



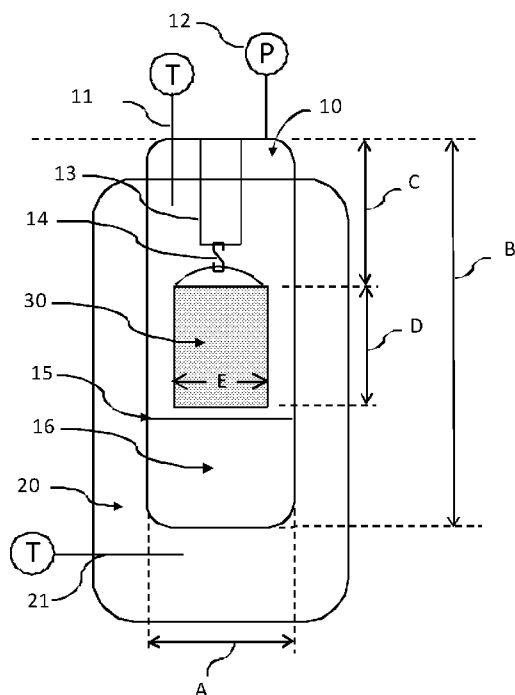
- (51) International Patent Classification:  
C09K 8/592 (2006.01) E21B 43/00 (2006.01)
- (21) International Application Number:  
PCT/US2016/041425
- (22) International Filing Date:  
8 July 2016 (08.07.2016)
- (25) Filing Language:  
English
- (26) Publication Language:  
English
- (30) Priority Data:  
62/192,107 14 July 2015 (14.07.2015) US
- (71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC**  
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).
- (72) Inventor: **WILLIAMSON, Alexander**; 2301 North  
Brazosport Blvd., Freeport, TX 77541 (US).
- (74) Agent: **CHRISTY, M. Robert**; The Dow Chemical Com-  
pany, Intellectual Property, P.O. Box 1967, Midland,  
Michigan 48641-1967 (US).

- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: THERMALLY UNSTABLE HYDROXYALKYL AMMONIUM CARBOXYLATES FOR ENHANCED OIL RECOVERY

FIG. 1



(57) Abstract: A process includes (a) injecting a steam composition into a subterranean location containing heavy hydrocarbons, preferably bitumen, wherein the steam composition comprises (i) steam and (ii) a hydroxyalkyl ammonium carboxylate and (b) recovering the heavy hydrocarbon from the subterranean location to above the ground. The process is preferably a cyclic steam stimulation (CSS) process, a steam assisted gravity drainage (SAGD), or a combination thereof.

**Published:**

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

THERMALLY UNSTABLE HYDROXYALKYL AMMONIUM CARBOXYLATES FOR  
ENHANCED OIL RECOVERY

FIELD OF THE INVENTION

5

The present invention relates to a steam composition useful for an *in situ* steam extraction method of removing heavy hydrocarbons, preferably bitumen, from underground locations. Said steam composition comprises steam and a hydroxyalkyl ammonium carboxylate.

10

BACKGROUND OF THE INVENTION

Bitumen recovery from oil sands is a challenging activity that requires accessing subterranean bitumen, extracting the bitumen from the subterranean sand and then recovering the bitumen from the subterranean location to above ground. There are numerous proposed methods for recovering bitumen from oil sands. The Background section of US Patent Application No. 2008/0139418 provides a review of many recovery methods including strip mining, cold flow technique, cyclic steam stimulation (CSS), steam assisted gravity drainage (SAGD) and vapor extraction process (VAPEX).

20 Strip mining removes bitumen together with sand from underground and then extracts bitumen from the sand while above the ground. Strip mining is not an *in situ* extraction method because it involves extracting bitumen from sand after removing the sand from the ground. *In situ* extraction of bitumen involves extracting bitumen from sand in its natural location underground. *In situ* extraction is more desirable than strip mining because  
25 it is less damaging to the landscape than strip mining.

The cold flow technique is only useful for recovering oils that have low enough viscosity to pump at reservoir conditions. Bitumen is too viscous in most subterranean oil sand deposits to allow the cold flow technique to be a reasonable method for recovering bitumen from oil sands.

30 VAPEX is a method that requires injecting hydrocarbon solvents into a first horizontal well that extends into subterranean oil sands. The solvents penetrate into the oil sands, reduce the viscosity of bitumen by dilution and enable the bitumen/solvent mixture to

drain into a second horizontal well below the first from which recovery of the bitumen/solvent mixture occurs. Desirably, hydrocarbon solvent is removed from the bitumen above ground and desirably recycled. The VAPEX method is a “cold” process, which means the material injected into the well is not heated any appreciable amount as opposed to “hot” processes (commonly known as, thermal methods) such as CSS and SAGD where steam is injected into a well. Cold processes such as the VAPEX method are less efficient at extracting bitumen than hot processes such as CSS and SAGD processes because bitumen viscosity is higher at lower temperatures. Therefore, to be effective, the VAPEX method requires injection of large amounts of hydrocarbon solvents into the well in order to sufficiently dilute the bitumen to achieve drainage.

Use of hydrocarbon solvents, particularly high concentrations of hydrocarbon solvents, can be undesirable in *in situ* bitumen recovery processes. Hydrocarbons can cause asphaltenes to precipitate from bitumen and the precipitated asphaltenes can undesirably reduce the reservoir permeability. Additionally, hydrocarbon solvent can be lost into the surrounding subterranean environment, which can result in environmental contamination concerns and increased processing costs. Use of large amounts of hydrocarbon solvents, necessary for suitable solvating of bitumen, also requires an extra process step to recover the hydrocarbon from the bitumen upon extraction of the bitumen. Therefore, it is desirable to avoid both “cold” process methods and the use of hydrocarbons during *in-situ* bitumen recovery.

CSS and SAGD processes are “hot” processes (that is, thermal methods) that use hot steam to decrease the viscosity of subterranean bitumen. In these processes steam is injected down a first well into subterranean oil sands. The steam penetrates the sands and lowers the viscosity of bitumen by heating the oil sands, which facilitates flow of the bitumen through the sands into either the first well (CSS) or to a second well (SAGD) from which recovery of the bitumen occurs. With the CSS method, steam is injected into a well at temperatures of 250°C-400°C. The well then sits for days or weeks during which time the steam heats bitumen in the subterranean environment around the well causing bitumen to drain into the well and after which hot oil mixed with condensed steam is pumped out from the well for weeks or months. Then the process is repeated. In the SAGD process two horizontal wells are drilled, one below the other (generally approximately five meters apart). Steam is injected into the upper well, heating bitumen in the surrounding subterranean

environment thereby lowering the viscosity of the bitumen causing it to flow into the lower well. The resulting bitumen and condensed steam mixture is subsequently pumped to the surface from the bottom well. According to US Patent Application No. 2008/0139418, recovery of bitumen from an oil sands reservoir by CSS is typically only about 20-25 percent (%) while recovery in SAGD processes is reportedly up to about 60% of the available bitumen in the oil sands reservoir.

Typically, steam alone (without additives) is used for oil recovery in SAGD. The latent heat of condensation at the steam chamber edges lowers the viscosity of the bitumen sufficiently to allow gravity drainage. This process is however, slow and steam to oil ratios (SOR) of about 3:1 are typically needed. It is thought that an additive that enhances the formation of oil-in-water emulsions would enhance the rate of drainage through the porous chamber (due to smaller emulsion droplets) and perhaps allow less water usage by decreasing the SOR.

A modified version of the SAGD process is also known. USP 6,230,814 describes what has become known as the expanding solvent steam assisted gravity drainage (ES-SAGD) process. The ES-SAGD process requires combining hydrocarbons with steam in a SAGD-type process so the hydrocarbons can solubilize bitumen in subterranean oil sands to further reduce bitumen viscosity to facilitate the drainage of bitumen into a second well hole for recovery to above ground. The reference identifies suitable additives as hydrocarbons having from one to 25 carbons. However, as explained above, it is desirable to avoid injecting hydrocarbons into a well in order to facilitate removal of bitumen.

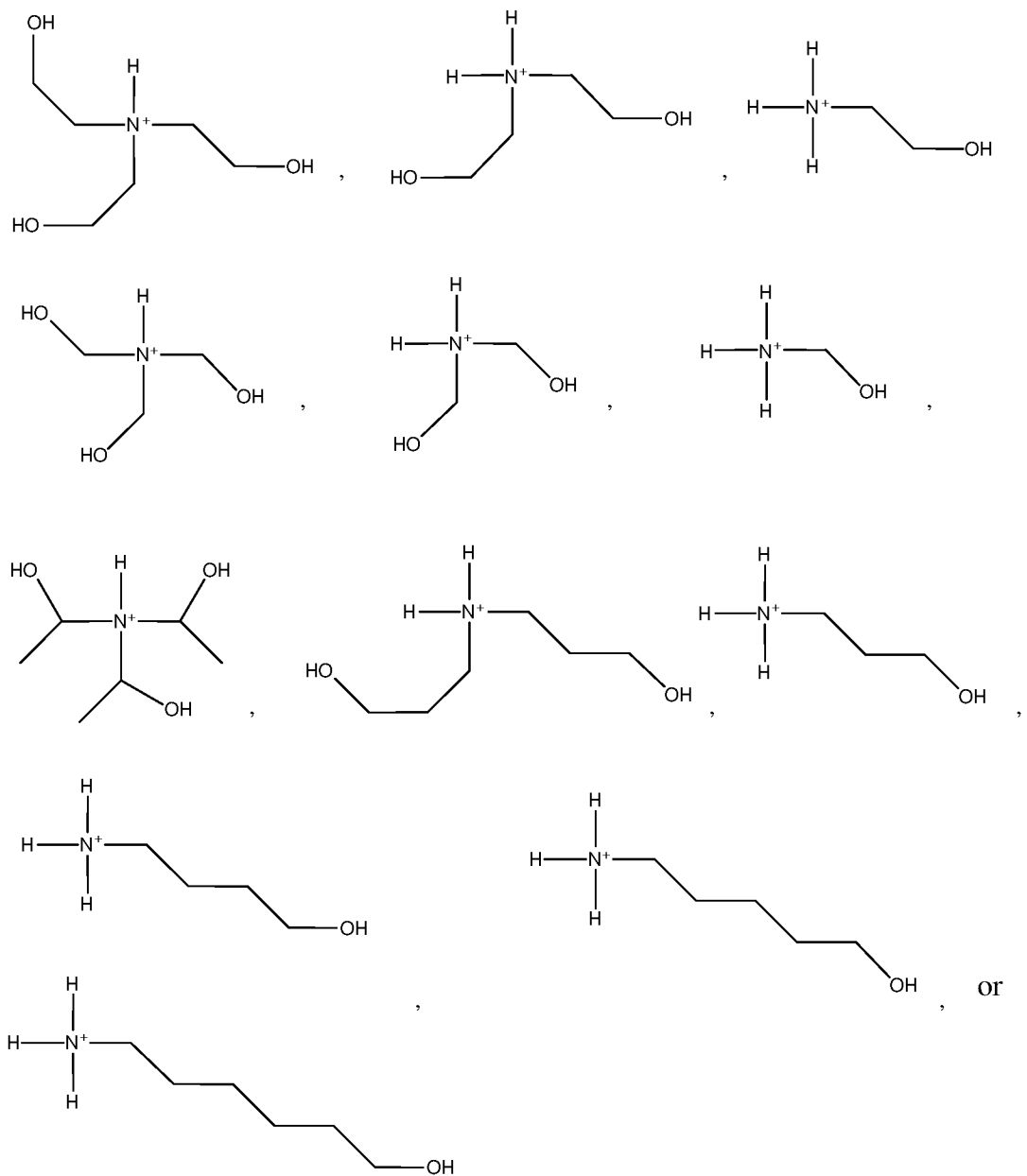
Conventional alkaline enhanced oil recovery agents such as NaOH, NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> are not volatile, and thus do not reach steam chamber edges (even though they could in theory be carried to the bottom of the chamber by dissolving in residual hot water in the Injector Well).

Thermally unstable ammonium carboxylates useful for an *in situ* steam extraction method of removing heavy hydrocarbons from underground locations is disclosed in US Serial No. 62/053446.

It is desirable to identify an *in situ* (that is, subterranean) method for recovering heavy hydrocarbons, such as bitumen from oil sands, that does not require injecting hydrocarbons into subterranean oil sands but that offers a greater recovery percentage than current CSS and SAGD processes.



In a preferred embodiment of the process of the present invention disclosed herein above, the hydroxyalkyl ammonium carboxylate is any combination of one or more of the following ammonium ions represented by the following structures:



with one or more of the following carboxylate ions: acetate, propionate, butanoate, 2-methylpropionate, pentanoate, 2-methylbutanoate, 3-methylbutanoate, 2,2-dimethylpropionate, hexanoate, 2-methylpentanoate, 3-methylpentanoate, 4-

methylpentanoate, 3,3-dimethylbutanoate, heptanoate, 2-methyl hexanoate, octanoate, 2-ethylhexanoate, 2-methylheptanoate, 2-propylpentanoate, nonanoate, decanoate, undecanoate, dodecanoate, benzoate, phenylacetate, or methylbenzoate.

In one embodiment of the process of the present invention disclosed herein above  
5 the carboxylate ion in the form of its free carboxylic acid (i.e., in its acid form) has a boiling point of equal to or less than 300°C at ambient pressure and the ammonium ion in the form of its free amine has a boiling point of equal to or less than 300°C at ambient pressure.

In one embodiment of the process of the present invention disclosed herein above,  
10 the process is cyclic steam stimulation (CSS) process where the recovered heavy hydrocarbon is pumped up the same well that the steam composition is injected down.

In another embodiment of the process of the present invention disclosed herein above, the process is a steam assisted gravity drainage (SAGD) process and the steam composition is injected into the ground through a first well and the heavy hydrocarbon that is displaced from the ground is recovered to above ground through a second well.

15

#### BRIEF DESCRIPTION OF THE DRAWINGS

**FIG. 1** provides an illustration of a vessel used to determine bitumen extraction efficiency in Experiment.

20

#### DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention is a method for producing a heavy hydrocarbon. For the purposes of this application, a heavy hydrocarbon includes dense or  
25 high viscosity crude oils and bitumen.

Heavy hydrocarbons can be difficult to produce. These hydrocarbons are very viscous and often cannot be produced using oil wells that are powered only by formation pressures. One method of lowering the viscosity of heavy hydrocarbons in subterranean formations is to flood the formation with steam. Steam increases the temperature of the hydrocarbons in the formation, which lowers their viscosity, allowing them to drain or be  
30 swept towards an oil well and be produced. Steam can also condense into water, which can

then act as a low viscosity carrier phase for an emulsion of oil, thereby allowing heavy hydrocarbons to be more easily produced.

In one embodiment, the invention is a method of recovering heavy hydrocarbons using an oil well. In this embodiment, the hydrocarbon in a subterranean formation is  
5 contacted with an admixture of steam and a hydroxyalkyl ammonium carboxylate, a primary hydroxyalkyl ammonium carboxylate, a secondary hydroxyalkyl ammonium carboxylate, a tertiary hydroxyalkyl ammonium carboxylate, or mixtures thereof. The hydroxyalkyl ammonium carboxylate compound of the present invention comprises a hydroxyalkyl ammonium ion derived from its free amine and a carboxylate ion derived from a carboxylic  
10 acid (i.e., in its free acid form). The steam and thermally unstable ammonia carboxylate admixture is introduced downhole using either the same well used for production or other wells used to introduce the steam into the formation. Either way, the steam condenses and forms an aqueous phase which can help liberate the heavy hydrocarbon from the mineral and carry it towards the production well.

15 In another embodiment, the invention is a method of recovering heavy hydrocarbons, especially bitumen, where the heavy hydrocarbon is recovered from a hydrocarbon bearing ore. One such ore is the bitumen rich ore commonly known as oil sand(s) or tar sand(s).

Enormous hydrocarbon reserves exist in the form of oil sands. The asphalt-like glassy bitumen found therein is often more difficult to produce than more liquid forms of  
20 underground hydrocarbons. Oilsand bitumen does not flow out of the ground in primary production. Such ore may be mined in open pits, the bitumen separated from the mineral *ex situ* using at least warm water, sometimes heated with steam, in giant vessels on the surface. Or the ore can be heated with steam *in situ*, and the bitumen separated from the formation matrix while still underground with the water condensed from the steam.

25 Unlike conventional heavy crude oils, the bitumen in oil sands is not continuous but in discrete bits intimately mixed with silt or capsules encasing individual grains of water wet sand. These bituminous hydrocarbons are considerably more viscous than even conventional heavy crude oils and there is typically even less of it in the formation-even rich oilsand ores bear only 10 to 15 percent hydrocarbon.

30 One method of recovering such bitumen is to clear the earthen overburden, scoop up the ore from the open pit mine, and then use heated water to wash away the sand and silt *ex situ*, in a series of arduous separation steps.

A more recent process separates the hydrocarbons from the sand in situ using horizontal well pairs drilled into the deeper oilsand formations. High pressure, 500°C, dry steam is injected into an upper (injector) well, which extends lengthwise through the upper part of the oilsand deposit. The steam condenses, releasing its latent and sensible heat  
5 which melts and fluidizes the bitumen near the injector well. As the oil and water, now at about 130 to about 230°C, drains, a dry steam chamber forms above the drainage zone.

One disadvantage to this method of hydrocarbon production is that new steam, along with any additives that it may include, may have to travel ever longer distances through this porous sand and clay to reach the progressing interface between the dry steam chamber and  
10 the zone where the oil and water drainage commences (a production front). This process is known as steam assisted gravity drainage and is commonly referred to by its acronym, "SAGD".

Unlike a conventional steam drive, the pressure of the steam is not primarily used to push the oil to the producer well; rather, the latent heat of the steam is used to reduce the  
15 viscosity of the bitumen so that it drains, along with the water condensed from the steam, to the lower, producer well by gravity. Since, at the production temperature of about 150°C, pure water is about 300 times less viscous than pure bitumen, and the typically water-wet formation can't hydrophobically impede the flow of water, the water drains much faster through the formation than the melted bitumen.

20 In a typical SAGD start-up, water is the first thing out of the ground. The concentration of hydrocarbon in the production fluid increases with time until eventually the oil concentration levels out at about 25 to 35 percent of the produced fluid. Thus the limiting "steam to oil ratio" or SOR is about 2 to 3.

Whatever the condition of the fluids underground, what reaches the first phase  
25 separator on the surface may not be two bulk phases, that is, an oil-based emulsion and a water-based emulsion. Instead, the predominant emulsion is usually oil-in-water. This emulsion typically carries with it is the most bitumen it can carry without flipping states, or inverting, into a water-in-oil emulsion.

In practice then, the SOR, and thus the oil production rate, may be more limited by  
30 the fluid flux (i.e., the transfer of motion to the oil via the water flow) than the thermal flux (i.e., the transfer of heat to the oil via steam). Increasing the fraction of oil carried by the water, then, produces more oil for same steam, and is thus highly desirable.

Two advantages of the method of the invention are that the use of a hydroxyalkyl ammonium carboxylate can increase both the efficiency and the effectiveness with which heavy hydrocarbons are dispersed into (and thus carried by) water. Increased efficiency results in lower steam requirements, which results in lower energy costs. In some fields, heavy crude oil is recovered at a cost of 1/3 of the oil produced being used to generate steam. It would be desirable in the art to lower steam requirements thereby lowering the use of recovered hydrocarbons or purchased energy in the form of natural gas for producing heavy hydrocarbons. Increased effectiveness results in greater total recovery of bitumen from the formation. Less oil is left wasted in the ground. This increases the return for the fixed capital invested to produce it.

Typically, an additive for SAGD is volatile under the SAGD operating conditions so that it can travel with the steam to the edges of the steam chamber where it can interact with the bitumen. This volatility constraint limits the selection of additive to non-ionic chemicals, as ionic chemicals are usually solids and not volatile, and therefore would not be transported with the steam to the edge of the steam chamber.

The improvement in the present invention is the use of hydroxyalkyl ammonium carboxylates where the free carboxylic acid is relatively volatile and the ammonia or the free amine is also relatively volatile. Hydroxyalkyl ammonium carboxylates are thermally unstable and, on heating, will reversibly decompose to the free ammonia or amine and the free carboxylic acid. Not to be held by any particular theory, we believe that when injected into an injector well, the non-volatile hydroxyalkyl ammonium carboxylate will decompose to form a volatile ammonia/amine and a volatile carboxylic acid which will be transported together to the edges of the steam chamber. Once at the edge of the steam chamber, the ammonia/amine and the carboxylic acid will reversibly recombine, hence reversibly forming an anionic surface active agent at the edge of the steam chamber. An advantage of an anionic surface active agent over typical non-ionic surface active agents is that they have a higher hydrophobic-lipophilic balance (HLB) which promotes formation of oil-in-water emulsions which are preferable over water-in-oil emulsions that tend to be formed by volatile non-ionic surface active agents. Some non-ionic surface active agents, such as glycol ethers, also tend to precipitate from solution at higher temperatures by reaching their cloud-point.

The hydroxyalkyl ammonium carboxylate, once in salt form and dissolved in the condensed water at the steam chamber edge, can exchange with salts which are found naturally in groundwater, such as sodium chloride. The resultant sodium carboxylate will also act as a good surface active agent and aid the formation of oil-in-water emulsions.

5 In another embodiment of the process of the invention the ammonia or amine which is released from the hydroxyalkyl ammonium carboxylate can interact with naphthenic acids in bitumen to form surface active agents.

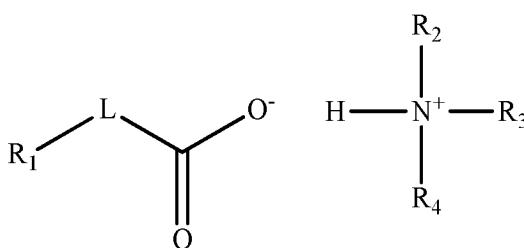
The process of the present invention requires injecting a steam composition through a well into a subterranean location containing bitumen. The subterranean location is  
10 desirably in or proximate to an oil sand deposit. Oil sand is also known as tar sands or bituminous sands. Oil sand is loose sand, or partially consolidated sandstone containing mixtures of sand, clay and water that includes bitumen. Canada, Kazakhstan and Russia all contain large quantities of oil sand deposits. The process of the present invention extracts bitumen from other components of the oil sands in a subterranean location by injecting a  
15 steam composition into the subterranean oil sand deposit to increase the flowability of the bitumen, thereby enabling the bitumen to drain from the oil sand components and eventually be recovered by pumping above ground. The process of the present invention avoids first having to remove oil sand from underground in order to extract bitumen from the removed oil sand as is required in a strip mining process. Instead, the present invention extracts  
20 bitumen from oil sands *in situ*, that is, in the subterranean location of the oil sand.

The steam composition of the present invention comprises both steam and a hydroxyalkyl ammonium carboxylate. The composition is desirably injected at a temperature and pressure sufficient to provide a steam composition at a temperature of 150°C or higher, preferably 180°C or higher and at the same time desirably a temperature of  
25 300°C or lower, preferably 260°C or lower.

The steam in the steam composition can be superheated steam, saturated steam, less than 100 percent quality steam or any combination thereof. "Superheated steam" is steam that is at a temperature above the vapor-liquid equilibrium point of water. "Saturated steam" is synonymous with 100 percent quality steam. The quality of steam is a  
30 characteristic of how much liquid water phase is present in the steam. 100 percent quality steam has zero percent liquid phase water present. "Less than 100 percent quality steam" has liquid water present. A steam composition that is less than 100 percent quality steam

can include the resulting composition from feeding a steam feed and a liquid aqueous phase feed together (as is done, for example, in Examples 1-5 herein).

In the broadest scope of the present invention, the hydroxyalkyl ammonium carboxylate is not limited in composition, preferably it is a hydroxyalkyl ammonium carboxylate, a primary hydroxyalkyl ammonium carboxylate, a secondary hydroxyalkyl ammonium carboxylate, a tertiary hydroxyalkyl ammonium carboxylate, or mixtures thereof. In general, the hydroxyalkyl ammonium carboxylate has the following chemical formula:



10

wherein L represents a methylene group, an alkyl ether group, preferably  $-\text{CH}_2\text{CH}_2\text{O}-$ ,  $-\text{CHMeCH}_2\text{O}-$ , or  $-\text{CH}_2\text{CHMeO}-$ , an aryl group, an aryloxy group preferably  $-\text{C}_6\text{H}_4\text{O}-$ , an alkyl aryl group preferably  $-\text{CH}_2\text{C}_6\text{H}_4-$ , or alkyl aryloxy group preferably  $-\text{CH}_2\text{C}_6\text{H}_4\text{O}-$ , optionally the L group may be substituted with alkyl groups, branched alkyl groups, or heteroatom containing groups such as hydroxyl, acetoxy, alkyl ether, or halogen,

15

$\text{R}_1$  is hydrogen or a linear or branched alkyl group having a primary chain length equal to or greater than 1 carbon and equal to or less than 15 carbons, preferably equal to or greater than 3 carbons and equal to or less than less than 15 carbons, more preferably equal to or greater than 5 carbons and equal to or less than less than 15 carbons

20

and

$\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are independently a hydrogen, a linear alkyl group, or a branched alkyl group, preferably a linear alkyl group having 1 to 12 carbons or a branched alkyl group having 3 to 12 carbons with the proviso that at least one of  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  is not hydrogen and is a linear alkyl group or a branched alkyl group comprising one or more hydroxyl group.

25

Preferred substituted methylene groups suitable for L are  $-\text{CHMe}-$ ,  $-\text{CMe}_2-$ ,  $-\text{CHEt}-$ ,  $-\text{CHPr}-$ , or  $-\text{CH}(\text{OH})-$ .

Preferred alkyl ether groups for L are ethyleneoxy or propyleneoxy, where the oxygen is attached directly to  $\text{R}_1$ .

5 Preferred aryl groups suitable for L are substituted or non-substituted phenylene groups.

Preferred aryloxy groups are  $-\text{C}_6\text{H}_4\text{O}-$  where the oxygen is attached directly to  $\text{R}_1$ .

Preferred alkylaryl groups are  $-\text{CH}_2\text{C}_6\text{H}_4-$ , or  $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4-$  where the aryl group is attached directly to  $\text{R}_1$ .

10 Preferred alkylaryloxy groups are  $-\text{CH}_2\text{C}_6\text{H}_4\text{O}-$ , or  $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{O}-$  where the oxygen is attached directly to  $\text{R}_1$ .

Preferred linear alkyl groups suitable for  $\text{R}_1$  are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, or undecyl.

Preferred branched alkyl groups suitable for  $\text{R}_1$  are  $-\text{CHMe}_2$ ,  $-\text{CHMeEt}$ ,  $-\text{CH}_2\text{CHMe}_2$ , or  $-\text{CMe}_3$ .

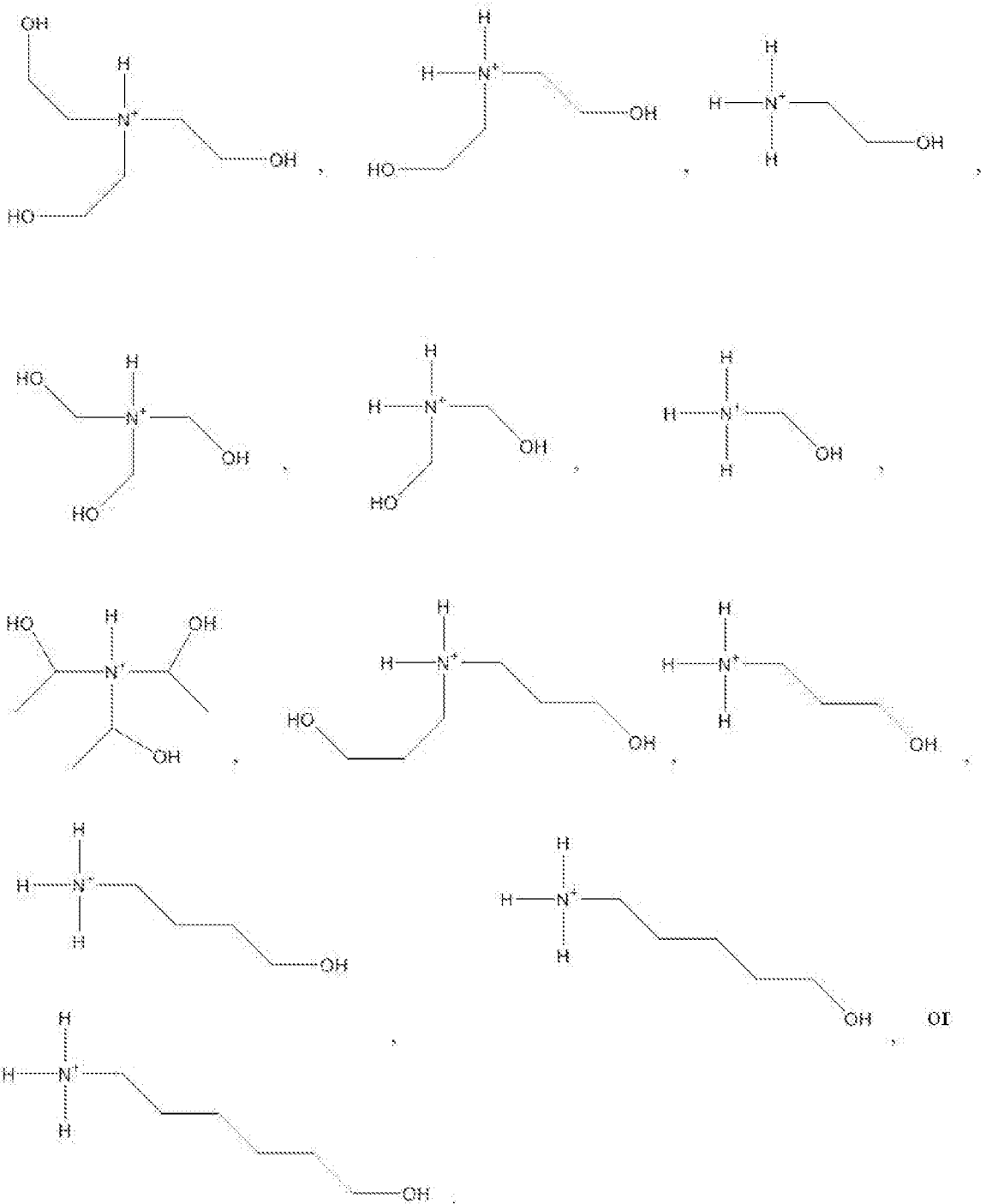
Preferred linear alkyl groups suitable for  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl.

Preferred branched alkyl groups suitable for  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, 2-methylbutyl, 1-ethylpropyl, or 1,2-dimethylpropyl.

20 Preferred linear hydroxyalkyl groups suitable for  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are 1-hydroxymethyl; 1-hydroxyethyl; 2-hydroxyethyl; 1-hydroxypropyl; 2-hydroxypropyl, 3-hydroxypropyl; 1-hydroxy-2-methylethyl; 1-hydroxybutyl; 2-hydroxybutyl; 3-hydroxybutyl; 4-hydroxybutyl; 5-hydroxypentyl; 6-hydroxyhexyl; 7-hydroxyheptyl; 8-hydroxyoctyl; 9-hydroxynonyl; 10-hydroxydecyl; 11-hydroxyundecyl; and 12-hydroxydodecyl.

25 Preferred branched hydroxyalkyl groups suitable for  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are 1-hydroxyisopropyl; 2-hydroxyisopropyl, 1-hydroxyisobutyl; 2-hydroxyisobutyl; 3-hydroxyisobutyl; 1-hydroxysec-butyl; 2-hydroxysec-butyl; 3-hydroxysec-butyl; 2-hydroxytert-butyl; 4-hydroxyisopentyl; and 4-hydroxy, 2-methylbutyl

30 Preferred hydroxyalkyl ammonium ions are represented by the structures herein below:



5 When an amine salt is used, the free amine should have a boiling point of equal to or less than 300°C, preferably equal to or less than 200°C, at ambient pressure.

Preferred carboxylates are derived from, but are not limited to, the following free acids: acetic acid, propionic acid, butanoic acid, 2-methylpropionic acid, pentanoic acid, 2-

methylbutanoic acid, 3-methylbutanoic acid, 2,2-dimethylpropionic acid, hexanoic acid, 2-methylpentanoic acid, 3-methylpentanoic acid, 4-methylpentanoic acid, 3,3-dimethylbutanoic acid, heptanoic acid, 2-methyl hexanoic acid, octanoic acid, 2-ethylhexanoic acid, 2-methylheptanoic acid, 2-propylpentanoic acid, nonanoic acid,  
5 decanoic acid, undecanoic acid, dodecanoic acid, benzoic acid, phenylacetic acid, or methylbenzoic acid.

The primary chain length of the carboxylic acid (aliphatic chain with highest number of carbon atoms tailing away from carboxylate head-group) should be at least 1 carbon, preferably 3 carbons, more preferably 5 carbons. The primary chain length of the carboxylic  
10 acid (aliphatic chain with highest number of carbon atoms tailing away from carboxylate head-group) preferably is equal to or less than 12 carbons, more preferably equal to or less than 11 carbons, more preferably equal to or less than 10 carbons, and more preferably equal to or less than 9 carbons.

Preferably, the free carboxylic acid (i.e., in acid form) has a boiling point of equal to  
15 or less than 300°C, preferably equal to or less than 275°C, at ambient pressure.

Preferred carboxylate ions are, but not limited to, acetate, propionate, butanoate, 2-methylpropionate, pentanoate, 2-methylbutanoate, 3-methylbutanoate, 2,2-dimethylpropionate, hexanoate, 2-methylpentanoate, 3-methylpentanoate, 4-methylpentanoate, 3,3-dimethylbutanoate, heptanoate, 2-methyl hexanoate, octanoate, 2-ethylhexanoate, 2-methylheptanoate, 2-propylpentanoate, nonanoate, decanoate,  
20 undecanoate, dodecanoate, benzoate, phenylacetate, or methylbenzoate.

The steam composition can contain one hydroxyalkyl ammonium carboxylate or a mixture of more than one kind of hydroxyalkyl ammonium carboxylate.

The amount of hydroxyalkyl ammonium carboxylate required in the steam  
25 composition to achieve improvement in bitumen extraction over steam alone is surprisingly low. The steam composition can contain as little as 0.005 weight percent (wt%) of hydroxyalkyl ammonium carboxylate and still demonstrate an improvement in bitumen extraction over use to steam alone in the same process, preferably, the steam composition contains 0.05 wt% or more, more preferably 0.1 wt% or more, more preferably 0.2 wt% or  
30 more, more preferably 0.3 wt% or more, more preferably 0.4 wt% or more, or more preferably 0.5 wt% or more hydroxyalkyl ammonium carboxylate. The steam composition can contain 25 wt% or less, preferably 20 wt% or less, more preferably 15 wt% or less, more

preferably 10 wt% or less, more preferably 5 wt%, and more preferably 1 wt% or less hydroxyalkyl ammonium carboxylate. Excessive amounts of hydroxyalkyl ammonium carboxylate cause the cost of the process to increase so lower concentrations of the hydroxyalkyl ammonium carboxylate are desirable from a cost standpoint. The wt% of hydroxyalkyl ammonium carboxylate is based on total combined weight of steam and alkylene glycol ether.

Desirably, the steam composition is free of glycol ether amine. In general, the process of the present invention is desirably free of glycol ether amine as an extraction aid.

The steam composition can be free from hydrocarbons when injecting the steam composition into a subterranean location. The process of the present invention can be free of injecting hydrocarbons in any manner, whether in a steam composition or otherwise, into a well. Use of hydrocarbons is unnecessary in the present invention.

In its broadest scope, the present invention is independent from how to form the steam composition. For example, an aqueous solution of the hydroxyalkyl ammonium carboxylate can be boiled to create the steam composition; hydroxyalkyl ammonium carboxylate (neat or as an aqueous solution) can be introduced to steam, or any combination thereof.

After injecting the steam composition into a subterranean location containing heavy hydrocarbons, for example bitumen, the process further includes extracting the heavy hydrocarbon, i.e., bitumen, from the subterranean location to above the ground. The steam composition serves to cause the bitumen to become flowable allowing it to be pumped from underground to above ground. The process of the present invention can take the form of a cyclic steam stimulation (CSS) process where bitumen is pumped up the same well that the steam composition is injected, a steam assisted gravity drainage (SAGD) where bitumen is pumped up a second well (or production well) other than the well through which the steam composition is injected down a first well (or injection well) into the ground, or conceivable a combination of both CSS and SAGD type processes.

## EXAMPLES

30

Oil-sands samples are obtained from Syncrude Canada Ltd. and contained between 10 to 12.5 percent oil. The initial oil content of each oil sands sample is measured before

each experiment. Steam soaking experiments are done using a hanging **13/14** mesh basket **30** containing compressed oil sands in a Parr reactor **10** on a heating mantle **20**, as shown in **FIG. 1**. All baskets used in these experiments are made with 74 micron (200 mesh) openings, a height **D** of 48 mm (1.89 inches), and diameter **E** of 28 mm (1.10 inches). The

5 Parr reactor has one pressure gauge **12** and thermocouple **11** in the vapor space to monitor reactor conditions as well as a rupture disk connected to a knock-out pot. There is also a thermocouple in between the reactor and the heating mantle **21** to measure heating mantle surface temperature. A temperature controller (not shown in the drawing) is available to control the system temperature from either thermocouple (vapor or heating mantle surface).

10 Parr reactor vapor temperature, mantle temperature and vapor pressure are recorded during all experiments using a Siemens control system. A temperature controller controls the heating mantle using a vapor temperature set point of 188 °C. For all campaigns, the Parr reactor is loaded with a stainless steel sleeve **15** that holds 150 mL of deionized (DI) water **16** with or without additives.

15 Oil sand batches are homogenized (removal of large rocks, mixing of sands) before being used in experiments to ensure consistency between experiments. The oil sands inside the hanging mesh basket are mechanically compressed using an Instron machine 5543 at 235 lbf for 30 minutes (3 x 10 minute compression interspersed with 10 minute static times with no compression). Once the reactor and oil sands basket is assembled and closed, the

20 system is purged with nitrogen for a few minutes before beginning the heating procedure. Upon reaching 188°C (warm-up time is about 1 hour), where a max pressure of 190 to 195 psig is reached, the reactor is heated for 3 more hours and subsequently allowed to cool down overnight. The steady state pressure is between 150 to 165 psig.

25 Preparing solutions to start the experiment.

For the steam soaking experiments, water and additive are mixed and added to the stainless steel sleeve insert in the following amounts:

- water baseline trials: 150 mL of deionized (DI) water, no additive
- 2.5 wt.% additive experiments: 150 mL of DI water with 3.75 g of additive

30 Note that additive weight fractions are reported with respect to the mass of water present (rather than total solution mass).

*Sample Collection Procedure.*

After the reactor cools down, the heating mantle is lowered, and the Parr reactor is removed and unbolted. After the reactor is opened, the hanging basket of oil sands is placed in an aluminum pan and put into an oven at 110°C for 2 hours to dry out the water from the basket. Then the dried basket is placed into the desiccator for 30 min to cool to room temperature before being homogenized to eliminate any sand clumps. This sand is called the “spent sand sample” and analyzed for remaining oil content via toluene extraction (using 15 g of spent sand in 100 mL of toluene). The spent sand sample shows how much oil remains in the sand bed, and is used to calculate how much oil is extracted from the sand.

10

*Sand Analysis Procedure.*

Before analyzing the spent sand sample, it is placed in the hood for 1 hr to evaporate any trace water from the sample. Next, the sand sample is placed in a 110°C oven for 2 hours to evaporate any additional water. Then the samples are cooled overnight in the desiccator. The dried sand is then homogenized. 100 mL toluene is added to 15 g of the prepared spent sand sample and the sample is placed in a shaker for 30 min at 400 rpm. Two vial aliquots (about 2mL) of each oil/toluene sample are collected. Next, the mass of an empty aluminum pan is recorded. A pipette is used to transport the toluene/oil samples from both vials to an aluminum weigh pan. The pan is weighed immediately to obtain the weight of the initial samples (before too much toluene evaporates). The aluminum pans are then placed in the hood to allow the toluene to evaporate from the samples for at least 1 hour. After all of the visible liquid toluene has evaporated, the aluminum pans are placed in an 80°C oven overnight. The dried samples are weighed to quantify the amount of oil in the spent sands which is used to calculate the amount of produced oil and the results are summarized in Table 1.

25

In the following Examples and Comparative Example ammonium hydroxide is obtained as a 28 to 30% wt% solution in water from Sigma Aldrich, and is diluted with water to the desired concentration for the steam-soaking experiment.

Decanoic acid was obtained from Sigma Aldrich and diluted to the desired concentration for the steam-soaking experiments.

30

All other materials are synthesized as follows and are diluted to the desired concentration in water for the steam-soaking experiments.

#### Preparation of Acetic Acid-Ethanolamine Salt.

Into a 500 mL bottle is loaded deionized water (200 grams), glacial acetic acid (33.05 grams, 0.5504 mole), and ethanolamine (33.62 grams, 0.5504 mole). The mixture is agitated with a stir bar, and the resulting solution used as prepared. This yields an aqueous solution of 25% acetic acid-ethanolamine salt (Example 1).

#### Preparation of Decanoic Acid-Diethanolamine Salt.

Into a 1000 mL flask is loaded deionized water (200 grams), diethanolamine (25.27 grams, 0.2403 mole), and molten decanoic acid (41.40 grams, 0.2403 mole). The flask is placed on a hot-plate with a glass stir-shaft stir blade inserted for overhead stirring. The solution is stirred at room temperature for about 2 hours and then gently warmed until all solids dissolve. The solution is cooled to room temperature and used as prepared. This yields an aqueous solution of 25% decanoic acid-diethanolamine salt (Example 2).

15

#### Preparation of Decanoic Acid-Trimethylamine Salt.

Into a 500 mL bottle is loaded deionized water (120.5 grams), molten decanoic acid (40.95 grams, 0.2377 mole), and 24.0 wt% trimethylamine in water (58.55 grams, 0.2377 mole trimethylamine). The bottle is warmed in 55°C oven with occasional agitation until a solution results. The solution is then cooled to room temperature and used as prepared. This yields an aqueous solution of 25% decanoic acid-trimethylamine salt (Example 3).

20

#### Preparation of Decanoic Acid-Tributylamine Salt.

Into a 500 mL bottle is loaded deionized water (165.0 grams), molten decanoic acid (26.49 grams, 0.1538 mole), and tributylamine (28.51 grams, 0.1538 mole). The bottle is warmed in 55°C oven overnight with occasional agitation to form a dispersion. The dispersion is cooled to room temperature and used as prepared. This yields a dispersion of 25% decanoic acid-tributylamine salt in water (Example 4).

25

Table 1

Example	Additive	Oil Recovery, %
Comp Ex A	no additive	17
Example 1	2.5 wt% acetic acid-ethanolamine salt	17
Example 2	2.5% wt% decanoic acid-diethanolamine salt	22
Com Ex B	2.5 wt% decanoic acid-trimethylamine salt	21
Com Ex C	2.5 wt% decanoic acid-tributylamine salt	36





methylpentanoate, 3,3-dimethylbutanoate, heptanoate, 2-methyl hexanoate, octanoate, 2-ethylhexanoate, 2-methylheptanoate, 2-propylpentanoate, nonanoate, decanoate, undecanoate, dodecanoate, benzoate, phenylacetate, or methylbenzoate.

4. The process of Claim 1 wherein  $R_1$  is a linear or branched alkyl group having a  
5 primary chain length equal to or greater than 5 carbons and equal to or less than 15 carbons.

5 The process of Claim 1 wherein the carboxylate ion in the form of its free carboxylic acid (i.e., in its acid form) has a boiling point of equal to or less than 300°C at ambient pressure and the ammonium ion in the form of its free amine has a boiling point of equal to or less than 300°C at ambient pressure.

10 6. The process of Claim 1 wherein the process is cyclic steam stimulation (CSS) process where the recovered heavy hydrocarbon is pumped up the same well that the steam composition is injected down.

7. The process of Claim 1, wherein the process is a steam assisted gravity drainage (SAGD) process and the steam composition is injected into the ground through a first well  
15 and the heavy hydrocarbon that is displaced from the ground is recovered to above ground through a second well.

8. The process of any previous Claim 1 wherein the heavy hydrocarbon is bitumen.



**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2016/041425

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C09K8/592 E21B43/00  
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, COMPENDEX, INSPEC, 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 4 572 296 A (WATKINS DAVID R [US]) 25 February 1986 (1986-02-25) column 1 - column 5; claims; examples -----	1-8
X	US 4 714 112 A (NIGRINI ANDREW [US] ET AL) 22 December 1987 (1987-12-22) column 4 - column 5; claims; examples -----	1,4-7
A	US 2014/367098 A1 (LIKHAANOVA NATALYA VICTOROVNA [MX] ET AL) 18 December 2014 (2014-12-18) the whole document -----	1-8
A	WO 2014/149524 A1 (SCHLUMBERGER CA LTD [CA]; SCHLUMBERGER SERVICES PETROL [FR]; SCHLUMBER) 25 September 2014 (2014-09-25) the whole document -----	1-8

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  7 October 2016	Date of mailing of the international search report  17/10/2016
---	--

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  Doslik, Natasa
--	--

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2016/041425
---

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4572296	A	25-02-1986	NONE	
US 4714112	A	22-12-1987	NONE	
US 2014367098	A1	18-12-2014	BR 102014014759 A2 US 2014367098 A1	21-07-2015 18-12-2014
WO 2014149524	A1	25-09-2014	AR 095301 A1 WO 2014149524 A1	07-10-2015 25-09-2014