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(71) Applicant *(for US only)*: **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463 (US).

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, 2596 The Hague (NL).

(72) Inventors: **TATAVALLI-MITTADAR, Nirmal**; 20900 FM 1093 Rd Apt# 8208, Richmond, Texas 77407 (US). **ASHTEKAR, Sunil**; Shell Technology India Pvt Ltd, RMZ Centennial Campus, B # 8B, Kundanahalli Main Road, Bangalore 560048 (IN). **JAIN, Shekhar**; 2020 Eldridge Pkwy, Apt. # 706, Houston, Texas 77077 (US). **LU, Jian**; 4413 Vivian, Bellaire, Texas 77401 (US). **DE-GALEESAN, Sujatha**; 22419 David's Crest Court, Katy, Texas 77450 (US).

(74) Agent: **HITCHCOCK, Thomas, S.**; Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463 (US).

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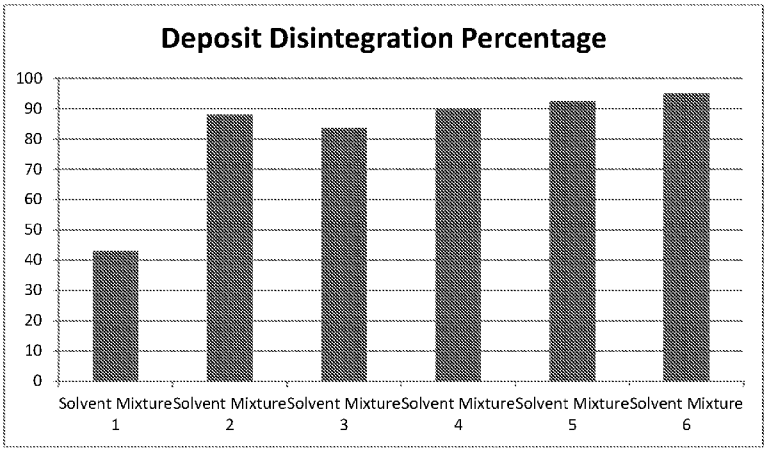
[Continued on next page]

(54) Title: DEPOSIT DISINTEGRATOR COMPOSITIONS

FIGURE 1



(57) Abstract: A solvent mixture comprising a solvent and a polar additive and associated methods.

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DEPOSIT DISINTEGRATOR COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/322,430, filed April 14, 2016, which is incorporated herein by reference.

BACKGROUND

[0002] The present disclosure relates generally to deposit disintegrator compositions. More specifically, in certain embodiments, the present disclosure relates to deposit disintegrator compositions useful in disintegrating deposits in subsea oil and gas pipelines and associated methods.

[0003] Oil and gas produced from wells frequently contain wax which may deposit in the wellbore and in equipment utilized for producing and transporting the oil and gas. The wax may also accumulate in pipelines, storage vessels, and other oil field equipment. The accumulation of wax and other deposits is a serious problem in that the deposits interfere with the production, transportation, storage, and processing of the oil and gas. In certain instances, the deposits may grow to a size where production is completely interrupted or flowline flow is stopped.

[0004] The problem of removing wax deposits from pumping wells and flowlines has been attacked in a number of ways. For example, flowlines may be cleaned mechanically, e.g. by scraping the flowlines with a pig. However, such methods may result in lost production time and high labor costs and may require special tools, the costs of which may be too expensive to be economically feasible methods to remove wax deposits.

[0005] Other common methods include cleaning flowlines with chemical solvents. Xylene is an example of a commonly used solvent used. While xylene may be effective in removing some deposits, xylene has a slow rate of deposit dissolution which reduces its effectiveness. In addition, xylene and other conventional solvent compositions may not be effective for use with all types of deposits.

[0006] It is desirable to develop a solvent composition that is more effective in disintegrating deposits than conventional solvents.

SUMMARY

[0007] The present disclosure relates generally to deposit disintegrator compositions. More specifically, in certain embodiments, the present disclosure relates to deposit disintegrator compositions useful in disintegrating deposits in subsea oil and gas pipelines and associated methods.

[0008] In one embodiment the present disclosure provides a solvent mixture comprising a solvent and a polar additive.

[0009] In another embodiment, the present disclosure provides a method comprising: providing a solvent mixture, wherein the solvent mixture comprises a solvent and a polar additive and injecting the solvent mixture into a subsea well or pipeline.

[0010] In another embodiment, the present disclosure provides a method comprising: providing a solvent mixture, wherein the solvent mixture comprises a solvent and a polar additive; contacting a deposit with the solvent mixture; and allowing the solvent mixture to disintegrate the deposit.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] A more complete and thorough understanding of the present embodiments and advantages thereof may be acquired by referring to the following description taken in conjunction with the accompanying drawings.

[0012] Figure 1 is a chart showing the effectiveness of different solvent mixtures in disintegrating a deposit.

[0013] Figure 2 is a chart showing the effectiveness of different solvent mixtures in disintegrating a deposit.

[0014] Figure 3 is a chart showing the effectiveness of different solvent mixtures in disintegrating a deposit.

[0015] Figure 4 is a chart showing the effectiveness of different solvent mixtures in disintegrating a deposit.

[0016] The features and advantages of the present disclosure will be readily apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the disclosure.

DETAILED DESCRIPTION

[0017] The description that follows includes exemplary apparatuses, methods, techniques, and/or instruction sequences that embody techniques of the inventive subject matter. However, it is understood that the described embodiments may be practiced without these specific details.

[0018] The present disclosure relates generally to deposit disintegrator compositions. More specifically, in certain embodiments, the present disclosure relates to deposit disintegrator compositions useful in disintegrating deposits in subsea oil and gas pipelines and associated methods.

[0019] Some desirable attributes of the compositions and methods discussed herein are that they may be more capable of disintegrating a deposit than conventional solvent compositions. In certain embodiments, the solvent mixtures described herein may be tailored to specific deposits by varying the concentration of the polar additives. In certain embodiments, the solvent mixtures described herein are capable of disintegrating deposits that comprise any combination of the following: wax, occluded crude oil, water, inorganics, and production chemicals.

[0020] In certain embodiments, the present disclosure provides a solvent mixture comprising a solvent and a polar additive.

[0021] In certain embodiments, the solvent may comprise any bulk solvent. In certain embodiments, the bulk solvent may comprise xylene, tetralin, decalin, toluene, terpene, naphtha, or diesel. In certain embodiments, the solvent may comprise a combination of bulk solvents.

[0022] In certain embodiments, amount of solvent present in the solvent mixture may be an amount in the range of from 30% to 98% by volume of the solvent mixture. In certain embodiments, amount of solvent present in the solvent mixture may be an amount in the range of from 75% to 95% by volume of the solvent mixture. In certain embodiments, amount of solvent present in the solvent mixture may be an amount in the range of from 80% to 90% by volume of the solvent mixture. In certain embodiments, amount of solvent present in the solvent mixture may be an amount in the range of from 85% to 90% by volume of the solvent mixture.

[0023] In certain embodiments, the polar additive may comprise any polar additive. In certain embodiments, the polar additive may comprise a protic polar additive or an aprotic polar additive. In certain embodiments, the polar additive may comprise di-methyl

sulfoxide, dimethyl carbonate, dimethyl formamide, or nitromethane. In certain embodiments, the polar additive may comprise a combination of polar additives.

[0024] In certain embodiments, the amount of polar additive in the solvent mixture may be an amount in the range of from 2% to 60% by volume of the solvent mixture. In certain embodiments, the amount of polar additive in the solvent mixture may be an amount in the range of from 5% to 20% by volume of the solvent mixture. In certain embodiments, the amount of polar additive in the solvent mixture may be an amount in the range of from 10% to 20% by volume of the solvent mixture. In certain embodiments, the amount of polar additive in the solvent mixture may be an amount in the range of from 10% to 15% by volume of the solvent mixture.

[0025] In certain embodiments, the volume ratio of polar additive to solvent in the solvent mixture may be a ratio in the range of from 0.01 to 0.6. In certain embodiments, the volume ratio of polar additive to solvent in the solvent mixture may be a ratio in the range of from 0.05 to 0.2. In certain embodiments, the volume ratio of polar additive to solvent in the solvent mixture may be a ratio in the range of from 0.05 to 0.15. In certain embodiments, the volume ratio of polar additive to solvent in the solvent mixture may be a ratio in the range of from 0.1 to 0.15.

[0026] In certain embodiments, the solvent mixture may further comprise a second polar additive. In certain embodiments, the second polar additive may comprise a protic polar additive or an aprotic polar additive. In certain embodiments, the second polar additive may be strongly polar or a moderately polar. In certain embodiments, the second polar additive may comprise di-methyl sulfoxide, methanol, acetone, iso-butanal, or teatrahydrofuran. In certain embodiments, the polar second additive may comprise a combination of second polar additives.

[0027] In certain embodiments, the concentration of second polar additive in the solvent mixture may be a concentration in the range of from 2% to 40% by volume of the solvent mixture. In certain embodiments, the concentration of second polar additive in the solvent mixture may be a concentration in the range of from 5% to 15% by volume of the solvent mixture.

[0028] In certain embodiments, the solvent mixture may further comprise a second bulk solvent. In certain embodiments, the second bulk solvent may comprise a non-polar solvent. In certain embodiments, the second bulk solvent may comprise naphtha, terpene, decalin, a C5-C11 alkane, diesel, a cyclic aromatic compound, or a bicyclic aromatic

compound. In certain embodiments the second bulk solvent may comprise a combination of second bulk solvents.

[0029] In certain embodiments, the concentration of second bulk solvent in in the solvent mixture may be a concentration in the range of 2% to 40% by volume of the solvent mixture. In certain embodiments, the concentration of second bulk solvent in in the solvent mixture may be a concentration in the range of 5% to 15% by volume of the solvent mixture.

[0030] In certain embodiments, the particular combination of bulk solvent and polar additive (and optionally second bulk solvent and/or second polar additive) present in the solvent mixture may be selected based on the type of deposit to be disintegrated by the solvent mixture. The types of deposits to be disintegrated by the solvent mixture may vary in their relative compositions of wax, entrapped oil, water, asphaltenes, and other inorganics.

[0031] In certain embodiments, the solvent mixture may have a density in the range of 0.75 g/cc to 1.1 g/cc. In certain embodiments, the solvent mixture may have a density in the range of from 0.8 g/cc to 1.0 g/cc. In certain embodiments, the solvent mixture may have a density in the range of from 0.85 g/cc to 0.95 g/cc.

[0032] In certain embodiments, the present invention provides a method comprising: providing a solvent mixture, wherein the solvent mixture comprises a solvent and a polar additive and injecting the solvent mixture into a subsea well or pipeline.

[0033] In certain embodiments, the solvent mixture may comprise any solvent mixture discussed above. In certain embodiments, the solvent mixture may be a specifically tailored solvent mixture. For example, in certain embodiments, the solvent mixture may be tailored based upon the type of deposit to be disintegrated.

[0034] In certain embodiments, the solvent mixture may further comprise a dispersing agent and/or a wetting agent. In certain embodiments, the solvent mixture may further comprise a rheology modifier.

[0035] In certain embodiments, injecting the solvent mixture into the subsea well or pipeline may comprise injecting the solvent mixture into the subsea well or pipeline by any conventional means. In certain embodiments, the solvent mixture may be injected into the subsea well or pipeline when the subsea well or pipeline is in a shut-in condition. In other embodiments, the solvent mixture may be injected into the subsea well or pipeline while the subsea well or pipeline is in a flowing condition.

[0036] In certain embodiments, a deposit site may be identified before the solvent mixture is injected into the subsea well or pipeline. In certain embodiments, the deposit site may be identified by any conventional surveillance method.

[0037] In certain embodiments, a spacer fluid may be injected into the subsea well or pipeline before and/or after the solvent mixture is injected into the subsea well or pipeline.

[0038] In certain embodiments, the solvent mixture may be injected sequentially with pre-flush and separator blocks. In certain embodiments, different and/or separate solvent mixtures may be injected into the subsea well or pipeline sequentially.

[0039] In certain embodiments, the method may further comprise allowing the solvent mixture to contact a deposit. In certain embodiments, the deposit may comprise any combination of the following: wax, occluded crude oil, water, inorganics, and production chemicals. In certain embodiments, the deposit may be located along a sidewall of a pipeline or may be blocking the pipeline. In certain embodiments, the deposit may be located in a valve, a tank, or any other piece of oilfield equipment. In certain embodiments, the method may further comprise allowing the solvent mixture to disintegrate the deposit.

[0040] In certain embodiments, the method may further comprise using wire-lining technology and/or pressure pulsing technologies while the solvent mixture disintegrates the deposit.

[0041] In certain embodiments, the solvent mixture may be heated to a temperature in the range of from 100°F to 200°F before it is injected into the subsea well or pipeline. In certain embodiments, the solvent mixture may be heated to a temperature in the range of from 150°F to 200°F before it is injected into the subsea well or pipeline. In certain embodiments, the solvent mixture may be heated to a temperature in the range of from 175°F to 200°F before it is injected into the subsea well or pipeline.

[0042] In certain embodiments the solvent mixture can be couple with additional methods that help in efficient suspension and flow of the dispersed deposit.

[0043] In certain embodiments, the solvent mixture may be recovered after the deposit is disintegrated. In certain embodiments, the solvent mixture may be re-injected into the subsea well or pipeline. In certain embodiments, effluents formed from the disintegration of the deposit may be discarded after the solvent mixture is recovered. In other embodiments, the solvent mixture and effluents may be flown along with the

produced fluids without recovery.

[0044] In certain embodiments, the present disclosure provides a method comprising: providing a solvent mixture, wherein the solvent mixture comprises a solvent and a polar additive; contacting a deposit with the solvent mixture; and allowing the solvent mixture to disintegrate the deposit.

[0045] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

Examples

[0046] Example 1

[0047] Six 50 mL solvent mixtures with varying ratios of solvent and polar additives were prepared. Solvent mixture 1 comprised 100% xylene. Solvent mixture 2 comprised 90% xylene and 10 % methanol. Solvent mixture 3 comprised 95% xylene and 5% di-methyl sulfoxide. Solvent mixture 4 comprised 90% xylene and 10% di-methyl sulfoxide. Solvent mixture 5 comprised 85% xylene and 15% di-methyl sulfoxide. Solvent mixture 6 comprised 80% xylene and 20% di-methyl sulfoxide.

[0048] A 1 cm diameter disk comprising 0.2 grams of a gannet deposit was placed into each of the solvent mixtures. The gannet deposits comprised 46% occluded oil, 45% wax, 1% asphaltene, 5% water, and 3% inorganic matter.

[0049] The deposits were kept in the solutions for four hours. The deposits were then removed from the solvent mixtures, and the percentage of deposit disintegration was measured and plotted in Figure 1.

[0050] As can be seen by Figure 1, the solvent mixture comprising 80% xylene and 20% di-methyl sulfoxide outperformed the other solvent mixtures.

[0051] Example 2

[0052] Six 50 mL solvent mixtures with varying ratios of solvent and polar additives were prepared. Solvent mixture 1 comprised 100% xylene. Solvent mixture 2 comprised 90% xylene and 10 % methanol. Solvent mixture 3 comprised 95% xylene and 5% di-methyl sulfoxide. Solvent mixture 4 comprised 90% xylene and 10% di-methyl sulfoxide. Solvent mixture 5 comprised 85% xylene and 15% di-methyl sulfoxide. Solvent mixture 6 comprised 80% xylene and 20% di-methyl sulfoxide.

[0053] A 1 cm diameter disk comprising 0.2 grams of Sierra Blanca deposit was placed into each of these solutions. The Sierra Blanca deposits comprised 38% occluded

oil, 55% wax, 3% asphaltene, 2% water, and 2% inorganic matter.

[0054] The deposits were kept in the solutions for four hours. The deposits were then removed from the solvent mixtures, and the percentage of deposit disintegration was measured and plotted in Figure 2.

[0055] As can be seen by Figure 2, the solvent mixture comprising 80% xylene and 20% di-methyl sulfoxide outperformed the other solvent mixtures.

[0056] Example 3

[0057] Five 50 mL solvent mixtures with varying ratios of solvent and polar additives were prepared. Solvent mixture 1 comprised 100% xylene. Solvent mixture 2 comprised 85% xylene, 10% di-methyl sulfoxide, and 5% methanol. Solvent mixture 3 comprised 80% xylene, 15% di-methyl sulfoxide, and 5% methanol. Solvent mixture 4 comprised 90% terpene, 5% di-methyl sulfoxide, and 5% isobutanol. Solvent mixture 5 comprised 85% tetralin, 10% di-methyl sulfoxide, and 5% methanol.

[0058] A 1 cm diameter disk comprising 0.2 grams of a gannet deposit was placed into each of the solvent mixtures. The gannet deposits comprised 46% occluded oil, 45% wax, 1% asphaltene, 5% water, and 3% inorganic matter.

[0059] The deposits were kept in the solutions for four hours. The deposits were then removed from the solvent mixtures, and the percentage of deposit disintegration was measured and plotted in Figure 3.

[0060] As can be seen by Figure 3, the solvent mixture comprising 85% xylene, 10% di-methyl sulfoxide, and 5% methanol outperformed the other solvent mixtures.

[0061] Example 4

[0062] Five 50 mL solvent mixtures with varying ratios of solvent and polar additives were prepared. Solvent mixture 1 comprised 100% xylene. Solvent mixture 2 comprised 85% xylene, 10% dimethyl sulfoxide, and 5% methanol. Solvent mixture 3 comprised 80% xylene, 15% dimethyl sulfoxide, and 5% methanol. Solvent mixture 4 comprised 90% terpene, 5% dimethyl sulfoxide, and 5% isobutanol. Solvent mixture 5 comprised 85% tetralin, 10% dimethyl sulfoxide, and 5% methanol.

[0063] A 1 cm diameter disk comprising 0.2 grams of Sierra Blanca deposit was placed into each of these solutions. The Sierra Blanca deposits comprised 38% occluded oil, 55% wax, 3% asphaltene, 2% water, and 2% inorganic matter.

[0064] The deposits were kept in the solutions for four hours. The deposits were then removed from the solvent mixtures, and the percentage of deposit disintegration was

measured and plotted in Figure 4.

[0065] As can be seen by Figure 4, the solvent mixture comprising 90% terpene, 5% dimethyl sulfoxide, and 5% isobutanol outperformed the other solvent mixture.

[0066] While the embodiments are described with reference to various implementations and exploitations, it will be understood that these embodiments are illustrative and that the scope of the inventive subject matter is not limited to them. Many variations, modifications, additions and improvements are possible.

[0067] Plural instances may be provided for components, operations or structures described herein as a single instance. In general, structures and functionality presented as separate components in the exemplary configurations may be implemented as a combined structure or component. Similarly, structures and functionality presented as a single component may be implemented as separate components. These and other variations, modifications, additions, and improvements may fall within the scope of the inventive subject matter.

What is claimed is:

1. A method comprising: providing a solvent mixture, wherein the solvent mixture comprises a solvent and a polar additive and injecting the solvent mixture into a subsea pipeline or well.

2. The method of claim 1, wherein the solvent comprises xylene, tetralin, decalin, toluene, terpene, naphtha, or diesel.

3. The method of claim 1, wherein the solvent is present in the solvent mixture in an amount in the range of from 30% to 98% by volume of the solvent mixture.

4. The method of claim 1, wherein the polar additive is di-methyl sulfoxide, dimethyl carbonate, dimethyl formamide, or nitromethane.

5. The method of claim 1, wherein the polar additive is present in the solvent mixture in an amount in the range of from 2% to 60% by volume of the solvent mixture.

6. The method of claim 1, wherein the volume ratio of polar additive to solvent in the solvent mixture is in the range of from 0.01 to 0.6.

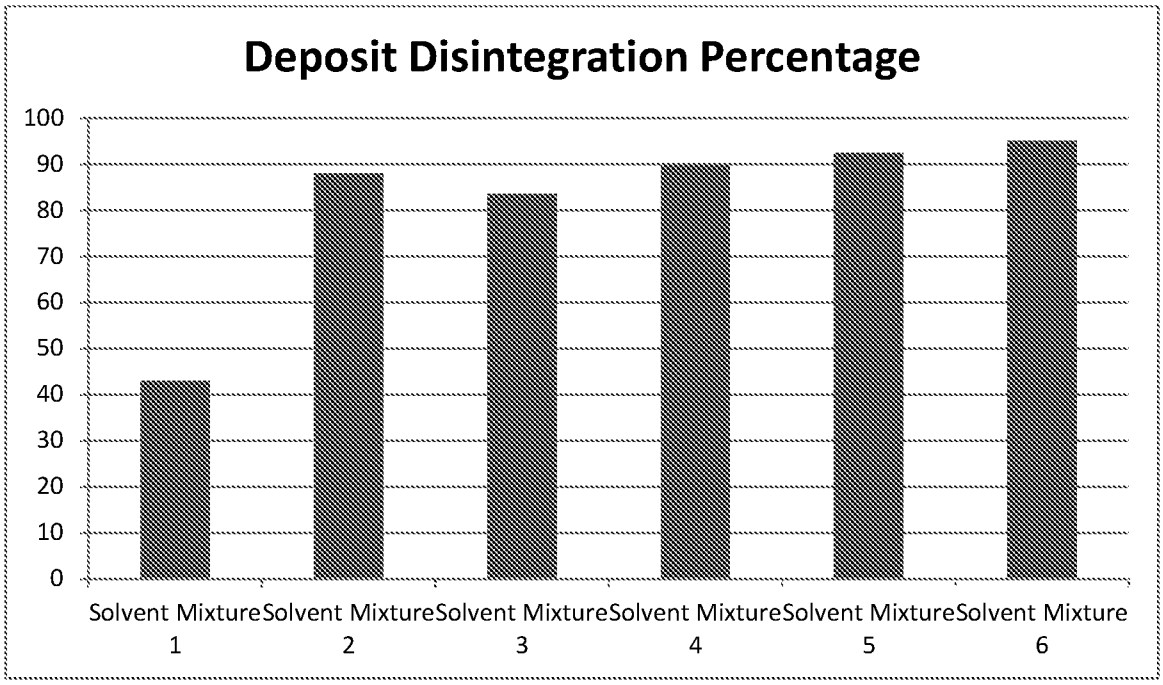
7. The method of claim 1, wherein the solvent mixture further comprises a second bulk solvent.

8. The method of claim 7, wherein the second bulk solvent is naphtha, terpene, decalin, a C5-C11 alkane, diesel, a cyclic aromatic compound, or a bicyclic aromatic compound.

9. The method of claim 8, wherein the second bulk solvent is present in the solvent mixture in an amount in the range of from 2% to 40% by volume of the solvent mixture.

10. The method of claim 1, further comprising allowing the solvent mixture to contact a deposit.

FIGURE 1


Deposit Disintegration Percentage
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80
70
60
50
40
30
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10
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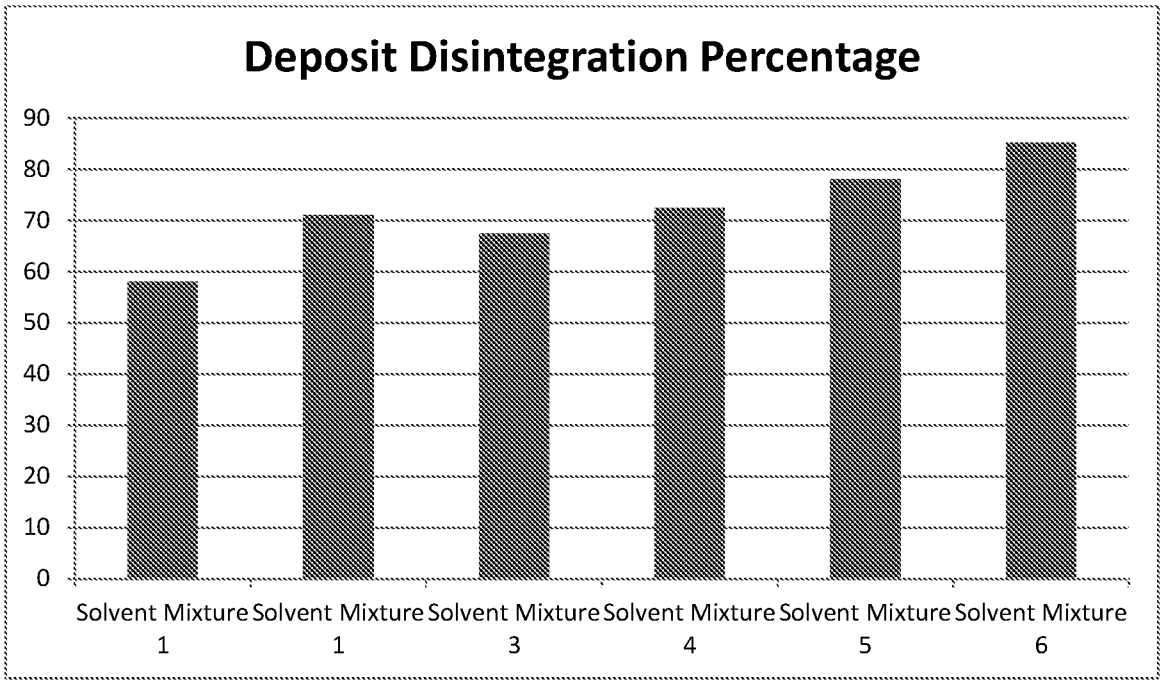
Solvent Mixture 1
Solvent Mixture 2
Solvent Mixture 3
Solvent Mixture 4
Solvent Mixture 5
Solvent Mixture 6

FIGURE 2


Deposit Disintegration Percentage
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60
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40
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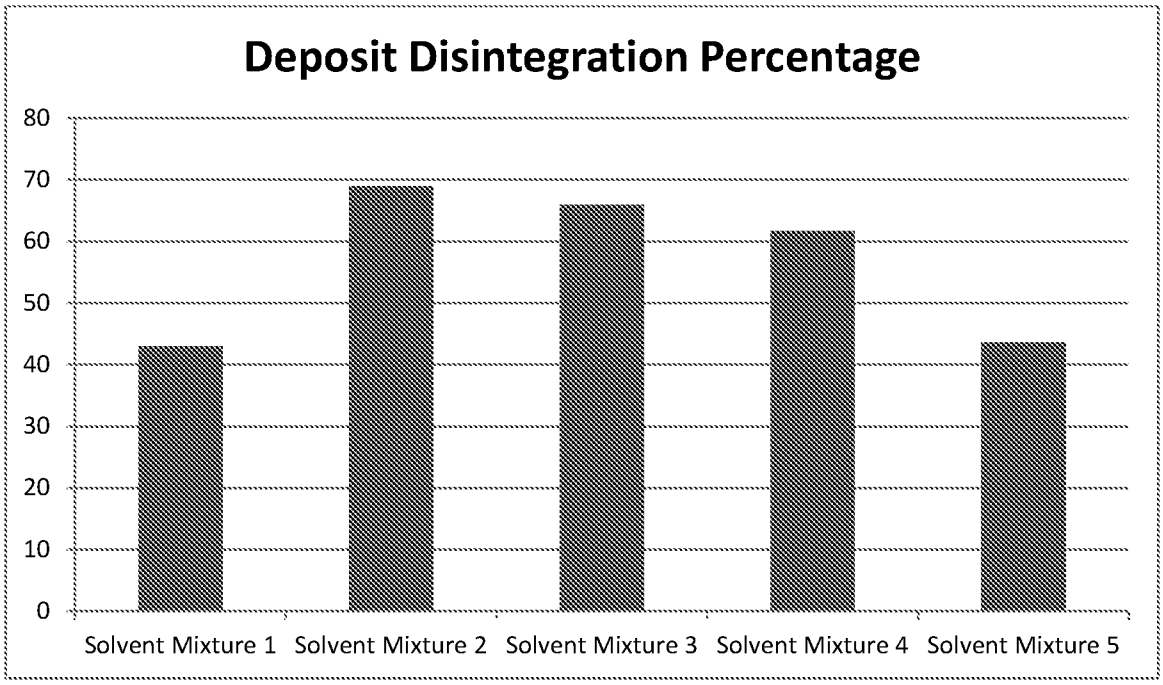
Solvent Mixture 1
Solvent Mixture 1
Solvent Mixture 3
Solvent Mixture 4
Solvent Mixture 5
Solvent Mixture 6

FIGURE 3


Deposit Disintegration Percentage
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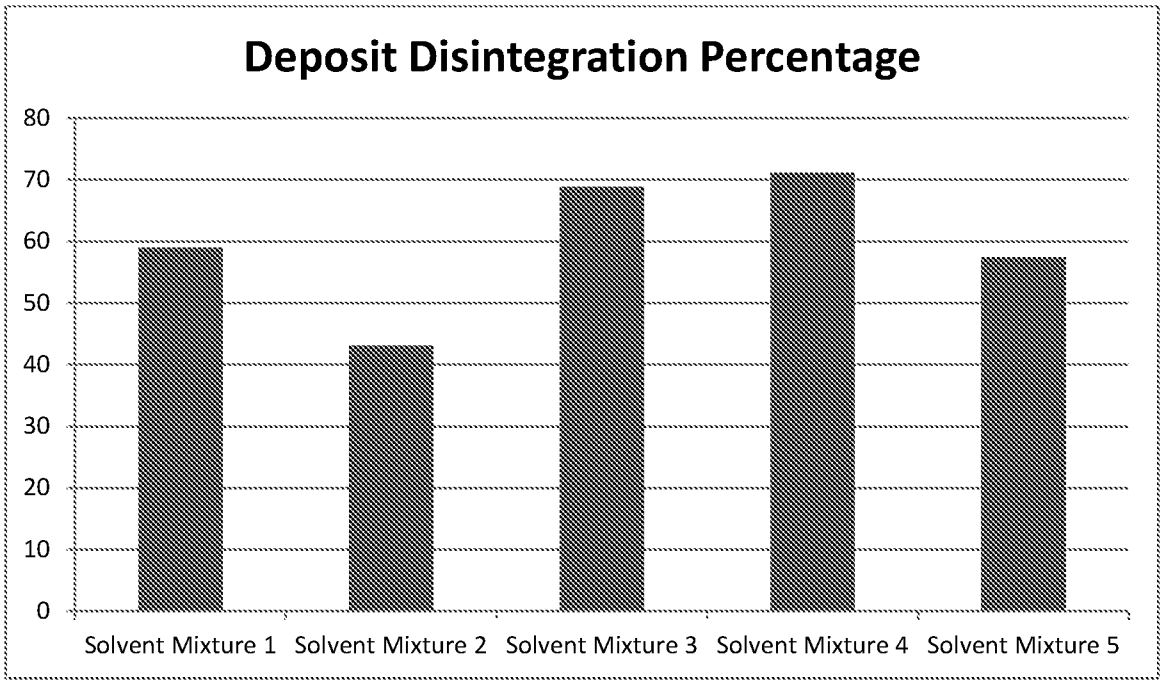
Solvent Mixture 1
Solvent Mixture 2
Solvent Mixture 3
Solvent Mixture 4
Solvent Mixture 5

FIGURE 4


Deposit Disintegration Percentage
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Solvent Mixture 1
Solvent Mixture 2
Solvent Mixture 3
Solvent Mixture 4
Solvent Mixture 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/027203

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/52
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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 504 063 A (BECKER HAROLD L [US] ET AL) 2 April 1996 (1996-04-02) claim 1; example V; table IIIB	1-7,9,10
X	US 3 830 737 A (FRIEDMAN R ET AL) 20 August 1974 (1974-08-20) column 1, lines 25-56; claims 1,2; example 2	1-10
X	US 2010/314117 A1 (LI JACK [US] ET AL) 16 December 2010 (2010-12-16) claims 1,5; table 1	1-3,5-10
X	US 2010/130389 A1 (LIGHTFORD STEPHEN CHARLES [GB] ET AL) 27 May 2010 (2010-05-27) claims 1,7; table 1; compound D	1-3,5,6, 8-10

☐ 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

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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 June 2017	21/06/2017

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

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/027203

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