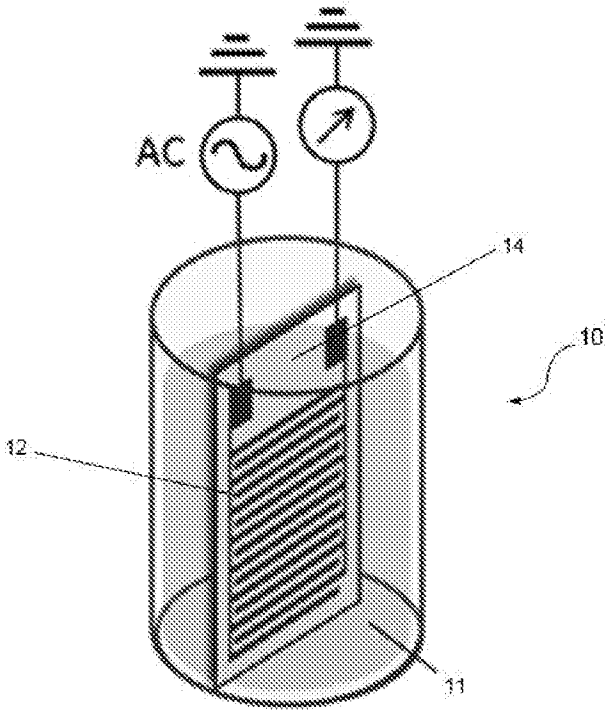


FIG. 1

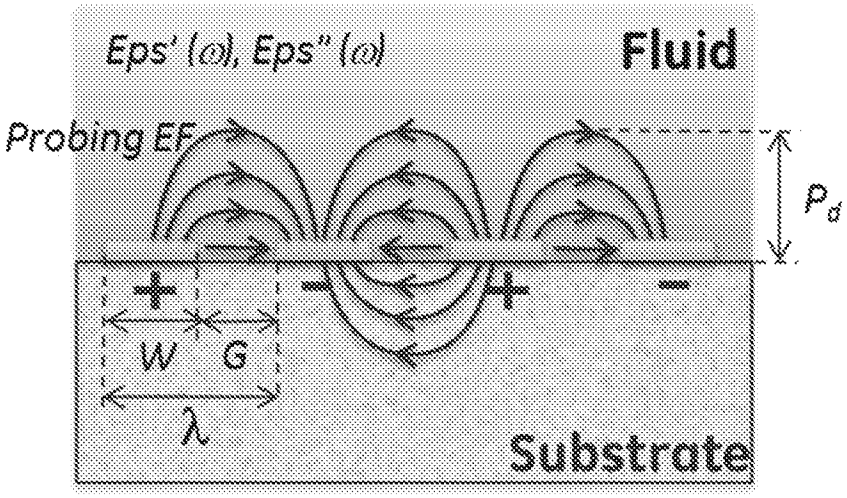


FIG. 2

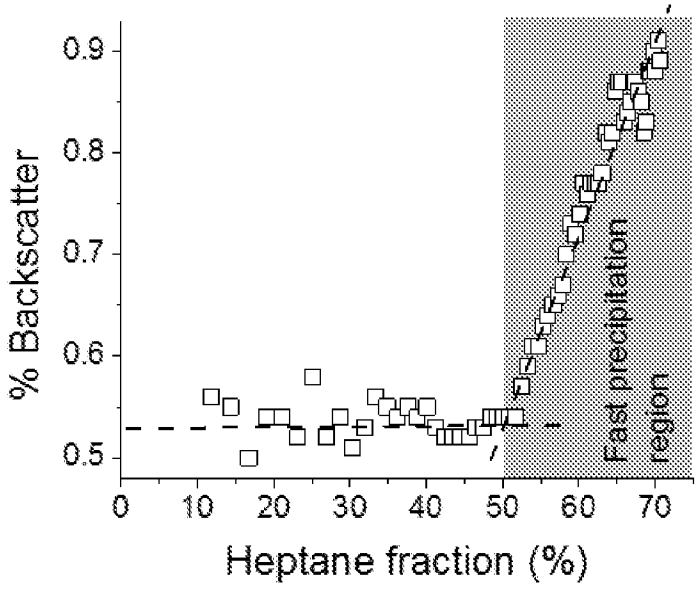
% Backscatter
0.9
0.8
0.7
0.6
0.5
0
10
20
30
40
50
60
70
Heptane fraction (%)
Fast precipitation region

FIG. 3A

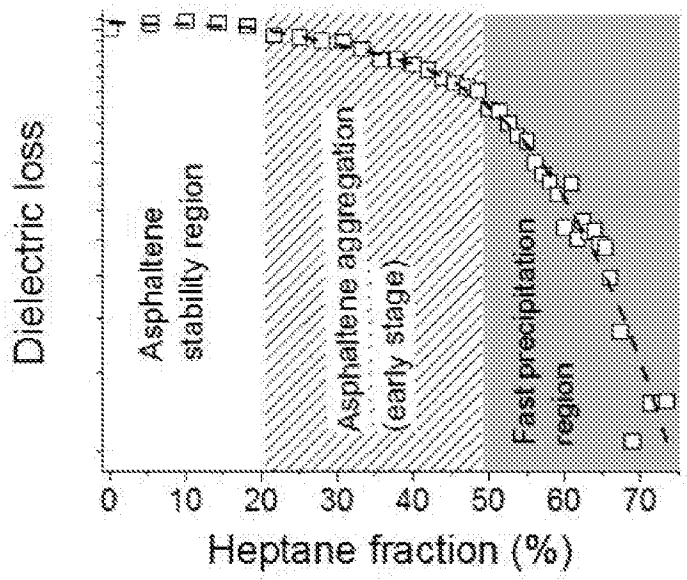
Dielectric loss
Asphaltene stability region
Asphaltene aggregation (early stage)
Fast precipitation region
0
10
20
30
40
50
60
70
Heptane fraction (%)

FIG. 3B

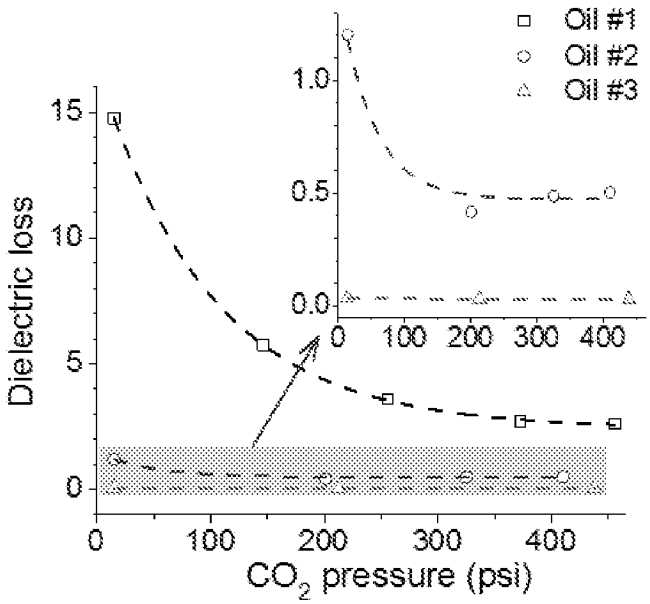
Oil #1
Oil #2
Oil #3
Dielectric loss
CO2 pressure (psi)

FIG. 4A

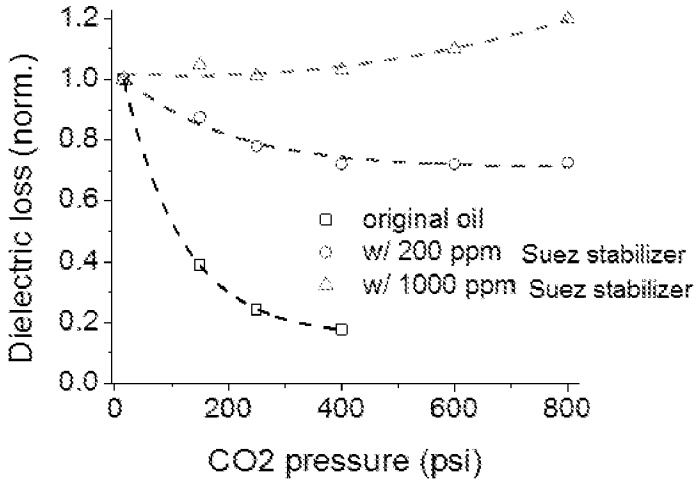
Dielectric loss (norm.)
original oil
w/ 200 ppm Suez stabilizer
w/ 1000 ppm Suez stabilizer
CO2 pressure (psi)

FIG. 4B

# INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/067000

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/02 E21B47/10 G01N15/02 G01N33/28
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)
G01N 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 practicable, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X<br><br>Y | EP 0 544 354 A1 (NORSK HYDRO TECHNOLOGY [NL]) 2 June 1993 (1993-06-02)<br>column 2, line 56 - column 3, line 5<br>column 3, line 38 - column 4, line 56<br>column 8, line 1 - line 30<br>figure 6<br>-----<br>-/-- | 1,5-10, 18,22,23<br>2-4, 11-17, 19-21 |

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

[X] See patent family annex.

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

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 16 September 2019 | 25/09/2019 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Joyce, David |

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