



(51) International Patent Classification:

C10G 9/16 (2006.01) C10G 75/04 (2006.01)

(21) International Application Number:

PCT/US2024/032476

(22) International Filing Date:

05 June 2024 (05.06.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/507,635 12 June 2023 (12.06.2023) US

(71) Applicant: **BL TECHNOLOGIES, INC.** [US/US]; 5951
Clearwater Drive, Minnetonka, Minnesota 55343 (US).(72) Inventors: **CROM, Bryan**; 5951 Clearwater Drive, Min-
netonka, Minnesota 55343 (US). **LE, Eric**; 5951 Clearwa-
ter Drive, Minnetonka, Minnesota 55343 (US). **PATEL,**
Nimeshkumar; 5951 Clearwater Drive, Minnetonka, Min-
nesota 55343 (US). **DEES, Joop**; Interleuvenlaan 25, 3001
Leuven (BE).(74) Agent: **KING, Hui-Shan Sandra et al.**; Armstrong Teas-
dale LLP, 7700 Forsyth Blvd., Suite 1800, St. Louis, Mis-
souri 63105-1847 (US).

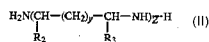
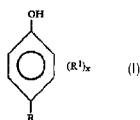
(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IQ, 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, MU, 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, CV,
GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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).

Declarations under Rule 4.17:

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

(54) Title: ETHYLENE TAR DISPERSANTS AND CHARGE GAS COMPRESSOR SURFACE MODIFIERS



(57) Abstract: A method of preventing fouling in a quench system or charge gas compressor of an ethylene plant comprising adding to the system and/or compressor a dispersant chemistry comprising an effective amount of a reaction product formed by reaction of reactants (A), (B), and (C), wherein (A) comprises an alkyl substituted phenol of the structure Formula (I), (B) comprises a polyamine of the structure, Formula (II), and (C) comprising an aldehyde of the structure, Formula (III).

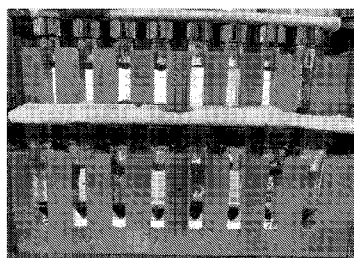


FIG. 1A

Published:

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

ETHYLENE TAR DISPERSANTS AND CHARGE GAS COMPRESSOR SURFACE MODIFIERS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States Provisional Patent Application No. 63/507,635, filed on June 12, 2023, which is incorporated by reference herein in its entirety.

10

FIELD

[0002] The disclosed technology relates generally to compositions and methods for preventing fouling, deposition, and/or emulsification in ethylene plant quench systems and charge gas compressors. More specifically, the disclosed technology relates to compositions and methods for preventing fouling, deposition, and/or emulsification in ethylene plant quench systems and charge gas compressors by adding a dispersant chemistry.

15

BACKGROUND

[0003] During the thermal cracking of feedstock (naphtha, LPG, ethane, shale gas, etc.) to produce ethylene, several secondary substances are also generated, including a relatively heavy condensable material, referred to by varied names such as tar, pyrolysis tar, ethylene tar, py-tar, cracker tar, residue, ethylene cracker residue, etc., and can manifest itself as solids or viscous liquids. This heavy material/tar is condensable in the quench section of the ethylene production plant, and can lead to considerable fouling throughout the quench system and dilution steam system. This heavy material/tar may also migrate to the hydrocarbon-water interface in the quench water separator and cause emulsification issues. When the cracking feedstock is light, such as shale gas, ethane, or LPG, less of this heavy material/tar is generated in the cracker, but somewhat counterintuitively, the problems caused by this heavy material/tar can be worse when cracking light feedstock because there is also a reduction in other condensable hydrocarbons that can help solubilize and naturally disperse the heavy material/tar. Fouled quench system components and emulsification issues in the quench water separator can

20

25

30

lead to reduced production throughput, operational challenges, reduced run lengths, and expensive cleaning operations.

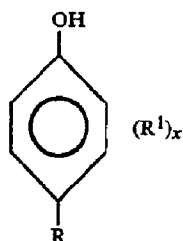
[0004] Additionally, Charge Gas Compressors (CGCs) of ethylene production plants can experience fouling with a similar type material that will lead to throughput
5 reductions and plant shutdowns for cleaning.

[0005] Improved chemistries to prevent fouling of these systems are needed.

SUMMARY

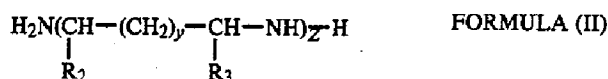
[0006] The disclosed technology provides for compositions and methods for
10 preventing fouling, deposition, and/or emulsification in ethylene plant quench systems and charge gas compressors.

[0007] Various aspects of the disclosure relate to a method of preventing fouling, deposition, plugging and/or emulsification in a quench system of an ethylene plant comprising adding to the system a dispersant chemistry comprising an effective amount of
15 a reaction product formed by reaction of reactants (A), (B), and (C), wherein (A) comprises an alkyl substituted phenol of the structure



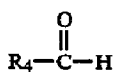
FORMULA I

[0008] wherein R and R¹ are the same or different and are independently selected from alkyl, aryl, alkaryl, or arylalkyl of from about 1 to 20 carbon atoms and x is 0 or 1;
20 (B) comprises a polyamine of the structure



FORMULA (II)

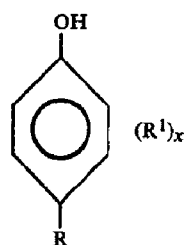
[0009] wherein Z is a positive integer, R₂ and R₃ are the same or different and are independently selected from H, alkyl, aryl, aralkyl, or alkaryl having from 1 to 20 carbon atoms, y being 0 or 1; and (C) comprising an aldehyde of the structure



FORMULA (III)

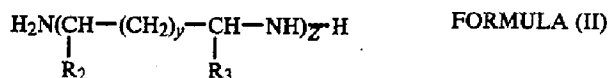
[0010] wherein R_4 comprises H or C_1 - C_6 alkyl.

[0011] Various aspects of the disclosure relate to a method of preventing fouling in a charge gas compressor (CGC) of an ethylene plant comprising adding to the compressor a dispersant chemistry comprising an effective amount of a reaction product formed by reaction of reactants (A), (B), and (C), wherein (A) comprises an alkyl substituted phenol of the structure



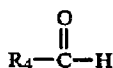
FORMULA I

[0012] wherein R and R^1 are the same or different and are independently selected from alkyl, aryl, alkaryl, or arylalkyl of from about 1 to 20 carbon atoms and x is 0 or 1;
 (B) comprises a polyamine of the structure



FORMULA (II)

[0013] wherein Z is a positive integer, R_2 and R_3 are the same or different and are independently selected from H, alkyl, aryl, aralkyl, or alkaryl having from 1 to 20 carbon atoms, y being 0 or 1; and (C) comprising an aldehyde of the structure



FORMULA (III)

[0014] wherein R_4 comprises H or C_1 - C_6 alkyl.

[0015] In various aspects, the fouling may be caused by solid or viscous liquids comprising ethylene tar or polymers formed through radical-induced polymerization reactions.

BRIEF DESCRIPTION OF THE FIGURES

[0016] Those of skill in the art will understand that the figures, described below, are for illustrative purposes only. The figures are not intended to limit the scope of the present teachings in any way.

[0017] FIGS. 1A-1H illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in caustic water as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIGS. 1A and 1B), t=4 minutes after shaking (FIGS. 1C and 1D), t=120 minutes after shaking (FIGS. 1E and 1F), and t=24 hours after shaking (FIGS. 1G and 1H).

[0018] FIGS. 2A-2G illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in A-150 as compared to untreated and comparative chemistries before shaking (FIG. 2A), at t=0 minutes after shaking (FIGS. 2B and 2C), at t=15 minutes after shaking (FIGS. 2D and 2E), and at t=60 minutes after shaking (FIGS. 2F and 2G).

[0019] FIGS. 3A-3D illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in caustic water as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIGS. 3A and 3B) and t=30 minutes after shaking (FIGS. 3C and 3D).

[0020] FIGS. 4A-4E illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in A-150 as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIG. 4A), at t=10 minutes after shaking (FIG. 4B), at t=45 minutes after shaking (FIG. 4C and 4D), and at t=65 minutes after shaking (FIG. 4E).

[0021] FIGS. 5A-5C illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in caustic water as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIG. 5A), and at t=120 minutes after shaking (FIG. 5B and 5C).

[0022] FIGS. 6A and 6B illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in A-150 as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIG. 6A), and at t=35 minutes after shaking (FIG. 6B).

[0023] FIGS. 7A and 7B illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in A-150 as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIG. 7A), and at t=35 minutes after shaking (FIG. 7B).

[0024] FIGS. 8A and 8B illustrate the treatment effectiveness of an embodiment of the dispersant chemistry of the disclosure on a tar sample in caustic water as compared to untreated and comparative chemistries at t=0 minutes after shaking (FIG. 8A), and at t=3 minutes after shaking (FIG. 8B).

5

DETAILED DESCRIPTION

[0025] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as “about”, is not limited to the precise value specified. In at least some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Range limitations may be combined and/or interchanged, and such ranges are identified and include all the sub-ranges stated herein unless context or language indicates otherwise. Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions and the like, used in the specification and the claims, are to be understood as modified in all instances by the term “about”.

[0026] “Optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, or that the subsequently identified material may or may not be present, and that the description includes instances where the event or circumstance occurs or where the material is present, and instances where the event or circumstance does not occur or the material is not present.

[0027] As used herein, the terms “comprises”, “comprising”, “includes”, “including”, “has”, “having”, or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article or apparatus that comprises a list of elements is not necessarily limited to only those elements, but may include other elements not expressly listed or inherent to such process, method, article, or apparatus.

[0028] The singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise.

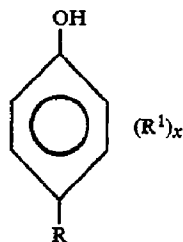
[0029] The disclosed technology provides for compositions and methods for preventing fouling, deposition, and/or emulsification in ethylene plant quench systems and charge gas compressors.

[0030] The compositions and methods disclosed herein provide a solution for ethylene plant quench systems that experience fouling, deposition, plugging, or emulsification issues caused by solids or viscous liquids (often referred to by terms such as tar, ethylene tar, pyrolysis tar, py-tar, residue, cracker residue, and other terms) by providing a dispersant chemistry that dissolves or disperses the solids and/or viscous liquids into an aqueous or hydrocarbon continuous phase, preventing the deposition of the solids and/or viscous liquids within the quench system and/or preventing the migration of the solids and/or viscous liquids to the hydrocarbon-water interface of a quench water separator. Without being bound by theory, by dispersing the heavy material/tar into either the bulk hydrocarbon phase or the bulk caustic phase, the heavy material/tar is not allowed to deposit/foul the quench system or the charge gas compressor. By also keeping the material in the bulk phase, it cannot migrate to the oil-hydrocarbon interface of the quench water separator, and thus cannot contribute to emulsion issues.

[0031] As used herein, the term “an effective amount” refers to any amount of the disclosed dispersant chemistry that is effective in preventing fouling, deposition, and/or emulsification in ethylene plant quench systems and charge gas compressors caused by fouling substances such as ethylene tar and/or polymers formed through radical-induced polymerization reactions.

[0032] As used herein, the term “tar” or “ethylene tar” refers to the by-product of thermal cracking feedstock (ethane, natural gas, naphtha, heavy gas oil, etc.) to produce ethylene. It may be in the form of a heavy solid or viscous liquid that often has a high carbon content and is often highly aromatic. In some cases, tar may also include inorganic components that are entrained in the feedstock or are byproducts of corrosion within the feedstock processing equipment.

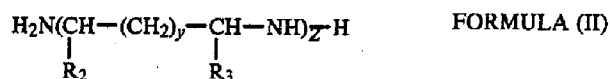
[0033] In various aspects of the disclosed technology, a method of preventing fouling, deposition, and/or emulsification in ethylene plant quench systems or charge gas compressors is disclosed. In various aspects, the method comprises adding to the system or compressor a dispersant chemistry comprising an effective amount of a reaction product formed by reaction of reactants (A), (B), and (C), wherein (A) comprises an alkyl substituted phenol of the structure



FORMULA I

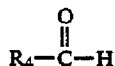
[0034] wherein R and R¹ are the same or different and are independently selected from alkyl, aryl, alkaryl, or arylalkyl of from about 1 to 20 carbon atoms, and x is 0 or 1;

[0035] wherein (B) comprises a polyamine of the structure



FORMULA (II)

[0036] wherein Z is a positive integer, R₂ and R₃ may be the same or different and are independently selected from H, alkyl, aryl, aralkyl, or alkaryl having from 1 to 20 carbon atoms, y may be 0 or 1; and wherein (C) comprises an aldehyde of the structure



FORMULA (III)

[0037] wherein R₄ may be selected from hydrogen and alkyl having 1 to 6 carbon atoms.

[0038] In various aspects, exemplary compounds that may fall within the scope of Formula I include p-cresol, 4-ethylphenol, 4-t-butylphenol, 4-t-amylphenol, 4-t-octylphenol, 4-dodecylphenol, 2,4-di-t-butylphenol, 2,4-di-t-amylphenol, and 4-nonylphenol.

[0039] In various aspects, exemplary polyamines which may be used in accordance with Formula II include ethylenediamine, propylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentaamine and the like.

[0040] In various aspects, the aldehyde component may comprise formaldehyde, acetaldehyde, propanaldehyde, butyraldehyde, hexaldehyde, heptaldehyde, and the like. In some aspects, the formaldehyde may be used in its monomeric form, or its polymeric form, i.e., paraformaldehyde.

[0041] In various aspects, the reaction may proceed at temperatures from about 50°C to about 200°C, or between about 75°C to about 175°C. In various aspects, the time

required for completion of the reaction may vary from about 1 to about 8 hours, varying based on the specific reactants chosen and the reaction temperature.

[0042] In various aspects, the molar range of components (A):(B):(C) may fall within 0.5-5:1:0.5-5, or from about 1-2:1:1-2, or from about 2:1:2.

5 [0043] In various aspects, the dispersant chemistries of the disclosure may be added in an amount of about 0.05 to 50,000 ppm, or from about 0.5; 1; 50; 100; 200; 300; 400; 500; 600; 700; 800; 900; 1,000; 2,000; 3,000; 4,000; 5,000; 10,000; 20,000; 30,000; 40,000; or 50,000 ppm, or about 1 ppm to about 10,000 ppm, or about 5 ppm to about 500 ppm, or about 200 ppm, or any value between any of these amounts.

10 [0044] In various aspects, the methods may further comprise adding to the system or compressor, a wash oil.

[0045] In various aspects of the disclosed methods, the fouling, deposition, and/or emulsification may be caused by solid or viscous liquids comprising ethylene tar or polymers formed through radical-induced polymerization reactions.

15 [0046] In various aspects, the disclosed method may be used in quench systems of an ethylene plant, charge gas compressors, or any other system that would benefit from the disclosed methods.

EXAMPLES

20 [0047] 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 disclosed technology or limit the scope to any particular embodiments.

[0048] Examples

[0049] Preparation of Reaction Products

25 [0050] 15.9 gm of Paraform (92% active), 61 gm (technical grade) of nonylphenol, and 40 gm of solvent A-150 were placed in a flask. The mixture was stirred and 15.4 (99% active) gm of ethylenediamine (EDA) was added. The temperature was allowed to rise from 15°C to 70°C. The reaction mixture was heated to 125°C while distilling off an azeotropic mixture of water and A-150. After 9 gm of water and 3 gm of A-150 were
30 removed, the reaction was kept at 140°C for two additional hours. The mixture was cooled to the desired temperature and loaded into a storage container.

[0051] General Testing Methods

[0052] Ethylene tar deposits were examined either in an aqueous phase or organic phase environment. A solution of caustic water with pH=10 represented the aqueous phase, while an A-150 solution represented the organic phase.

[0053] The tar was pre-heated at 80°C for 20 minutes and then shaken for 1 minute at a constant rate. After shaking, and under continued heating, the settling rate between the untreated sample and each treatment sample was compared. To better assist the observation, a LED light panel was placed behind the Combi instrument. The guideline below explains how the best treatment was selected.

[0054] Case A: Untreated Tar sample was settled immediately

[0055] 1) Any treatment vials that blocked the light were considered effective.

[0056] 2) The effective treatments were ranked by how long they blocked the light. The treatment vial that blocked the light the longest was considered the best.

[0057] Case B: Untreated Tar sample was slowly settled

[0058] 1) Ineffective treatment vials that allowed the light fully to pass through were eliminated.

[0059] 2) At specific periods, treatments were compared by the darkness of the solution and the volume of dark materials at the tip of the vials. The darkest solution with the least materials volume at the tip of a vial was considered the best treatment.

[0060] 3) Compared to the untreated sample vial, the best treatment was effective if it blocked the light longer than the untreated sample vial. The effective treatments were determined by the long blocking time and/or less amount of settling deposit.

[0061] Example 1

[0062] 0.2 g of tar was individually added into a set of 24 5 mL combi vials. 4 mL of a pH=10 caustic water and various treatment chemistries, as listed in Table 1 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. Photos were taken and the effectiveness of the treatments were compared.

[0063] Table 1

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Comparative Treatment 1	5000
3	Comparative Treatment 1	1000
4	Comparative Treatment 1	200
5	Comparative Treatment 2	200

6	Comparative Treatment 3	200
7	Comparative Treatment 4	200
8	Comparative Treatment 5	200
9	Untreated	
10	Comparative Treatment 6	200
11	Comparative Treatment 7	200
12	Comparative Treatment 8	200
13	Comparative Treatment 9	200
14	Comparative Treatment 10	200
15	Comparative Treatment 11	200
16	Comparative Treatment 12	200
17	Untreated	
18	Comparative Treatment 13	200
19	Comparative Treatment 14	200
20	Comparative Treatment 15	200
21	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
22	Comparative Treatment 16	200
23	Comparative Treatment 1	5000
24	Comparative Treatment 2	200

[0064] As shown in FIGS. 1A-1H, vial 21, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity when compared to the untreated vials 1, 9 and 17 and the comparative vials 2-8, 10-16, 18-20 and 22-24.

5 [0065] Example 2

[0066] 0.2 g of tar was individually added into a set of 24 5 mL combi vials. 4 mL of A-150 and various treatment chemistries, as listed in Table 2 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued heating, photos were taken and the effectiveness of the treatments were compared.

[0067] Table 2

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Comparative Treatment 1	5000
3	Comparative Treatment 1	1000
4	Comparative Treatment 1	200
5	Comparative Treatment 2	200
6	Comparative Treatment 3	200
7	Comparative Treatment 4	200
8	Comparative Treatment 5	200
9	Untreated	

10	Comparative Treatment 6	200
11	Comparative Treatment 7	200
12	Comparative Treatment 8	200
13	Comparative Treatment 9	200
14	Comparative Treatment 10	200
15	Comparative Treatment 11	200
16	Comparative Treatment 12	200
17	Untreated	
18	Comparative Treatment 13	200
19	Comparative Treatment 14	200
20	Comparative Treatment 15	200
21	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
22	Comparative Treatment 16	200
23	Comparative Treatment 1	5000
24	Comparative Treatment 2	200

[0068] As shown in FIGS. 2A-2G, vial 21, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 60 minutes when compared to the untreated vials 1, 9 and 17 and the comparative vials 2-8, 10-16, 18-20 and 22-24.

5 [0069] Example 3

[0070] 0.2 g of tar was individually added into a set of 11 5 mL combi vials numbered 12-22. 4 mL of caustic and various treatment chemistries, as listed in Table 3 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued heating, photos were taken and the effectiveness of the treatments were compared.

[0071] Table 3

Vial Number	Product	Dosage (ppmA)
12	Untreated	
13	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
14	Comparative Treatment 17	200
15	Comparative Treatment 7	200
16	Comparative Treatment 11	200
17	Comparative Treatment 2	200
18	Comparative Treatment 18	200
19	Comparative Treatment 18	200
20	Untreated	200
21	Comparative Treatment 19	200
22	Comparative Treatment 1	200

[0072] As shown in FIGS. 3A-3D, vial 13, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 30 minutes when compared to the untreated vials 12 and 20 and the comparative vials 14-19, 21 and 22.

5 [0073] Example 4

[0074] 0.2 g of tar was individually added into a set of 11 5 mL combi vials. 4 mL of A-150 and various treatment chemistries, as listed in Table 4 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued
10 heating, photos were taken and the effectiveness of the treatments were compared.

[0075] Table 4

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
3	Comparative Treatment 17	200
4	Comparative Treatment 7	200
5	Comparative Treatment 11	200
6	Untreated	
7	Comparative Treatment 2	200
8	Comparative Treatment 18	200
9	Comparative Treatment 18	200
10	Comparative Treatment 19	200
11	Comparative Treatment 1	200

[0076] As shown in FIGS. 4A-4E, vial 2, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 65 minutes when compared to the untreated vials 1 and 6 and the
15 comparative vials 3-5 and 7-11.

[0077] Example 5

[0078] 0.2 g of tar was individually added into a set of 11 5 mL combi vials. 4 mL of caustic water and various treatment chemistries, as listed in Table 5 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken
20 for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued heating, photos were taken and the effectiveness of the treatments were compared.

[0079] Table 5

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
3	Comparative Treatment 17	200
4	Comparative Treatment 7	200
5	Comparative Treatment 11	200
6	Untreated	
7	Comparative Treatment 2	200
8	Comparative Treatment 18	200
9	Comparative Treatment 18	200
10	Comparative Treatment 19	200
11	Comparative Treatment 1	200

[0080] As shown in FIGS. 5A-5C, vial 2, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 120 minutes when compared to the untreated vials 1 and 6 and the comparative vials 3-5 and 7-11.

5 [0081] Example 6

[0082] 0.2 g of tar was individually added into a set of 5 5 mL combi vials. 4 mL of A-150 and various treatment chemistries, as listed in Table 6 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued heating, photos were taken and the effectiveness of the treatments were compared.

10

[0083] Table 6

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
3	Comparative Treatment 20	200
4	Comparative Treatment 21	200
5	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200

[0084] As shown in FIGS. 6A-6B, vial 2, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 35 minutes when compared to the untreated vial 1 and the comparative vials 3-5.

15

[0085] Example 7

[0086] 0.2 g of tar was individually added into a set of 5 5 mL combi vials. 4 mL of A-150 and various treatment chemistries, as listed in Table 7 below, were added to each

vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued heating, photos were taken and the effectiveness of the treatments were compared.

[0087] Table 7

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
3	Comparative Treatment 22	200
4	Comparative Treatment 23	200
5	Comparative Treatment 24	200

5 [0088] As shown in FIGS. 7A-7B, vial 2, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 35 minutes when compared to the untreated vial 1 and the comparative vials 3-5.

[0089] Example 8

10 [0090] 0.2 g of tar was individually added into a set of 5 5 mL combi vials. 4 mL of caustic water and various treatment chemistries, as listed in Table 6 below, were added to each vial. The vials were preheated to 80°C for 20 minutes. The vials were then shaken for 1 minute at the level 4 mark on the Combi instrument. After shaking, and under continued heating, photos were taken and the effectiveness of the treatments were
15 compared.

[0091] Table 8

Vial Number	Product	Dosage (ppmA)
1	Untreated	
2	Reaction product of formaldehyde with 4-nonylphenol and ethylene diamine	200
3	Comparative Treatment 22	200
4	Comparative Treatment 23	200
5	Comparative Treatment 24	200

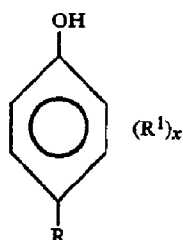
[0092] As shown in FIGS. 8A-8B, vial 2, which included an embodiment of the dispersant chemistry of the disclosure, exhibited superior light blocking activity over a period of time of up to 3 minutes when compared to the untreated vial 1 and the
20 comparative vials 3-5.

[0093] 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.

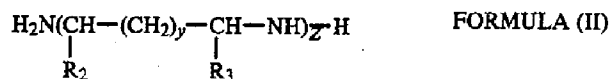
CLAIMS

1. A method of preventing fouling, deposition, plugging and/or emulsification in a quench system of an ethylene plant comprising adding to the system a dispersant chemistry comprising an effective amount of a reaction product formed by reaction of
 5 reactants (A), (B), and (C), wherein (A) comprises an alkyl substituted phenol of the structure



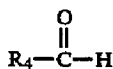
FORMULA I

- wherein R and R¹ are the same or different and are independently selected from alkyl, aryl,
 10 alkaryl, or arylalkyl of from about 1 to 20 carbon atoms and x is 0 or 1; (B) comprises a polyamine of the structure



FORMULA (II)

- wherein Z is a positive integer, R₂ and R₃ are the same or different and are independently
 15 selected from H, alkyl, aryl, aralkyl, or alkaryl having from 1 to 20 carbon atoms, y being 0 or 1; and (C) comprising an aldehyde of the structure

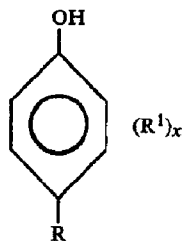


FORMULA (III)

wherein R₄ comprises H or C₁-C₆ alkyl.

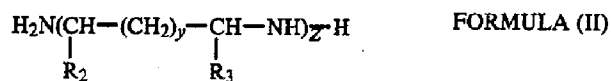
- 20 2. The method of claim 1, wherein the fouling, deposition, plugging and/or emulsification is caused by solid or viscous liquids comprising ethylene tar.
3. The method of claim 1, wherein the molar ratio of reactants (A):(B):(C) is 0.5-5:1:0.5-5.

4. The method of claim 1, wherein the reaction product is added to the quench system in an amount of from 0.5 to 50,000 ppm.
5. The method of claim 4, wherein the reaction product is added to the quench system in an amount of 1 to 10,000 ppm.
6. The method of claim 4, wherein the reaction product is added to the quench system in an amount of 5 to 500 ppm.
- 10 7. The method of claim 4, wherein the reaction product is added to the quench system in an amount of about 200 ppm.
8. The method of claim 1, wherein (A) comprises a member or members selected from the group consisting of p-cresol, 4-ethylphenol, 4-t-butylphenol, 4-t-amylphenol, 4-t-octylphenol, 4-dodecylphenol, 2,4-di-t-butylphenol, 2,4-di-t-amylphenol, and 4-nonylphenol.
9. The method of claim 1, wherein the polyamine (B) is selected from the group consisting of ethylenediamine and triethylenetetramine.
- 20 10. The method of claim 1, wherein the aldehyde (C) is selected from the group consisting of formaldehyde and paraformaldehyde.
11. A method of preventing fouling in a charge gas compressor (CGC) of an ethylene plant comprising adding to the compressor a dispersant chemistry comprising an effective amount of a reaction product formed by reaction of reactants (A), (B), and (C), wherein (A) comprises an alkyl substituted phenol of the structure



FORMULA I

wherein R and R¹ are the same or different and are independently selected from alkyl, aryl, alkaryl, or arylalkyl of from about 1 to 20 carbon atoms and x is 0 or 1; (B) comprises a polyamine of the structure



wherein Z is a positive integer, R₂ and R₃ are the same or different and are independently selected from H, alkyl, aryl, aralkyl, or alkaryl having from 1 to 20 carbon atoms, y being 0 or 1; and (C) comprising an aldehyde of the structure



wherein R₄ comprises H or C₁-C₆ alkyl.

12. The method of claim 11, wherein the fouling is caused by solid or viscous liquids comprising ethylene tar or polymers formed through radical-induced polymerization reactions.

13. The method of claim 11, wherein the molar ratio of reactants (A):(B):(C) is 0.5-5:1:0.5-5.

14. The method of claim 11, wherein the reaction product is added to the CGC in an amount of from 0.5 to 50,000 ppm.

15. The method of claim 14, wherein the reaction product is added to the CGC in an amount of 1 to 10,000 ppm.

16. The method of claim 14, wherein the reaction product is added to the CGC in an amount of 5 to 500 ppm.

17. The method of claim 14, wherein the reaction product is added to the CGC in an amount of about 200 ppm.

18. The method of claim 11, wherein (A) comprises a member or members selected from the group consisting of p-cresol, 4-ethylphenol, 4-t-butylphenol, 4-t-amylphenol, 4-t-octylphenol, 4-dodecylphenol, 2,4-di-t-butylphenol, 2,4-di-t-amylphenol, and 4-nonylphenol.
19. The method of claim 11, wherein the polyamine (B) is selected from the group consisting of ethylenediamine and triethylenetetramine.
20. The method of claim 11, wherein the aldehyde (C) is selected from the group consisting of formaldehyde and paraformaldehyde.
21. The method of claim 11, wherein the method further comprises adding a wash oil.

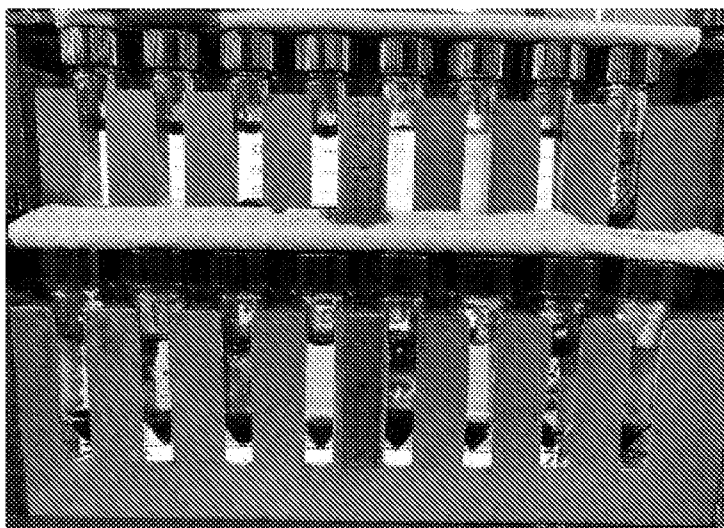


FIG. 1A

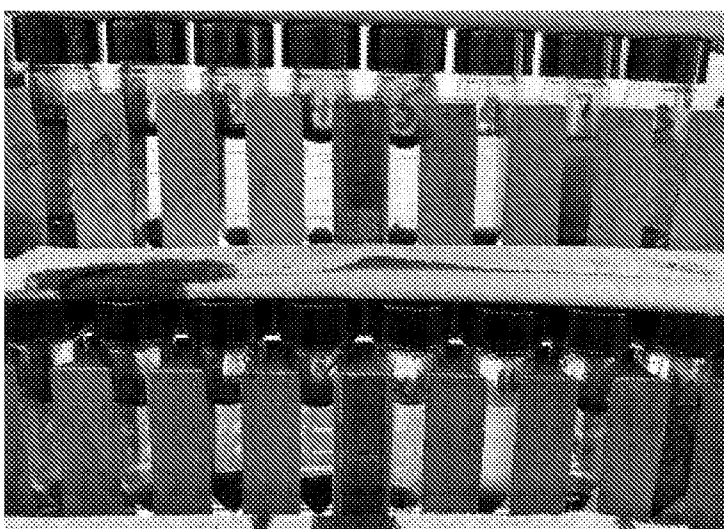


FIG. 1B

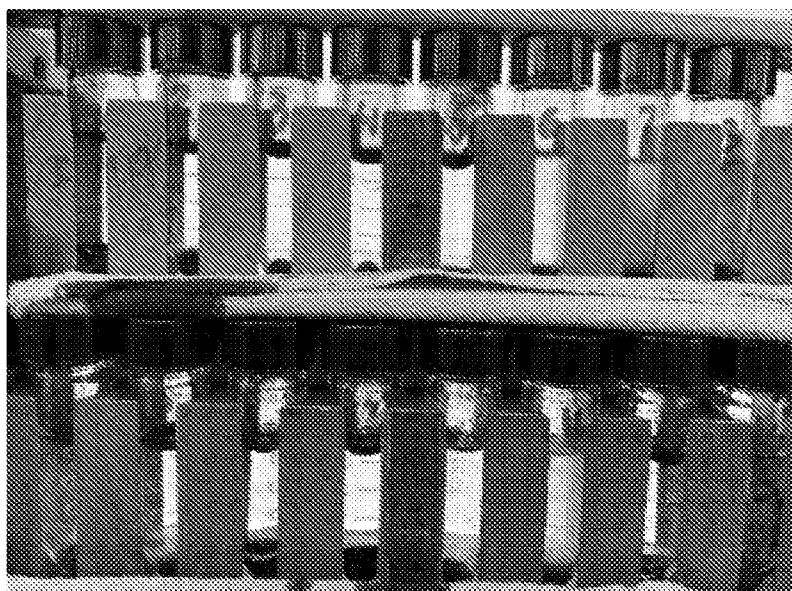


FIG. 1C

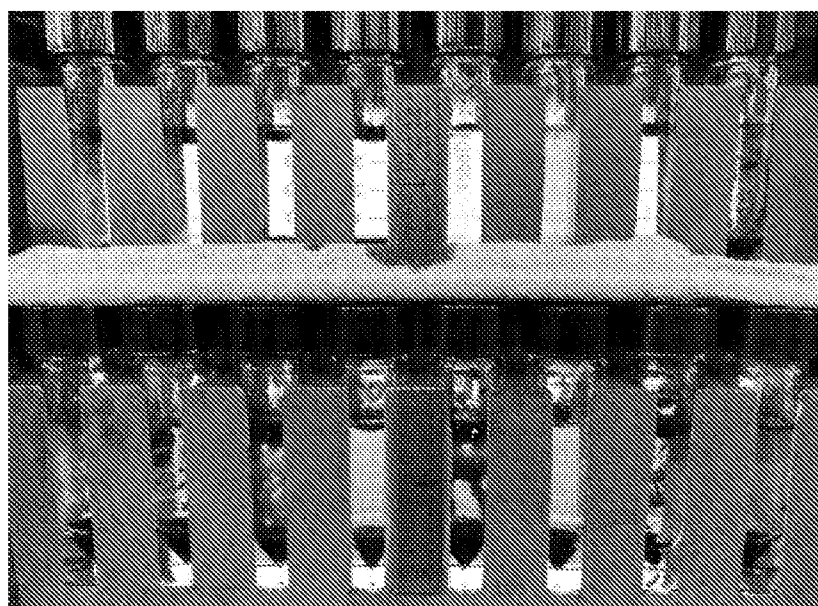


FIG. 1D

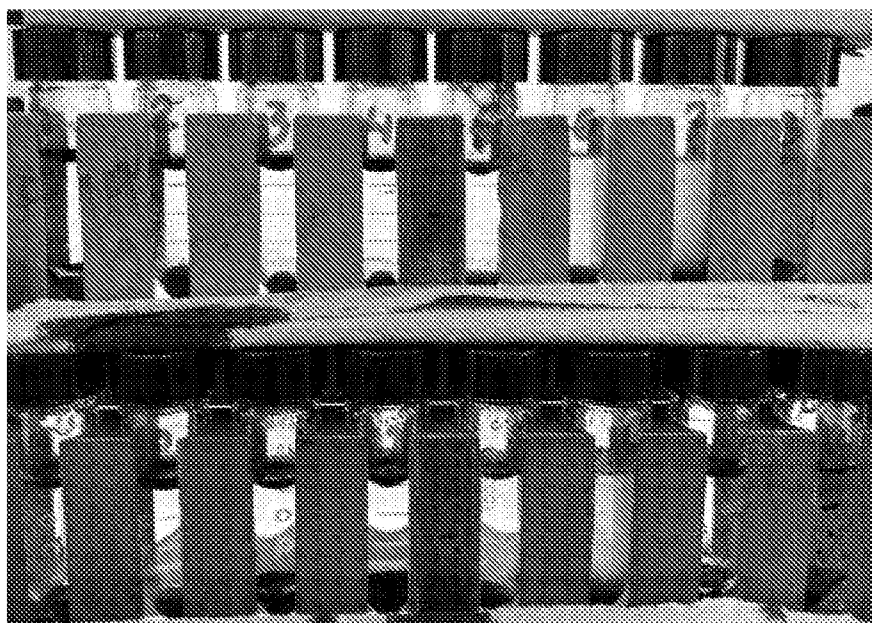


FIG. 1E

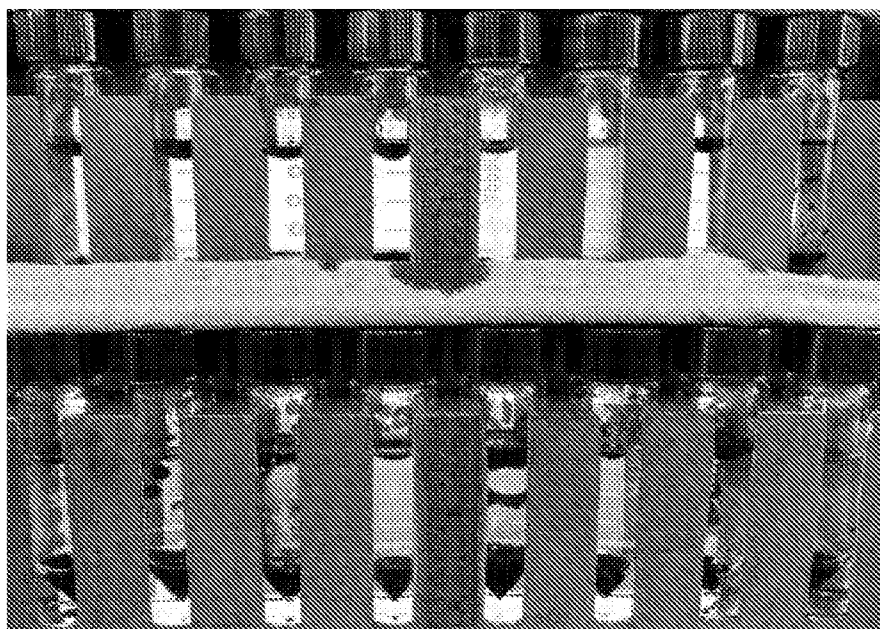


FIG. 1F

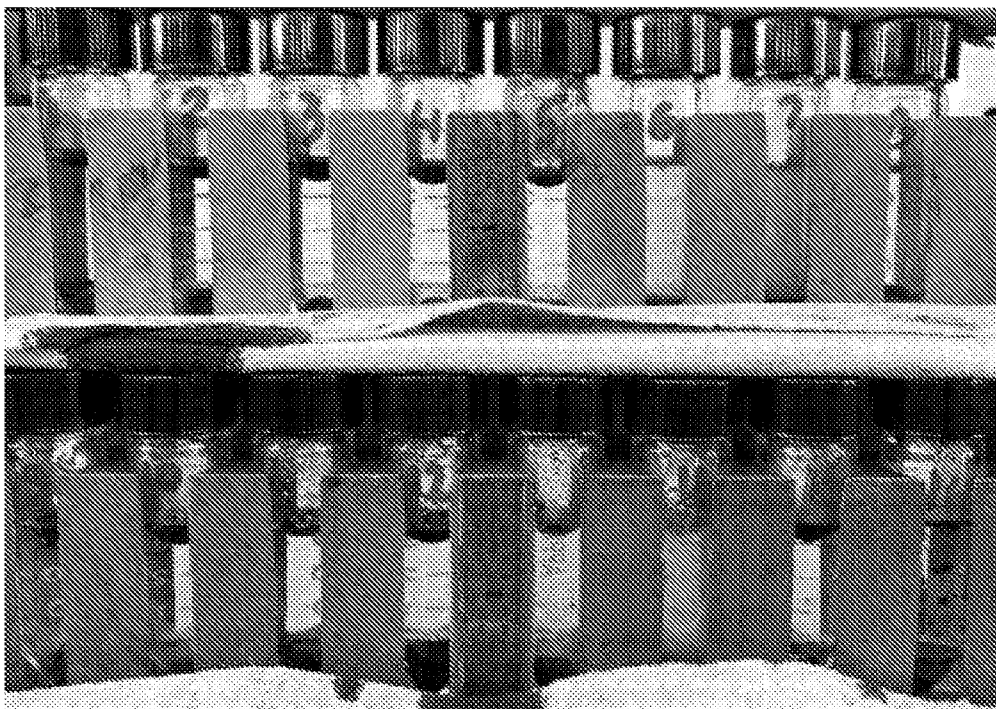


FIG. 1G



FIG. 1H

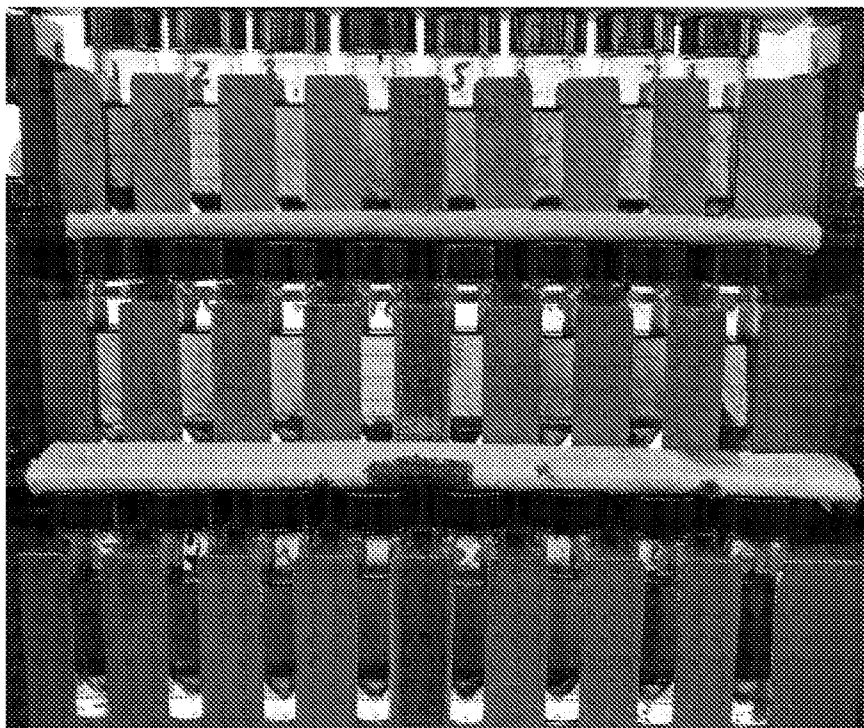


FIG. 2A

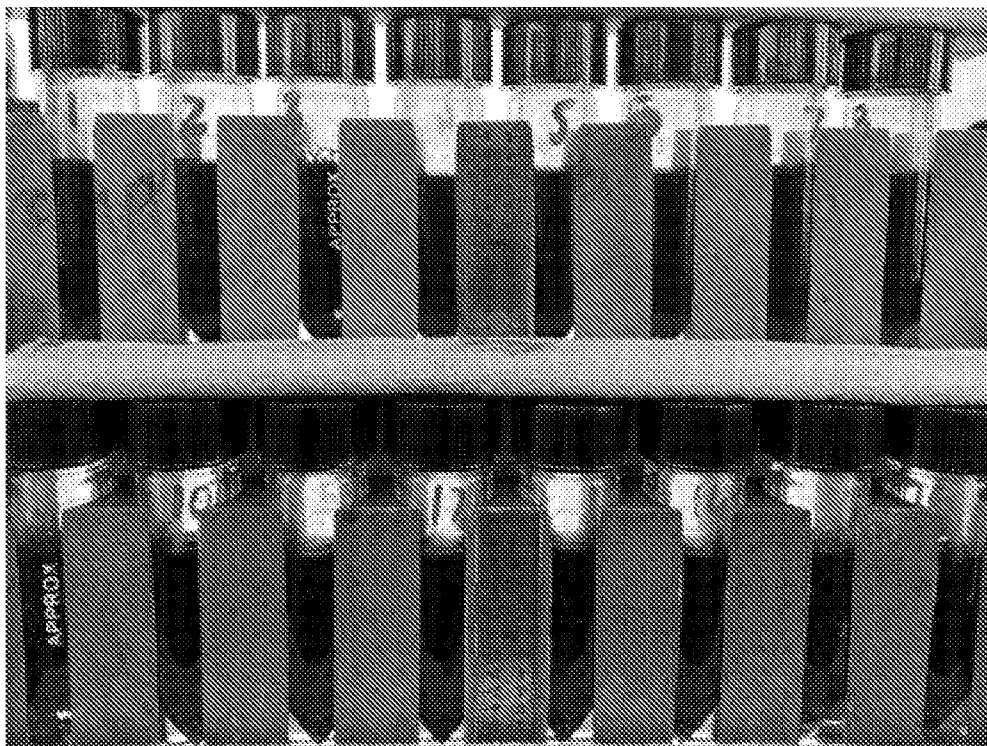


FIG. 2B

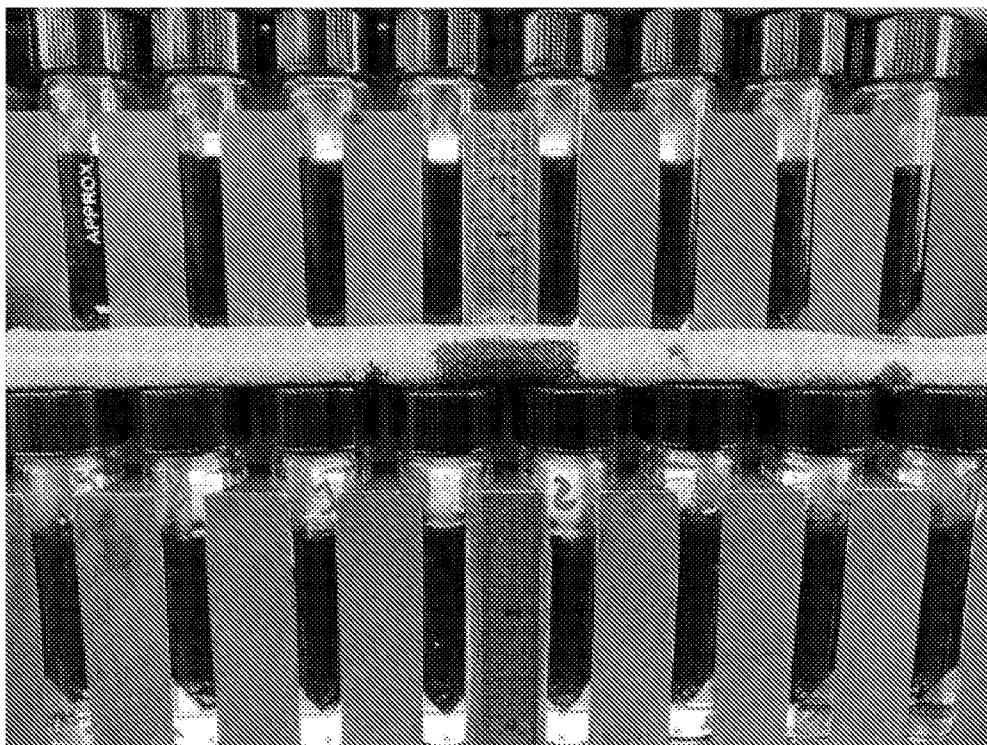


FIG. 2C

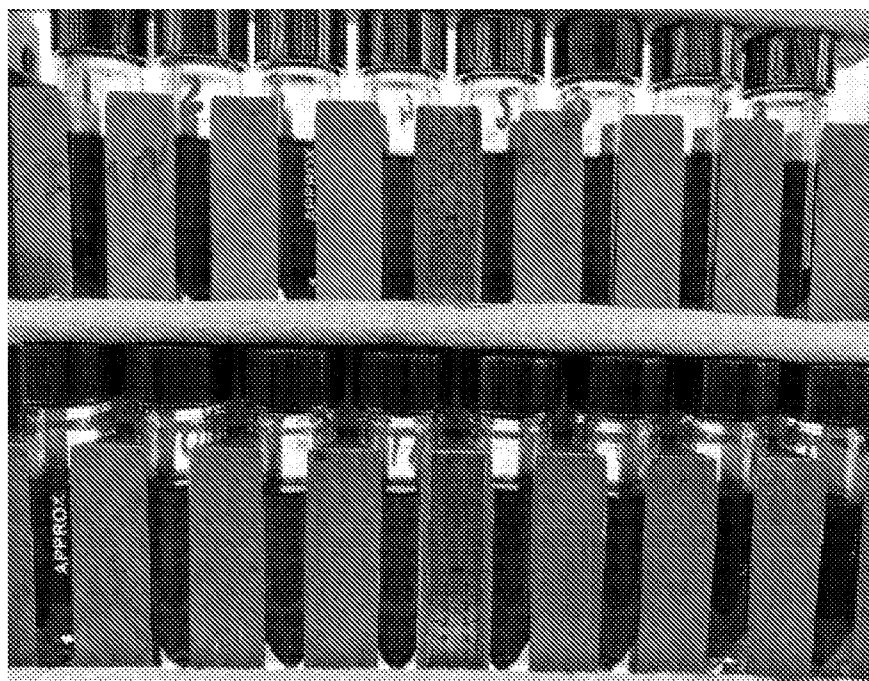


FIG. 2D

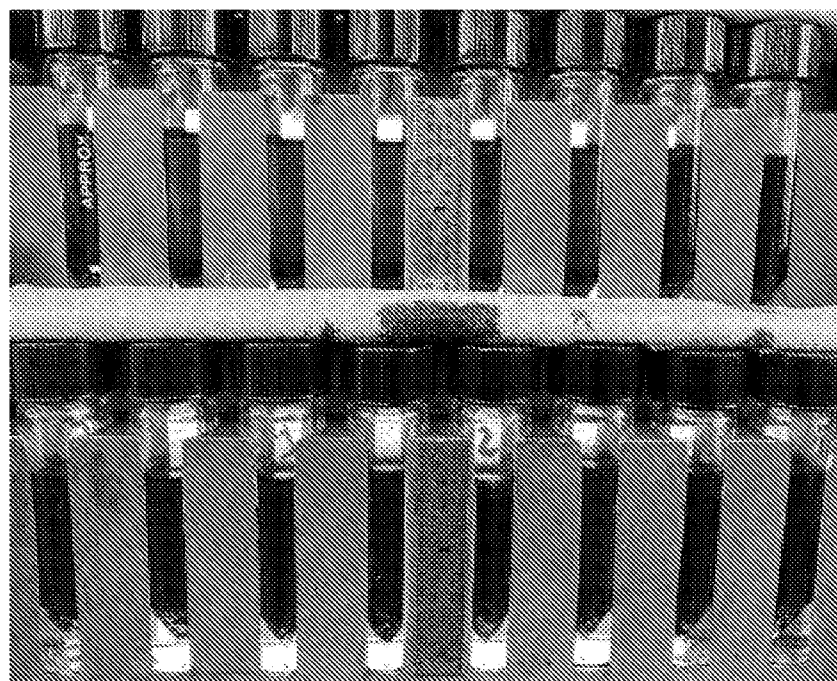


FIG. 2E

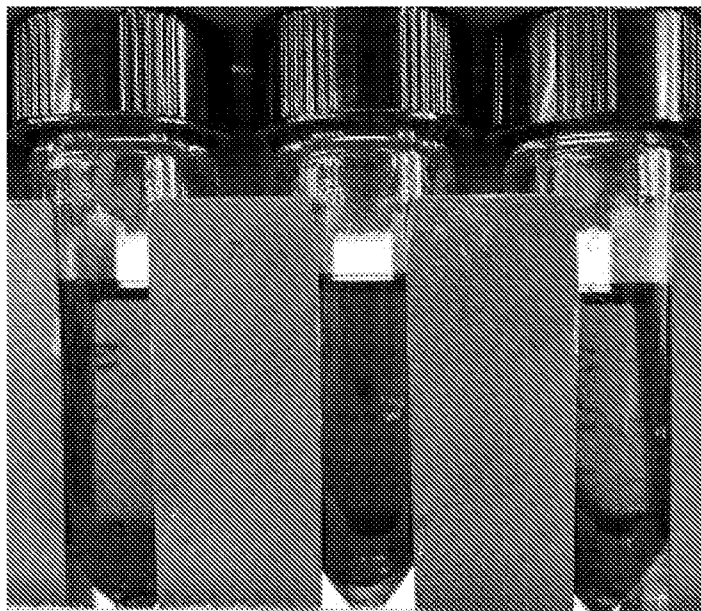


FIG. 2F



FIG. 2G

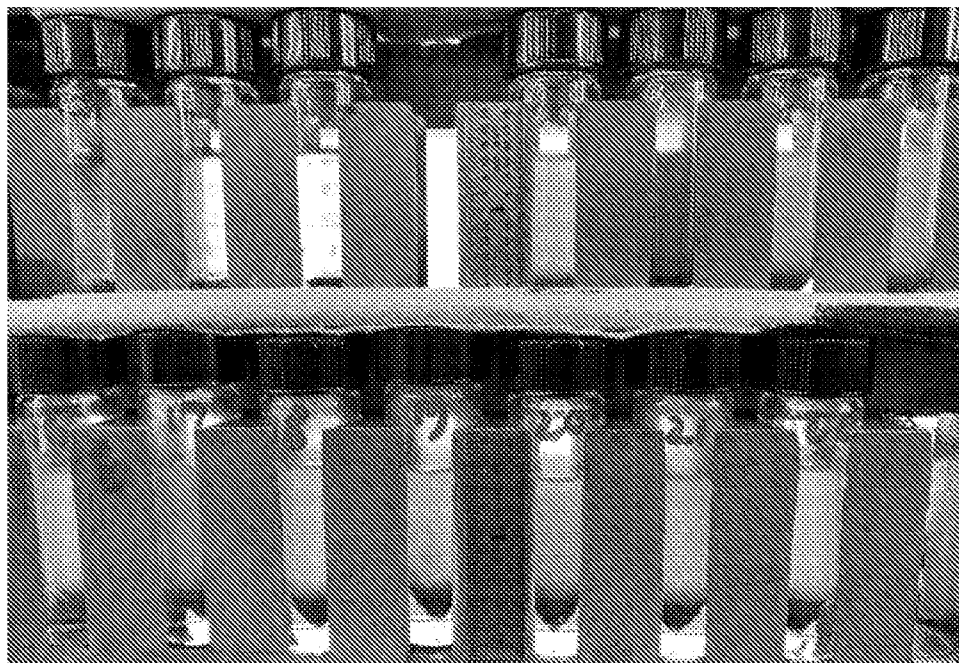


FIG. 3A

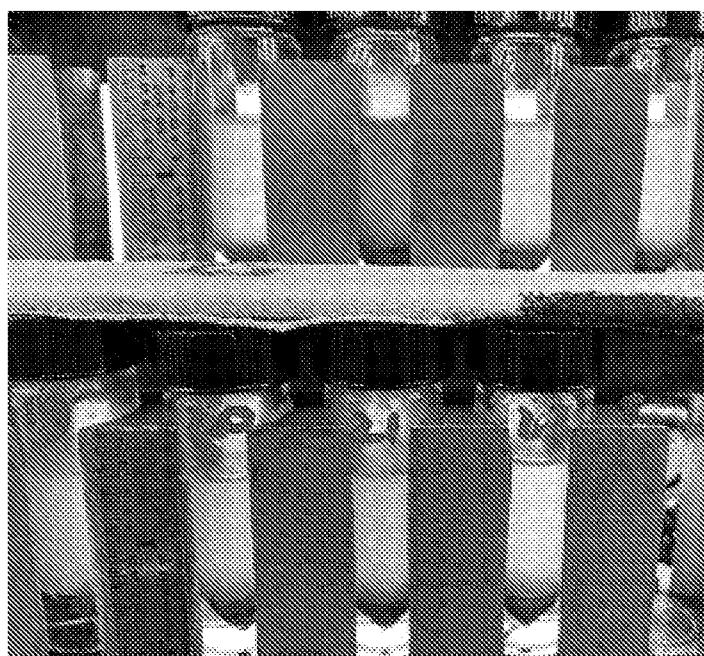


FIG. 3B

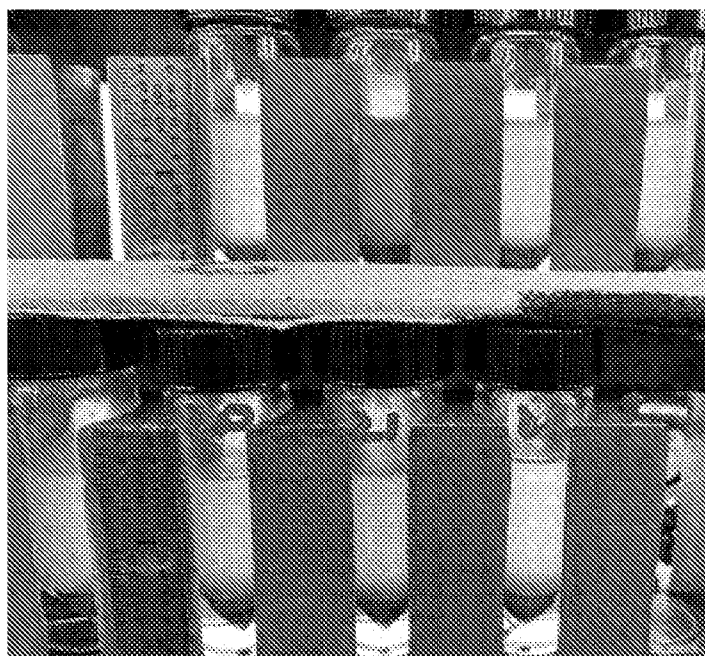


FIG. 3C



FIG. 3D

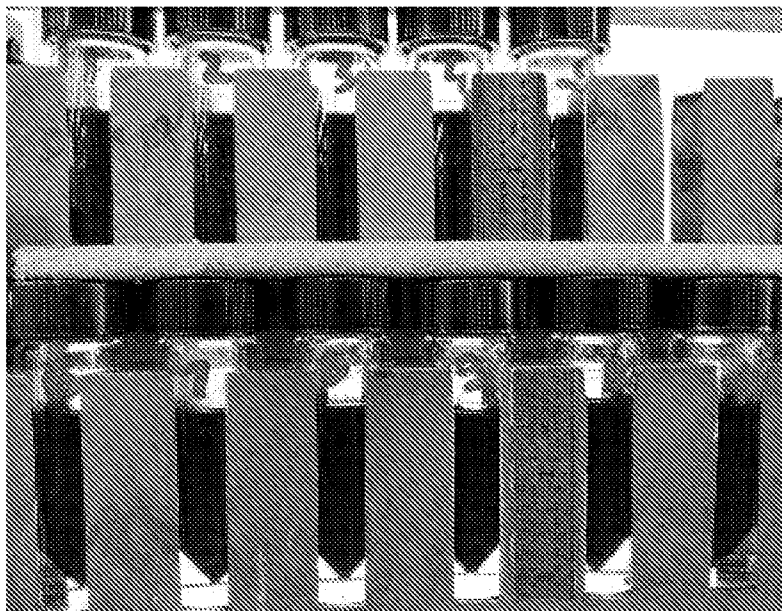


FIG. 4A

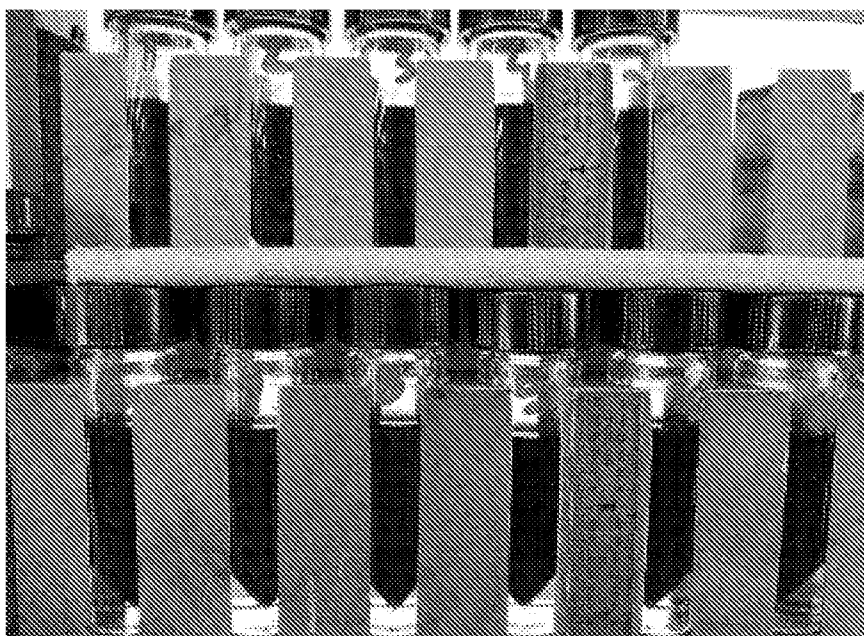


FIG. 4B

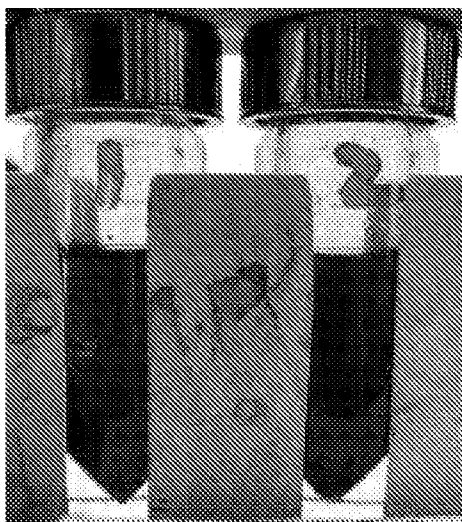


FIG. 4C

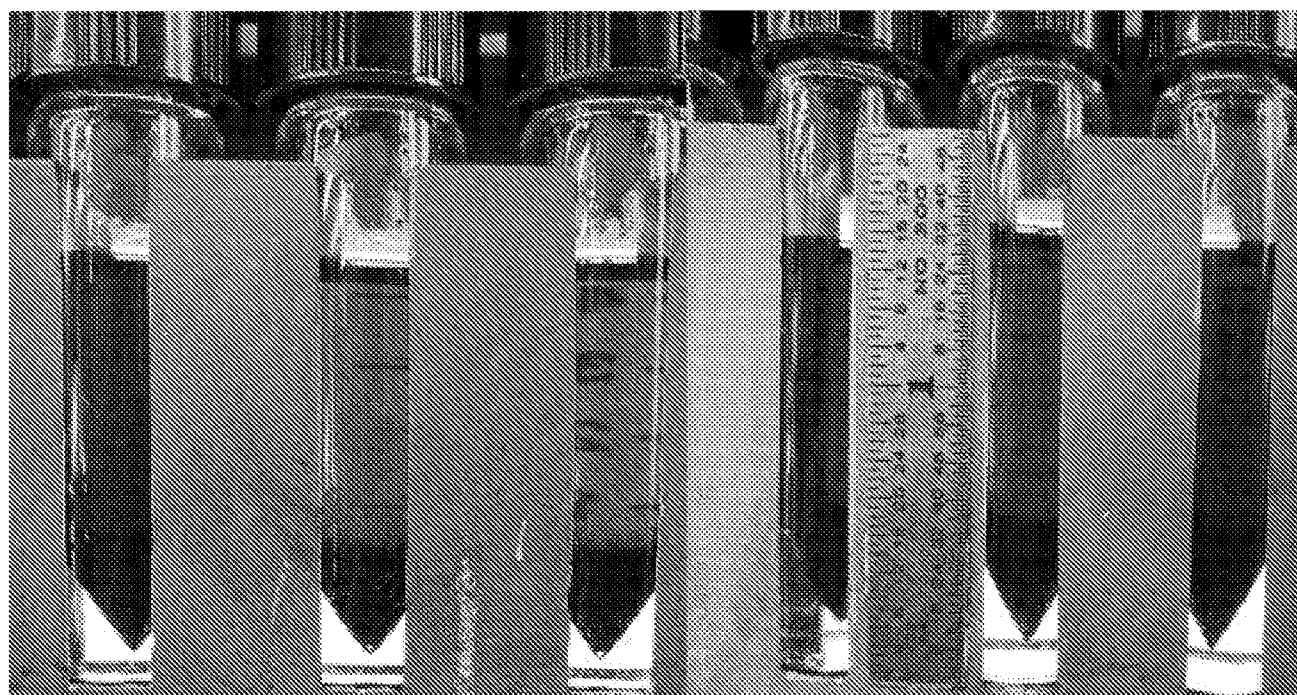


FIG. 4D

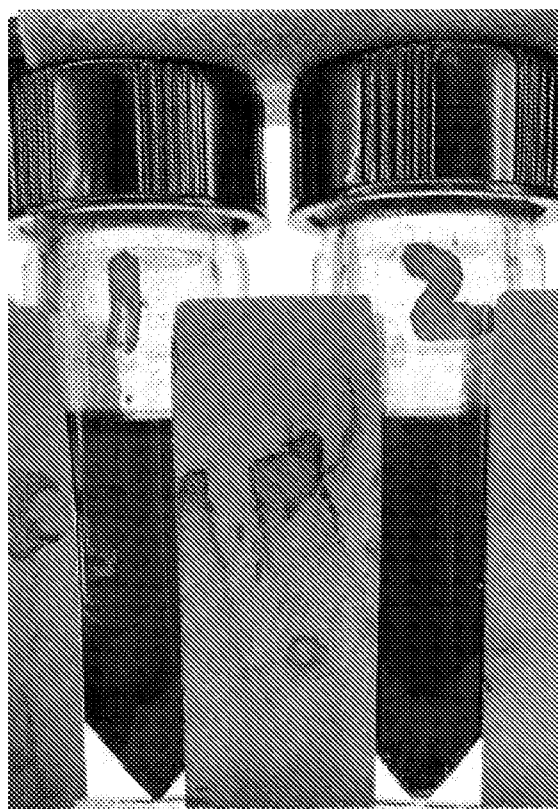


FIG. 4E



FIG. 5A

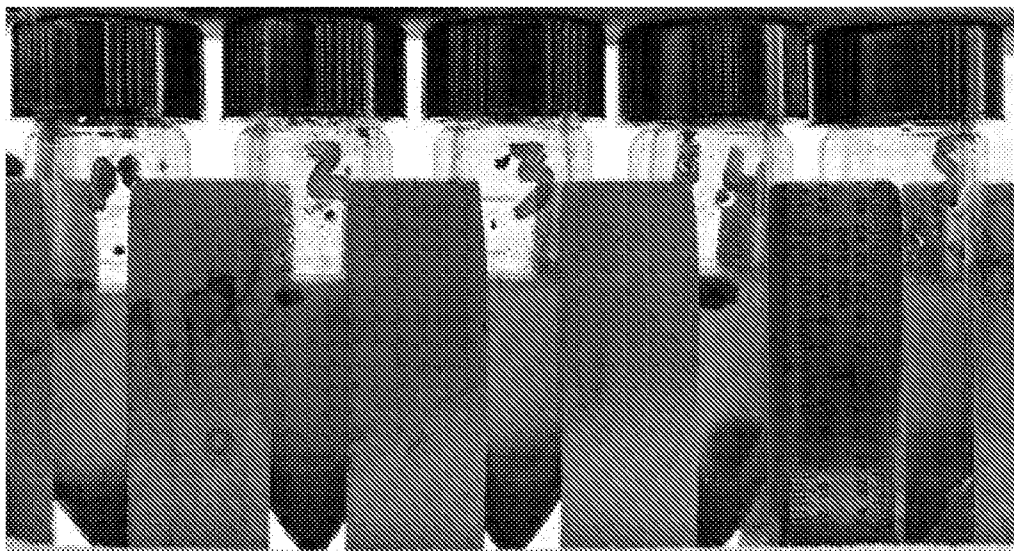


FIG. 5B



FIG. 5C



FIG. 6A



FIG. 6B



FIG. 7A

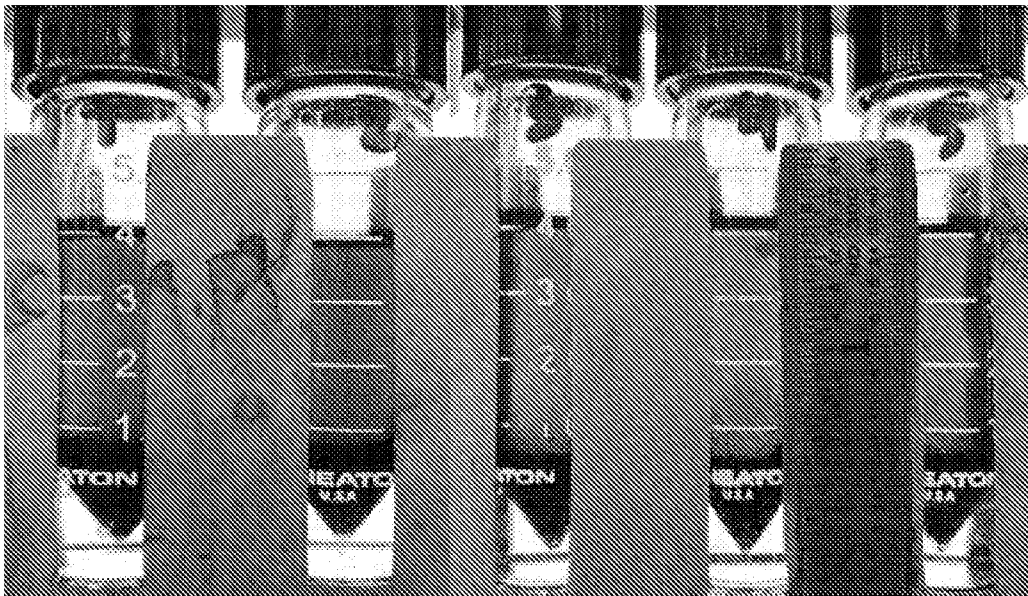


FIG. 7B



FIG. 8A



FIG. 8B

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/032476

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G9/16 C10G75/04

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)

C10G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 927 519 A (FORESTER DAVID R [US]) 22 May 1990 (1990-05-22) claim 1 column 4, lines 4-6, 16-24 column 9, lines 9-42 column 10, lines 26-28 Examples -----	11-21
X	US 9 505 988 B2 (MANEK MARIA BEATA [US]; SHAH MEHA H [US] ET AL.) 29 November 2016 (2016-11-29) column 2, lines 29-32 column 2, line 60 - column 3, line 3 column 3, lines 44-50 claim 1 ----- - / - -	1-10



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

"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

16 September 2024

Date of mailing of the international search report

30/09/2024

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

Authorized officer

Pardo Torre, J

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/032476

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:

see additional sheet

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 an 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.:

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/US2024/032476

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 797 329 B2 (BAKER HUGHES INC [US]) 28 September 2004 (2004-09-28) claims 1, 12 column 1, lines 53-63 column 3, lines 24-29 Examples -----	11 - 21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/032476

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4927519	A	22-05-1990	CA 1329163 C US 4927519 A	03-05-1994 22-05-1990

US 9505988	B2	29-11-2016	BR 112014006054 A2 CA 2844829 A1 CN 103827064 A EP 2768791 A1 ES 2615751 T3 JP 6068485 B2 JP 2014530934 A KR 20140079374 A MY 174253 A RU 2014110040 A SG 2014013312 A US 2013098466 A1 WO 2013058997 A1	11-04-2017 25-05-2013 28-05-2014 27-08-2014 08-06-2017 25-01-2017 20-11-2014 26-06-2014 01-04-2020 10-12-2015 30-07-2014 25-04-2013 25-04-2013

US 6797329	B2	28-09-2004	AU 2003287200 A1 CA 2503534 A1 EP 1556441 A1 ES 2349034 T3 JP 4362108 B2 JP 2006504846 A KR 20050067204 A PT 1556441 E US 2003129318 A1 WO 2004041932 A1	07-06-2004 21-05-2004 27-07-2005 22-12-2010 11-11-2009 09-02-2006 30-06-2005 09-08-2010 10-07-2003 21-05-2004

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-21

Preventing fouling

1.1. claims: 1-10

Preventing fouling in quench systems

1.2. claims: 11-21

Preventing fouling in charge gas compressors
