



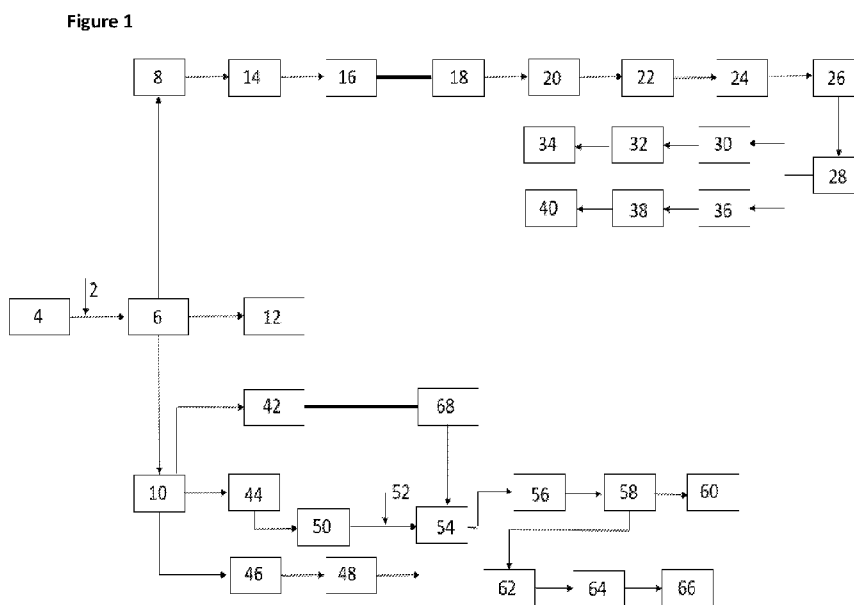
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- (71) **Applicant (for all designated States except US):**  
**PETROLIAM NASIONAL BERHAD (PETRONAS)** [MY/MY]; Tower 1, PETRONAS Twin Towers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY).
- (72) **Inventors; and**  
(71) **Applicants (for US only):** **WONG, Sharizal B Mohd Azam Shah** [MY/MY]; C/O Petroliam Nasional Berhad (PETRONAS), Tower 1, PETRONAS Twin Towers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY). **MAT, TG M Uzaini B TG** [MY/MY]; C/O Petroliam Nasional Berhad (PETRONAS), Tower 1, PETRONAS Twin Towers,

ers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY). **RAFEEN, M Syamzari B** [MY/MY]; C/O Petroliam Nasional Berhad (PETRONAS), Tower 1, PETRONAS Twin Towers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY). **SALAM, Safwan B A** [MY/MY]; C/O Petroliam Nasional Berhad (PETRONAS), Tower 1, PETRONAS Twin Towers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY). **HOLBREY, John** [GB/G-B]; C/O Petroliam Nasional Berhad (PETRONAS), Tower 1, PETRONAS Twin Towers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY). **BYRNE, Emily** [GB/G-B]; C/O Petroliam Nasional Berhad (PETRONAS), Tower 1, PETRONAS Twin Towers, Kuala Lumpur City Centre, Kuala Lumpur, 50088 (MY).

(74) **Agent: MATHYS & SQUIRE LLP;** The Shard, 32 London Bridge Street, London SE1 9SG (GB).

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(54) **Title:** MERCURY REMOVAL FROM HYDROCARBON FLUIDS



(57) **Abstract:** This invention relates to a process for removing mercury from mercury-containing hydrocarbon fluid feeds, and more specifically by use an active organic salt composition.

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## MERCURY REMOVAL FROM HYDROCARBON FLUIDS

### FIELD OF THE INVENTION

This invention relates to a process for removing mercury from mercury-containing hydrocarbon fluid feeds. More specifically, the invention relates to a process of extracting  
5 mercury from a hydrocarbon fluid feed using an active organic salt composition, methods for producing active organic salt compositions and uses thereof.

### BACKGROUND OF THE INVENTION

Liquid and gaseous hydrocarbons obtained from oil and gas fields are often contaminated  
10 with mercury. In particular, liquid and gaseous hydrocarbons obtained from oil and gas fields in and around the Netherlands, Germany, Canada, USA, Malaysia, Brunei and the UK are known to contain mercury. As reported by N. S. Bloom (Fresenius J. Anal. Chem., 2000, 366, 438-443), the mercury content of such hydrocarbons may take a variety of forms. Although elemental mercury tends to predominate, particulate mercury (i.e.  
15 mercury bound to particulate matter), organic mercury (e.g. dimethylmercury and diethylmercury) and ionic mercury (e.g. mercury dichloride) may also be found in naturally occurring hydrocarbon sources. The mercury concentration in crude oils can range from typically below 1 part per billion (ppb) to several thousand ppb depending on the well and location. Similarly, mercury concentrations in natural gas can range from below 1 ng·m<sup>-3</sup>  
20 to greater than 1000 µg·m<sup>-3</sup>.

The presence of mercury in hydrocarbons is problematic due to its toxicity. In addition, mercury is corrosive towards hydrocarbon processing equipment, such as that used in oil and gas refineries. Mercury can react with aluminium components of hydrocarbon  
25 processing equipment to form an amalgam, which can lead to equipment failure. For example, pipeline welds, cryogenic components, aluminium heat exchangers and hydrogenation catalysts can all be damaged by hydrocarbons contaminated with mercury. This can lead to plant shutdown, with severe economic implications, or, in extreme cases, to uncontrolled loss of containment or complete plant failure, with potentially catastrophic  
30 results. Furthermore, products with high levels of mercury contamination are considered to be of poorer quality, with the result that they command a lower price. Mercury can be found in both produced gaseous and liquid hydrocarbon streams. However, the bulk of

mercury tends to accumulate in produced liquid streams such as natural gas condensate and produced waters.

5 A number of approaches to the removal of mercury from hydrocarbons have been proposed. These include: scrubbing techniques using fixed bed columns containing sulfur, transition metal or heavy metal sulfides and iodides on an activated support; oxidation followed by complexation with sulfur-containing compounds; and oxidation followed by solvent extraction.

10 A typical method of processing hydrocarbon fluid feeds, such as natural gases, comprises the following steps. A feed gas is first cooled before entering a separator, wherein the gas is separated into a gas feed (consisting primarily of C<sub>1</sub> to C<sub>4</sub> alkanes), a condensate feed (predominantly comprising C<sub>5</sub> to C<sub>8</sub> alkanes) and a produced water feed. The condensate is then further processed by i) dewatering, ii) removal of solids through filtering and iii)  
15 mercury removal in a mercury removal unit (MRU) before the resulting product is exported. The produced water undergoes the processing steps of i) de-oiling, ii) degassing and iii) mercury removal in a mercury removal unit (MRU) before the treated water is either disposed of or recycled. Finally, the gas separated from the hydrocarbon feed is dehydrated and compressed before being exported.

20

The most common form of attempted mercury removal from both produced gaseous and liquid hydrocarbon fluids in the oil and gas industry is through the use of mercury removal units (MRUs) which are included as units attached to the conduits for transporting and processing hydrocarbon fluids. Mercury removal units involve the use of fixed bed  
25 adsorbents such as activated carbon, zeolite and alumina, through which hydrocarbon fluids comprising a mercury species can flow, removing at least a portion of mercury present, forming cinnabar (HgS) on the fixed bed.

30 Whilst the use of mercury removal units can in some instances be effective at lowering the concentration of mercury in hydrocarbon fluids, reliance on said units also has associated drawbacks. For example, as mercury removal units comprise adsorbents, the amount of mercury which can be removed from a hydrocarbon fluid is dependent, at least

in part, on the amount of adsorbent present and the amount of mercury-containing hydrocarbon fluid which has previously been treated. Accordingly, where the mercury concentration of the hydrocarbon fluids flowing into the units varies, treated hydrocarbon fluids may also have a large variance in mercury concentration. Another problem is that the adsorbents often require premature changing and replacement due to collapse of the solid support or leaching of the active chemical agent by the fluid flow of the hydrocarbons. Collapse of the solid support can also occur due to the presence of other contaminants in the hydrocarbon fluid. The process of replacing the adsorbents is complex and the handling of the spent adsorbents can be hazardous. The mercury removal units also occupy a large area and are heavy, making them unsuitable for inclusion in certain conduits and systems. These units can also be prone to large pressure drops across the adsorbent bed due to damage of adsorbent physical integrity which can result in problems with their operations. All of these issues contribute to high capital and operational costs as well as causing certain health and safety concerns.

15

Other approaches for removing mercury from hydrocarbon fluids, such as crude oil, can be seen for example in US 9,523,043. The process comprises the steps of i) fractionally distilling a crude product containing at least 50 ppbw mercury to form overhead vapor fractions comprising light naphtha having a first concentration of mercury; ii) contacting the overhead vapor fractions with a complexing agent to convert at least a portion of mercury into water soluble mercury in solution, producing a light naphtha product having a reduced concentration of mercury; iii) removing the solution containing water soluble mercury from the crude distillation unit; and iv) recovering the light naphtha product from an upper section of the distillation column. US '043 teaches that the complexing agent is selected from inorganic and organic polysulfides, such as sodium polysulfide, calcium polysulfide, ammonium polysulfide, di-tertbutyl polysulfide (TBPS) and amine polysulfide, or alternatively sodium thiocarbamate, sodium dithiocarbamate, ammonium thiocarbamate, ammonium dithiocarbamate, and mixtures thereof.

US 9,023,123 and US 8,790,427 disclose methods of removing mercury from hydrocarbon fluids such as natural gas. In particular, US 9,023,123 discloses a method comprising the steps of i) recovering a mixture of produced water and mercury-containing natural gas from an underground reservoir; ii) separating the mercury-containing natural gas from the

30

produced water; iii) scrubbing the natural gas with an aqueous solution in an absorber, wherein the aqueous solution comprises a water-soluble sulfur compound to react with at least a portion of mercury present, producing a treated natural gas with a reduced concentration of mercury and a mercury containing sulfur-depleted solution; iv) removing  
5 at least a portion of the mercury containing sulfur-depleted solution as a purge stream v) recirculating at least a portion of the mercury containing sulfur-depleted solution as a recirculating stream; and vi) providing a fresh source of water-soluble sulfur compound as a feed to the absorber for reaction with mercury in the natural gas. The water-soluble sulfur compounds may be selected from sodium hydrosulfide, potassium hydrosulfide,  
10 ammonium hydrosulfide, sodium sulfide, potassium sulfide, calcium sulfide, magnesium sulfide, ammonium sulfide, and mixtures thereof.

US 8,790,427 discloses a method comprising the step of incorporating a mercury removal process with an amine treating unit. In particular, a complexing agent is added to an  
15 adsorber comprising an amine scrubbing solution to remove acid gases such as hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide from the sour feed steam. In an alternative embodiment, the complexing agent is present in a glycol solution feed in a dehydrator unit. The complexing agent is preferably selected from amine polysulfides, sodium hydrosulfide, potassium hydrosulfide, ammonium hydrosulfide, sodium sulfide, potassium sulfide,  
20 calcium sulfide, magnesium sulfide, ammonium sulfide, sodium thiocarbamate, sodium dithiocarbamate, ammonium thiocarbamate, ammonium dithiocarbamate, and mixtures thereof or alternatively mercaptans, organic polysulfides (compounds of the general formula R-S<sub>x</sub>-R' where x is greater than 1 and R and R' are alkyl or aryl groups), sulfanes, and combinations thereof.

25

In addition, a limited number of approaches have been proposed for the removal of mercury from hydrocarbon fluids using ionic liquids. For example, the combination of metal-complexing ligands and ionic liquids coated onto an inert support as adsorbents to remove mercury from coal combustion flue gases has been described in US Patent  
30 Application 2007/0123660 and by Ji et al. (Water, Air, & Soil Pollution: Focus 2008, 8, 349-358 and Ind. Eng. Chem. Res., 2008, 47, 8396-8400).

The term “ionic liquid” as used herein refers to a liquid that is capable of being produced by melting a salt, and when so produced consists solely of ions. An ionic liquid may be formed from a homogeneous substance comprising one species of cation and one species of anion, or it can be composed of more than one species of cation and/or more than one species of anion. Thus, an ionic liquid may be composed of more than one species of cation and one species of anion. An ionic liquid may further be composed of one species of cation, and one or more species of anion. Still further, an ionic liquid may be composed of more than one species of cation and more than one species of anion.

10 The term “ionic liquid” includes compounds having both high melting points and compounds having low melting points, e.g. at or below room temperature. Thus, many ionic liquids have melting points below 200 °C, particularly below 100 °C, around room temperature (15 to 30 °C), or even below 0 °C. Ionic liquids having melting points below around 30 °C are commonly referred to as “room temperature ionic liquids” and are often  
15 derived from organic salts having nitrogen-containing heterocyclic cations, such as imidazolium and pyridinium-based cations. In room temperature ionic liquids, the structures of the cation and anion prevent the formation of an ordered crystalline structure and therefore the salt is liquid at room temperature.

20 Ionic liquids are most widely known as solvents. Many ionic liquids have been shown to have negligible vapour pressure, temperature stability, low flammability and recyclability. Due to the vast number of anion/cation combinations that are available it is possible to fine-tune the physical properties of the ionic liquid (e.g. melting point, density, viscosity, and miscibility with water or organic solvents) to suit the requirements of a particular  
25 application.

There is therefore a need for a more reliable and effective method of removing mercury from hydrocarbon feeds, particularly where the concentration of mercury at the inlet may be variable. In addition, it is desirable to provide a more cost-effective method of extracting  
30 mercury species from hydrocarbon fluids.

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The present invention is based on the surprising discovery that active organic salt compositions comprising a mixture of an ionic liquid and sulfur can be used to increase the amount of mercury extracted from mercury-containing hydrocarbon fluid feeds. It is believed that the use of an ionic liquid as defined herein facilitates an increased interaction  
5 between the activated sulfur species and the hydrocarbon feed, as well as any water present therein, resulting in an increased interaction between the sulfur species formed in the ionic liquid and mercury species present within these feeds. The present invention therefore provides a more effective and reliable method of producing hydrocarbon products meeting industry implemented limitations with regards to mercury concentration  
10 in a more time and cost-effective manner.

Thus, in a first aspect, the present invention provides a process for removing mercury from a mercury-containing hydrocarbon fluid feed, the process comprising the steps of:

(i) contacting the mercury containing hydrocarbon feed with an active organic salt  
15 composition comprising a mixture of an ionic liquid and sulfur, the ionic liquid having the formula:



wherein:  $[\text{Cat}^+]$  represents one or more cationic species; and

$[\text{X}^-]$  represents one or more alkyl carboxylic acid species; and

(ii) separating a hydrocarbon fluid product having a reduced mercury content  
20 compared to the mercury containing hydrocarbon feed.

The process of the invention may be applied to substantially any hydrocarbon feed which comprises mercury, and which is liquid or gaseous under the operating conditions of the  
25 process. Thus, hydrocarbon fluids that may be processed according to the present invention include liquid hydrocarbons, such as liquefied natural gas; light distillates, including liquid petroleum gas, gasoline, and/or naphtha; natural gas condensates; middle distillates, such as kerosene and/or diesel; heavy distillates, such as fuel oil; and crude oils. Hydrocarbon fluids that may be processed according to the present invention also  
30 include gaseous hydrocarbons, such as natural gas and refinery gas. Preferably the hydrocarbon fluid feed comprises a liquid hydrocarbon.

The above-mentioned process may be used as an alternative method of removing mercury from mercury-containing hydrocarbon fluid feeds compared to previous methods comprising the use of mercury removal units. In some embodiments, the process of removing mercury from a mercury-containing hydrocarbon fluid feed does not comprise the use of a mercury removal unit. In an alternative embodiment, the present invention may be used in combination with a mercury removal unit. The inclusion of a first step of at least partly removing mercury from a hydrocarbon feed in accordance with the present invention can reduce the occurrence of premature saturation of mercury adsorbents within the mercury removal unit. In addition the use of a process as defined herein in combination with a mercury removal unit allows greater control with regards to the concentration of mercury in the treated hydrocarbon fluid product, despite varying amounts of mercury within the feed material.

The step of contacting the hydrocarbon feed with an active organic salt composition may in principle be performed at any stage of processing the fluid hydrocarbon feed. In particular, an active organic salt composition as defined above may be injected directly into an underground reservoir. In an alternative embodiment, the active organic salt composition may be injected into the hydrocarbon feed prior to the feed entering a separator, for example to separate the hydrocarbon stream from water which may be present. In a further example, the active organic salt composition may be contacted with the separated condensate feed following a dewatering step, directly prior to the feed entering the mercury removal unit or directly prior to exporting the condensate product. In yet a still further example, the active organic salt composition may be contacted with the separated produced water feed following a de-oiling process step or directly prior to the feed entering the mercury removal unit. In embodiments where the process further comprises a mercury removal unit, the active organic salt composition is preferably contacted with the mercury containing hydrocarbon feed upstream of the mercury removal unit. By first contacting the hydrocarbon feed with the active organic salt composition, the life span of adsorbents present in the mercury removal unit is increased, thereby improving the cost efficiency of the overall process.

In accordance with the present invention, [X<sup>-</sup>] may be selected from one or more carboxylic acid species of a formula [R<sup>1</sup>-CO<sub>2</sub>]<sup>-</sup>, wherein R<sup>1</sup> is selected from a C<sub>1</sub> to C<sub>20</sub> branched or

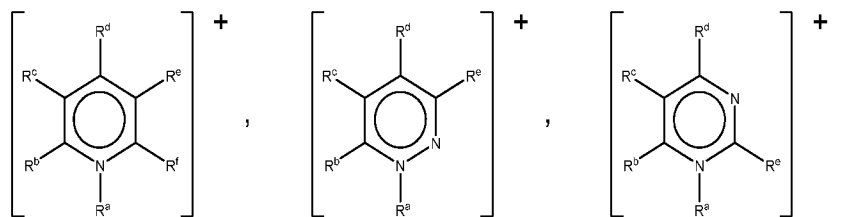
linear chain alkyl. Preferably, R<sup>1</sup> is selected from a C<sub>2</sub> to C<sub>14</sub> linear or branched alkyl, more preferably a C<sub>2</sub> to C<sub>12</sub> linear or branched alkyl. Most preferably, R<sup>1</sup> is selected from hexyl, heptyl, octyl, 2-ethylhexyl and decyl, and combinations thereof.

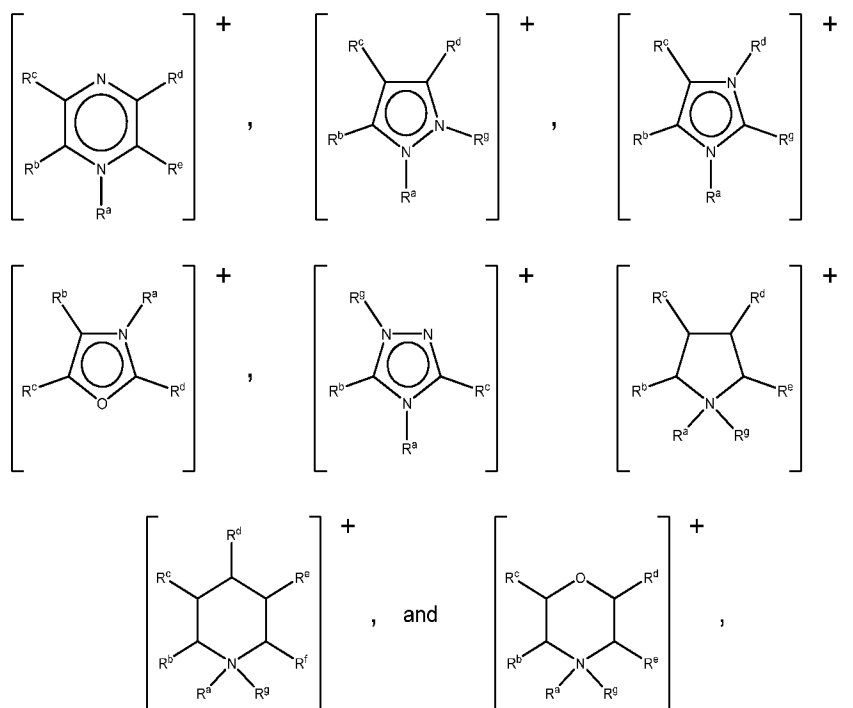
5 In accordance with the present invention, [Cat<sup>+</sup>] may comprise a cationic species selected from: ammonium, azaannulenium, azathiazolium, benzimidazolium, benzofuranium, benzotriazolium, borolium, cinnolinium, diazabicyclodecenium, diazabicyclononenium, diazabicyclo-undecenium, dithiazolium, furanium, imidazolium, indazolium, indolinium, indolium, morpholinium, oxaborolium, oxaphospholium, oxazinium, oxazolium, *iso*-  
 10 oxazolium, oxothiazolium, pentazolium, phospholium, phosphonium, phthalazinium, piperazinium, piperidinium, pyranium, pyrazinium, pyrazolium, pyridazinium, pyridinium, pyrimidinium, pyrrolidinium, pyrrolium, quinazolinium, quinolinium, *iso*-quinolinium, quinoxalinium, selenozolium, sulfonium, tetrazolium, *iso*-thiadiazolium, thiazinium, thiazolium, thiophenium, triazadecenium, triazinium, triazolium, and *iso*-triazolium.

15

In one preferred embodiment of the invention, [Cat<sup>+</sup>] comprises an aromatic heterocyclic cationic species selected from: benzimidazolium, benzofuranium, benzotriazolium, cinnolinium, diazabicyclodecenium, diazabicyclononenium, diazabicyclo-undecenium, dithiazolium, imidazolium, indazolium, indolinium, indolium, oxazinium, oxazolium, *iso*-  
 20 oxazolium, oxathiazolium, phthalazinium, pyrazinium, pyrazolium, pyridazinium, pyridinium, pyrimidinium, quinazolinium, quinolinium, *iso*-quinolinium, quinoxalinium, tetrazolium, *iso*-thiadiazolium, thiazinium, thiazolium, triazinium, triazolium, and *iso*-triazolium.

25 In one embodiment, [Cat<sup>+</sup>] may be selected from the group consisting of:





wherein:  $R^a$ ,  $R^b$ ,  $R^c$ ,  $R^d$ ,  $R^e$ ,  $R^f$  and  $R^g$  are each independently selected from  
 5 hydrogen, a  $C_1$  to  $C_{30}$ , straight chain or branched alkyl group, a  $C_3$  to  $C_8$  cycloalkyl group,  
 or a  $C_6$  to  $C_{10}$  aryl group, wherein said alkyl, cycloalkyl or aryl groups are unsubstituted or  
 may be substituted by one to three groups selected from:  $C_1$  to  $C_6$  alkoxy,  $C_2$  to  $C_{12}$   
 alkoxyalkoxy,  $C_3$  to  $C_8$  cycloalkyl,  $C_6$  to  $C_{10}$  aryl,  $-CN$ ,  $-OH$ ,  $-SH$ ,  $-NO_2$ ,  $C_6$  to  $C_{10}$  aryl and  
 $C_7$  to  $C_{10}$  alkaryl,  $-CO_2(C_1$  to  $C_6)alkyl$ ,  $-OC(O)(C_1$  to  $C_6)alkyl$ , or any two of  $R^b$ ,  $R^c$ ,  $R^d$ ,  $R^e$   
 10 and  $R^f$  attached to adjacent carbon atoms form a methylene chain  $-(CH_2)_q-$  wherein  $q$  is  
 from 3 to 6.

Preferably,  $R^a$ ,  $R^b$ ,  $R^c$ ,  $R^d$ ,  $R^e$ ,  $R^f$  and  $R^g$  are each independently selected from a  $C_1$  to  $C_{20}$   
 straight chain or branched alkyl group, a  $C_3$  to  $C_6$  cycloalkyl group, or a  $C_6$  aryl group,  
 15 wherein said alkyl, cycloalkyl or aryl groups are unsubstituted or may be substituted by  
 one to three groups selected from:  $C_1$  to  $C_6$  alkoxy,  $C_2$  to  $C_{12}$  alkoxyalkoxy,  $C_3$  to  $C_8$   
 cycloalkyl,  $C_6$  to  $C_{10}$  aryl,  $-CN$ ,  $-OH$ ,  $-SH$ ,  $-NO_2$ ,  $-CO_2(C_1$  to  $C_6)alkyl$ ,  $-OC(O)(C_1$  to  $C_6)alkyl$ ,  
 $C_6$  to  $C_{10}$  aryl and  $C_7$  to  $C_{10}$  alkaryl, and wherein one of  $R^b$ ,  $R^c$ ,  $R^d$ ,  $R^e$ ,  $R^f$  and  $R^g$  may also  
 be hydrogen.

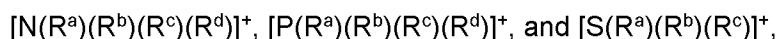
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R<sup>a</sup> is preferably selected from C<sub>1</sub> to C<sub>30</sub>, linear or branched, alkyl, more preferably C<sub>2</sub> to C<sub>20</sub> linear or branched alkyl, still more preferably, C<sub>2</sub> to C<sub>10</sub> linear or branched alkyl, and most preferably R<sup>a</sup> is selected from ethyl, n-butyl, n-hexyl and n-octyl. Further examples include wherein R<sup>a</sup> is selected from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl and n-octadecyl.

In the cations comprising an R<sup>g</sup> group, R<sup>g</sup> is preferably selected from C<sub>1</sub> to C<sub>10</sub> linear or branched alkyl, more preferably, C<sub>1</sub> to C<sub>5</sub> linear or branched alkyl, and most preferably R<sup>g</sup> is a methyl group.

In the cations comprising both an R<sup>a</sup> and an R<sup>g</sup> group, R<sup>a</sup> and R<sup>g</sup> are each preferably independently selected from C<sub>1</sub> to C<sub>30</sub>, linear or branched, alkyl, and one of R<sup>a</sup> and R<sup>g</sup> may also be hydrogen. More preferably, one of R<sup>a</sup> and R<sup>g</sup> may be selected from C<sub>2</sub> to C<sub>20</sub> linear or branched alkyl, still more preferably, C<sub>2</sub> to C<sub>10</sub> linear or branched alkyl, and most preferably C<sub>4</sub> to C<sub>8</sub> linear or branched alkyl, and the other one of R<sup>a</sup> and R<sup>g</sup> may be selected from C<sub>1</sub> to C<sub>10</sub> linear or branched alkyl, more preferably, C<sub>1</sub> to C<sub>5</sub> linear or branched alkyl, and most preferably a methyl group. In a further preferred embodiment, R<sup>a</sup> and R<sup>g</sup> may each be independently selected, where present, from C<sub>1</sub> to C<sub>30</sub> linear or branched alkyl and C<sub>1</sub> to C<sub>15</sub> alkoxyalkyl.

In another embodiment, the cation may be selected from the group consisting of:



wherein: R<sup>a</sup>, R<sup>b</sup>, R<sup>c</sup> and R<sup>d</sup> are as defined above.

25

Preferably, the cation is selected from:



wherein: R<sup>a</sup>, R<sup>b</sup>, R<sup>c</sup> and R<sup>d</sup> are each independently selected from C<sub>1</sub> to C<sub>8</sub>, straight or branched chain, alkyl, including C<sub>2</sub>, C<sub>4</sub> and C<sub>6</sub> alkyl.

30

Most preferably, the acyclic cation is  $[N(R^a)(R^b)(R^c)(R^d)]^+$ .

In a preferred embodiment,  $R^a$ ,  $R^b$ ,  $R^c$  and  $R^d$  are the same, and optionally selected from  $C_1$  to  $C_8$  straight chain alkyl (methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl), such as  $C_2$  to  $C_6$  alkyl (ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl).

In some embodiments,  $[Cat^+]$  may be selected from tetrabutylammonium.

In some embodiments, the ionic liquid,  $[Cat^+][X^-]$ , may be selected from one or more of tetrabutylammonium 2-ethylhexanoate, tetrabutylammonium heptanoate, tetrabutylammonium hexanoate, tetrabutylammonium octanoate and tetrabutylammonium decanoate, or combinations thereof. Preferably the ionic liquid is tetrabutylammonium hexanoate.

Ionic liquids for use according to the present invention preferably have a melting point of 250 °C or less, more preferably 150 °C or less, still more preferably 100 °C or less, still more preferably 80 °C or less, and most preferably, the ionic liquid has a melting point below 30 °C. However, any compound that meets the criteria of being a salt (consisting of a cation and an anion) and which is liquid at the operating temperature and pressure of the process, or exists in a fluid state during any stage of the reaction, may be defined as an ionic liquid for the purposes of the present invention. Most preferably, the ionic liquid is chosen so as to be substantially immiscible with the hydrocarbon fluid, particularly where the hydrocarbon fluid comprises a liquid hydrocarbon.

Ionic liquids for use in the present invention are generally formed via metathesis reactions, an acid-base neutralization reaction or direct combination. Each of these reactions are considered to be well-known within the present field, and so it would be within the knowledge of the skilled person to select suitable starting materials as well as reaction conditions to produce the desired ionic liquid.

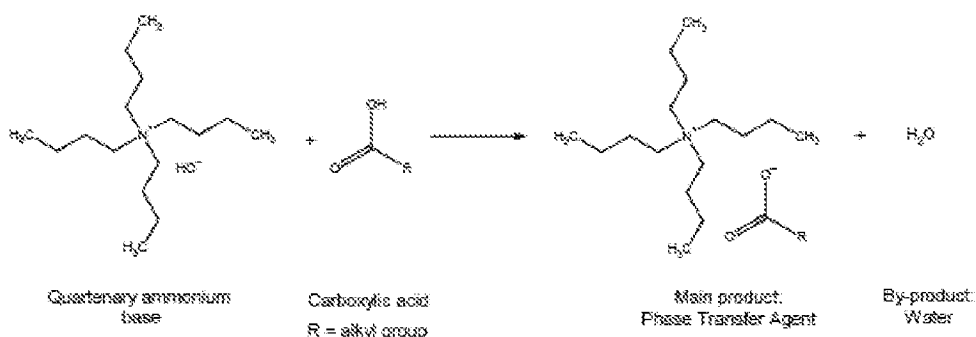
In preferred embodiments, ionic liquids of the present invention are formed using an acid-base neutralization method. Such methods generally comprise combining a hydroxide-

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based ionic liquid, such as a quaternary ammonium hydroxide, and an acid, such as a carboxylic acid. In some examples, the carboxylic acid comprises a formula  $R^1\text{-CO}_2\text{H}$ , wherein  $R^1$  is selected from a  $C_1$  to  $C_{20}$  branched or linear chain alkyl. Preferably,  $R^1$  is selected from a  $C_2$  to  $C_{14}$  linear or branched alkyl, more preferably a  $C_2$  to  $C_{12}$  linear or branched alkyl. Most preferably,  $R^1$  is selected from hexyl, heptyl, octyl, 2-ethylhexyl and decyl, and combinations thereof.

In some embodiments, the hydroxide-based ionic liquid and acid are added in a stoichiometric ratio, preferably at least 1:1 ratio, as illustrated in Reaction Scheme 1 below.

10 In some examples, the acid is present in a slight excess of the hydroxide-based ionic liquid, more preferably, the hydroxide-based ionic liquid and acid may be combined in a molar ratio of ratio of 1:1.5, preferably 1:1.2 and even 1:1.1.



15

Reaction Scheme 1

In general, acid is added dropwise to the hydroxide-based ionic liquid whilst stirring at room temperature ( $25\text{ }^\circ\text{C}$ ). During the reaction, the hydroxide-based ionic liquid and acid may be mixed at a rate of 50 to 500 rpm, preferably from 100 to 300 rpm.

20

In some embodiments, the ionic liquid formed may be selected from tetrabutylammonium 2-ethylhexanoate ([TBA][2-ethylhex]), tetrabutylammonium heptanoate ([TBA][Hep]), tetrabutylammonium hexanoate ([TBA][Hex]), tetrabutylammonium octanoate ([TBA][Octa]) or tetrabutylammonium decanoate ([TBA][Deca]).

Water produced as a by-product of the acid-base neutralisation process can be removed using standard techniques such as rotary evaporation, vacuum heating or distillation. It will be appreciated that it is environmentally friendly for the reaction by-product to be water, and also to avoid the unnecessary formation of halides – which has additional benefits as noted below.

In preferred embodiments, the ionic liquids formed are free of halides. At high temperatures and/or pressures, water may be hydrolyzed and acids, such as HCl, may be formed in the presence of halides. Corrosion caused by these acids can be economically costly, both in terms of replacement parts and process down-time. Furthermore, when working with bromine or chlorine under ambient or near-ambient temperatures and pressures, there are significant difficulties and hazards that are associated with the corrosivity and toxicity of both bromine and chlorine vapours. In addition, bromine is known to oxidise many metals to their corresponding bromide salts, with anhydrous bromine being less reactive toward many metals than hydrated bromine. Dry bromine reacts vigorously with aluminium, titanium, mercury as well as alkaline earths and alkali metals forming metal bromide salts. Accordingly, the presence of halides can result in the damage or failure of plant equipment leading to increased costs and, in extreme cases, plant shutdown.

Elemental sulfur is added to the above-mentioned ionic liquid in order to form activated sulfur compounds which comprise radical anions ( $[S_3]^{-\cdot}$ ) and  $[S_6]^{2-}$ , and combinations thereof. The sulfur radical anions and (poly)sulfide species formed react with elemental and molecular mercury (i.e. organic and inorganic mercury) forming an intermittent mercury (II) cation ( $Hg^{2+}$ ) and complexing with the poly(sulfide) dianions to form mercury (II) sulfide (HgS). Electronic paramagnetic resonance (EPR), also known as electron spin resonance (ESR) may be used to detect the presence of radical anions.

In some embodiments, an ionic liquid and sulfur are contacted with the mercury-containing hydrocarbon fluid feed concurrently, such that the active organic salt composition is formed in-situ. However, preferably, the active organic salt composition is formed by pre-

mixing the ionic liquid and sulfur and is subsequently contacted with the mercury-containing hydrocarbon fluid feed.

It will be understood that as the amount of sulfur present in the active organic salt composition increases, the relative effectiveness of the composition formed increases, and so the amount of sulfur present in the active organic salt composition is not particularly limited. For example, sulfur may be added to the solubility limit of the selected ionic liquid. In some embodiments, the amount of sulfur present in the active organic salt composition may be up to 1500 ppm, preferably up to 2000 ppm, more preferably up to 2500 ppm, even more preferably up to 3500 ppm. In some embodiments, the active organic salt composition comprises sulfur in an amount of from 500 ppm to 1750 ppm by weight preferably 750 ppm to 1250 ppm by weight, more preferably from 850 ppm to 1150 ppm by weight.

In order to reduce the reaction time for forming the pre-mixed active organic salt composition, the ionic liquid and sulfur may be heated to a temperature of 40 to 100 °C, preferably from 60 to 80°C, such as 65 to 75°C and/or the ionic liquid and sulfur may be mixed at a rate of 100 to 1000 rpm, preferably 150 to 800 rpm, more preferably 200 to 400 rpm.

In practice, the active salt composition is completely formed when the composition turns dark greenish-blue after addition of the sulfur source to the ionic liquid.

In preferred embodiments of the present invention, the active organic salt composition is free of halide ions. As discussed above, corrosion caused by the presence of halides can be economically costly, both in terms of replacement parts and process down-time.

The process of the invention may be applied to substantially any hydrocarbon feed which comprises mercury, and which is liquid or gaseous under the operating conditions of the process. Thus, hydrocarbon fluids that may be processed according to the present invention include liquid hydrocarbons, such as liquefied natural gas; light distillates, e.g.

comprising liquid petroleum gas, gasoline, and/or naphtha; natural gas condensates; middle distillates, e.g. comprising kerosene and/or diesel; heavy distillates, e.g. fuel oil; and crude oils. Hydrocarbon fluids that may be processed according to the present invention also include gaseous hydrocarbons, such as natural gas and refinery gas.

5 Preferably the hydrocarbon fluid comprises a liquid hydrocarbon.

Mercury-containing hydrocarbon fluids processed according to the present invention may comprise from 1 part per billion (ppb) weight of mercury to 1,000,000 ppb weight of mercury, for instance 1 to 250,000 ppb weight of mercury; or 500 to 100,000 ppb weight  
10 of mercury. The mercury content of naturally occurring hydrocarbon fluids may take a variety of forms, and the present invention can be applied to the removal of elemental mercury, particulate mercury, organic mercury or ionic mercury from hydrocarbon fluids. In one preferred embodiment, the mercury present is in the form of one or more of elemental, particulate or organic form. Still more preferably, the mercury is in elemental  
15 or organic form. Thus, in one embodiment, the mercury is in elemental form. In a further embodiment, the mercury is in organic form.

In some embodiments, the active organic salt composition and the liquid mercury-containing hydrocarbon fluid feed are contacted in a volume ratio of from 1:1 to 1:10,000,  
20 preferably 1:500 to 1:3000, more preferably 1:1500 to 1:2500.

The active organic salt composition may be added to the mercury-containing hydrocarbon fluid feed in an amount so as to form an active organic salt composition to mercury molar ratio of from 0.5:1 to 3:1, preferably from 1:1 to 2:1. In particular, the active organic salt  
25 composition is added to the mercury-containing hydrocarbon fluid feed in an amount so as to form an active organic salt composition to mercury molar ratio of 1:1.

The active organic salt may be heated prior to contacting the mercury-containing hydrocarbon fluid feed. For example, the active organic salt composition is contacted with  
30 the mercury-containing hydrocarbon fluid feed at a temperature of from 0°C to 250°C, preferably from 0°C to 150°C; more preferably from 25°C to 150°C and most preferably from 25 to 80°C.

As discussed above, upon contact with the sulfur species present in the active organic salt composition, mercury within the hydrocarbon feed may form an intermittent mercury (II) cation ( $\text{Hg}^{2+}$ ) followed by complexing with poly(sulfide) dianions to form mercury (II) sulfide ( $\text{HgS}$ ).  $\text{HgS}$  is a highly stable form of mercury which does not dissolve in either water or hydrocarbons. Upon aggregation with similar or dissimilar particles within the mixture, the hydrodynamic size of the particles exceeds the threshold for precipitation from solution and can then be subsequently removed.

10 Preferably, as a result of the process of the present invention, mercury is removed from the hydrocarbon fluid feed in the form of a mercury sulfide precipitate. Mercury (II) sulfide is found in two forms, cinnabar (alpha form) and metacinnabar (beta form), preferably mercury is removed as beta-mercury (II) sulfide (metacinnabar).

15 The presence of  $\beta$ - $\text{HgS}$  can be determined using powder x-ray diffraction (PXRD). It is expected that peaks at  $26.35^\circ$ ,  $30.52^\circ$ ,  $43.70^\circ$ ,  $51.75^\circ$  and  $54.24^\circ$  would be observed for  $\beta$ - $\text{HgS}$  corresponding to the diffraction planes of (111), (200), (220), (311) and (222) of the bulk  $\beta$ - $\text{HgS}$ .

20 Following contact with the active organic salt composition, the mercury salt precipitate may be at least partially separated from the hydrocarbon fluid product by filtration means (such as the use of a membrane or ceramic filter), centrifugation, cyclone or gravity separation.

25 In addition, or alternatively, mercury may be at least partially separated from the hydrocarbon fluid product by gravity separation, air flotation and electrophoresis separation means.

30 In order to reduce the time required for particulates of sufficient size to form and precipitate out of the hydrocarbon fluid product, the process may further comprise the addition of a flocculent to aid in removal of the mercury sulfide precipitate. Flocculants promote the

agglomeration of the small particulates formed into a 'floc', thereby accelerating the point at which the particulates reach a size sufficient to precipitate out of the hydrocarbon fluid feed.

5 In some embodiments, the flocculant comprises a polymeric flocculant and more preferably the polymeric flocculant comprises a cationic or anionic polymer flocculant. Where the flocculant is selected from a cationic polymer flocculant, the polymer preferably comprises a quaternary ammonium, quaternary sulfonium or quaternary phosphonium groups. In particular, the cationic polymer flocculant may be selected from a cationic  
10 polyacrylamide flocculant or one or more of methacryloyloxyethyl trimethylammonium chloride (DMC), acryloyloxyethyl trimethylammonium chloride (DAC), diallyldimethylammonium chloride (DADMAC), [2-(acryloyloxy)ethyl]trimethylammonium chloride (AETAC), and acrylamide propyl trimethyl ammonium chloride (APTAC).

15 Where the flocculant is selected from an anionic polymer flocculant, the polymer preferably comprises a carboxylate or sulphonate functional group. Preferably, the anionic polymer flocculant may be selected from poly(acrylic acid), poly(acrylamide) or poly(styrene sulfonic acid) (PSSA).

20 The process of the present invention can remove mercury in an amount of greater than 40 %, preferably greater than 50 %, more preferably greater than 60 %, even more preferably greater than 70 % and most preferably greater than 80 %, by weight as compared to the amount of mercury present in the mercury-containing hydrocarbon fluid feed. Without being bound by theory, it is believed that that presence of an ionic liquid  
25 enables translocation of the activated sulfur compounds, increasing interaction with the dissolved mercury in both the hydrocarbon (oleophilic) and aqueous (hydrophilic) phases of the hydrocarbon feed. Thereby increasing the amount of mercury extracted.

The mercury content of the hydrocarbon feed can be determined using various  
30 conventional analytical techniques known in the art, such as cold vapor atomic absorption spectroscopy (CV-AAS), inductively coupled plasma atomic emission spectroscopy (ICP-20 AES), X-ray fluorescence, or neutron activation. If the values produced by the above-

mentioned methods differ, the mercury content of the hydrocarbon feed is determined in accordance with ASTM D 6350.

In a second aspect of the present invention, there is provided a process for producing an active organic salt composition for use in a mercury removal process as defined above, wherein the process comprises the steps of:

- (i) providing a basic ionic liquid having a neutral cation and a basic anion of formula  $[\text{Cat}^+][\text{Bas}^-]$ ;
- 10 (ii) providing a carboxylic acid of formula  $\text{R}^1\text{-CO}_2\text{H}$ , wherein  $\text{R}^1$  is  $\text{C}_1$  to  $\text{C}_{20}$  branched or linear chain alkyl;
- (iii) combining the basic ionic liquid and carboxylic acid to produce an ionic liquid of formula  $[\text{Cat}^+][\text{R}^1\text{-CO}_2^-]$  and water;
- 15 (iv) providing a source of sulfur and adding to the ionic liquid formed in step (iii); and
- (v) obtaining an active organic salt composition.

In this embodiment of the invention, the ionic liquid of the active organic salt composition may be formed via an acid-base neutralization reaction, as described above.

20

The ionic liquid cation,  $[\text{Cat}^+]$ , may be any of the ionic liquid cations described above, and those cations described as preferred above are also preferred in this embodiment of the invention.  $[\text{Bas}^-]$  may be selected from any ionic liquid anion able to readily exchange with a carboxylate anion, for example  $[\text{Bas}^-]$  may be selected from a hydroxide.

25

As discussed above, the carboxylic acid comprises a formula  $\text{R}^1\text{-CO}_2\text{H}$ , wherein  $\text{R}^1$  is selected from  $\text{C}_1$  to  $\text{C}_{20}$  branched or linear chain alkyl. Preferably,  $\text{R}^1$  is selected from a  $\text{C}_2$  to  $\text{C}_{14}$  linear or branched alkyl, more preferably a  $\text{C}_2$  to  $\text{C}_{12}$  linear or branched alkyl.

Most preferably, R<sup>1</sup> is selected from hexyl, heptyl, octyl, 2-ethylhexyl and decyl, and combinations thereof.

In step (iii) of the process, the ionic liquid and carboxylic acid may be present in a stoichiometric ratio. Preferably, the carboxylic acid is present in a slight excess with respect to the ionic liquid, for example the ionic liquid and carboxylic acid may be combined in a molar ratio of ratio of 1:1.5, preferably 1:1.2 and even 1:1.1.

In some embodiments, the step of combining the basic ionic liquid and carboxylic acid to produce an ionic liquid of formula [Cat<sup>+</sup>][R<sup>1</sup>-CO<sub>2</sub><sup>-</sup>], may be accelerated by heating the basic ionic liquid and/or carboxylic acid prior to contacting. Alternatively, once combined, the basic ionic liquid and carboxylic acid may be heated in order to reduce the reaction time for forming an ionic liquid of formula [Cat<sup>+</sup>][R<sup>1</sup>-CO<sub>2</sub><sup>-</sup>] and water (as defined in step (iii)). Preferably, step (iii) is performed at a temperature of 10 to 50°C, such as 15 to 30°C, for example 20 to 25°C.

Alternatively or in addition to heating the basic ionic liquid and/or carboxylic acid, step (iii) may further comprise stirring in order to increase the interaction between the basic ionic liquid and carboxylic acid, thereby reducing the required reaction time for forming an ionic liquid of formula [Cat<sup>+</sup>][R<sup>1</sup>-CO<sub>2</sub><sup>-</sup>] and water. For example, step (iii) may be performed whilst stirring at a rate of from 50 to 500 rpm, more preferably 100 to 300 rpm.

The water formed in step (iii) of the process may be at least partially removed prior to adding a source of sulfur to the ionic liquid formed. Water produced as a by-product of step (iii) can be removed using standard techniques within this field such as, rotary evaporation, vacuum heating or distillation.

With regards to step (iv), the sulfur is preferably selected from elemental sulfur. It has been surprisingly found that significantly increased amounts of bulk mercury can be extracted from a mercury-containing hydrocarbon fluid feed when the sulfur source is selected from elemental sulfur.

In some embodiments, the amount of sulfur present in the active organic salt composition formed may be up to 1500 ppm, preferably 2000 ppm, more preferably 2500 ppm, even more preferably up to 3500 ppm. In some embodiments, the active organic salt composition comprises sulfur in an amount of from 500 ppm to 1750 ppm by weight preferably 750 ppm to 1250 ppm by weight, more preferably from 850 ppm to 1150 ppm by weight.

In order to reduce the reaction time for forming the active organic salt composition, the ionic liquid formed in step (iii) and sulfur may be heated to a temperature of 25 to 100°C, such as 40 to 90°C, for example 60 to 80°C and/or the ionic liquid and sulfur may be mixed at a rate of 100 to 1000 rpm, preferably 100 to 500 rpm, more preferably 200 to 400 rpm.

In a third aspect of the present invention, there is provided the use of an active organic salt composition as defined herein for the removal of mercury from a mercury-containing hydrocarbon fluid.

In a fourth aspect of the present invention, there is provided the use of an active organic salt composition as defined herein as a replacement for a mercury removal unit. The active organic salt of the present invention is capable of removing at least 50% of the mercury present in the hydrocarbon stream. Preferably, the active organic salt composition is capable of removing at least 80% of the mercury present in the hydrocarbon stream. More preferably, the active organic salt composition is capable of removing at least 85%, more preferably at least 90%, and even more preferably at least 95% of the mercury present in the hydrocarbon stream. In some embodiments of the invention, the active organic salt composition is capable of removing at least 96%, 97%, 98% and even at least 99% of the mercury present in the hydrocarbon stream.

In a fifth aspect of the present invention there is provided the use of an active organic salt composition as defined herein to reduce operating process damage to a mercury removal unit.

The present invention will now be described, by way of example only, with reference to the accompanying Figures, in which:

**Figure 1** is a flow cart illustrating a process of removing mercury from a mercury-containing hydrocarbon fluid feed, in accordance with the present invention;

**Figure 2a** illustrates sample vials containing five different ionic liquids;

**Figure 2b** illustrates five active organic salt compositions, in accordance with the present invention, formed by contacting the samples illustrated in Figure 2a with a sulfur source;

**Figure 3** is a UV-vis spectrum of each of the five active organic salt compositions illustrated in Figure 2b;

**Figure 4** shows a bar chart illustrating the amount of  $\text{Hg}^0$  remaining in an onshore condensate following treatment with various mercury extracting agents;

**Figure 5** shows a bar chart illustrating the amount of  $\text{HgCl}_2$  remaining in an onshore condensate following treatment with various mercury extracting agents;

**Figure 6** shows a bar chart illustrating the amount of  $\text{Hg}^0$  remaining in an offshore condensate following treatment with various mercury extracting agents;

**Figure 7** shows a bar chart illustrating the amount of  $\text{HgCl}_2$  remaining in an offshore condensate following treatment with various mercury extracting agents.

**Figure 8a** illustrates the formation of  $\beta$ -HgS precipitates when higher concentrations of an active organic salt composition in accordance with the present invention (PTA-4 + S) is added to a synthetic produced water;

**Figure 8b** illustrates the formation of  $\beta$ -HgS precipitates when lower concentrations of an active organic salt composition in accordance with the present invention (PTA-4 + S) is added to a synthetic produced water;

**Figure 9** illustrates the particle size distribution of  $\beta$ -HgS precipitates formed using active organic salt compositions in accordance with the present invention (PTA-1+S to PTA-4+S).

Figure 1 illustrates an embodiment of a process according to the present invention. In this particular embodiment, an active organic salt composition (2), as defined above, is contacted with a mercury-containing hydrocarbon fluid feed (4) extracted from an underground reservoir. The mercury-containing hydrocarbon fluid feed (4) may comprise a mixture of produced water and mercury-containing natural gas. Of course, in an alternative embodiment, the active organic salt composition may be injected directly into the underground reservoir. Upon reaction with the active organic salt composition, mercury salt precipitate is formed and may be at least partially separated from the hydrocarbon fluid product by filtration means (such as the use of a membrane or ceramic filter), centrifugation, cyclone, gravity separation, air flotation or electrophoresis separation means.

The reduced mercury hydrocarbon feed may subsequently be transferred to a separator (6), wherein the reduced mercury hydrocarbon feed is separated into a gas feed (8) (consisting primarily of C<sub>1</sub> to C<sub>4</sub> alkanes), a liquid feed (10) (comprising C<sub>5</sub> to C<sub>8</sub> alkanes) and solids (12).

Solids (12) present in the reduced mercury hydrocarbon feed may be separated by commonly used techniques within this field, including filtration means, centrifugation, cyclone or gravity separation.

The gaseous feed formed (8) is then transferred to a mercury removal unit (MRU) (14) in order to further reduce the concentration of any mercury species remaining following treatment with the active organic salt composition (2). The mercury removal units may comprise fixed bed adsorbents such as activated carbon, zeolite and alumina, through which the gaseous feed can flow, removing at least a portion of mercury present. In alternative embodiments, the presence of MRU following treatment with the active organic salt composition will not be required.

The gaseous feed can be further treated to meet industry standards by undergoing dewatering (16) and acid gas removal treatments (18) to at least partially remove H<sub>2</sub>S and/or CO<sub>2</sub> present.

Upgrading (20) of the semi-refined gaseous products in order to produce fuels may further be required. These upgrading processes may comprise one or more of catalytic reforming, isomerisation, fuel blending, hydrocracking and fluid catalytic cracking.

5

Following the upgrading process, the mixture of fuels may optionally be transferred to a further mercury removal unit (MRU) (22), if further reduction of mercury content is required.

10 The treated gas is then cooled using a heat-exchanger, such as a cold box (24), and undergoes low-temperature fractionation, for example cascade refrigeration using propylene and ethylene as refrigerants. Non-condensable gases, such as hydrogen, nitrogen, and carbon monoxide and relatively pure methane are first separated from the higher hydrocarbons present. At the next stage, C<sub>2</sub> hydrocarbons (ethylene and ethane)  
15 are separated from the remaining higher hydrocarbons (26). The separated C<sub>1</sub> and C<sub>2</sub> products (28) may be further processed. For example, ethylene (30) separated may undergo further mercury removal treatment by passing through a MRU (32) to produce a final ethylene product (34). Similarly, isolated methane may be used to form ammonia (36) via a Haber process. The ammonia formed may be further treated using a mercury  
20 removal unit (MRU) (38) to produce a final ammonia product (40).

The liquid feed (10) may be separated into crude oil (42), a condensate feed (44) (predominantly comprising C<sub>5</sub> to C<sub>8</sub> alkanes) and a produced water feed (46).

25 The produced water feed (46) may optionally be transferred to a further mercury removal unit (MRU) (48), if further reduction of mercury content is required. The treated produced water feed may then be either disposed of or recycled (as discussed further below).

The condensate feed (44) may also optionally be transferred to a further mercury removal  
30 unit (MRU) (50) and/or contacted with an active organic salt composition (52), as defined above, if further reduction of mercury content is required.

The treated condensate can then be separated (54) into hydrocarbon products for example using flash distillation or fractional distillation. The stream collected from the bottom of the distillation tower is heavy naphtha fuel (56).

5

The separated naphtha fuel (56) may optionally be transferred to a further mercury removal unit (MRU) (58), if further reduction of mercury content is required, to produce a final naphtha fuel product (60).

10 Following the further mercury removal treatment (58), where present, the reduced mercury naphtha formed may undergo additional refining/upgrading processes, including hydro-treating processes to reduce the amount of sulphur present, catalytic cracking and/or hydrocracking to reduce the presence of larger hydrocarbon compounds, and optionally  
15 blending with other streams (62), in order to produce a fuel meeting all of the requisite chemical, physical, economic and inventory requirements of the required hydrocarbon product. In addition, the refined/upgraded product may further undergo treatment in a mercury removal unit (MRU) (64), if necessary. The hydrocarbon product may then be separated (66) into hydrocarbon products, for example using flash distillation or fractional distillation.

20

With regards to the crude oil (42) separated, further processing in a desalter (68) is performed, wherein small inorganic salts, such as NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> are removed from the crude oil by extraction into an aqueous phase. In some embodiments, wastewater from the produced water feed (46) may be used to remove inorganic salts from crude oil.

25

The treated crude oil may then be combined with the treated condensate and separated (54) into hydrocarbon products for example using flash distillation or fractional distillation.

Alternatively or in addition to the above, in some embodiments the active organic salt  
30 composition may be contacted with the fluid feed directly prior to the feed entering the

mercury removal unit. In this way, the occurrence of premature saturation of mercury adsorbents within the mercury removal units can be reduced.

## **EXAMPLES**

5

### **Example 1**

#### **Formation of active organic salt compositions**

Active organic salt compositions according to the present invention are formed by contacting an ionic liquid having the formula  $[\text{Cat}^+][\text{X}^-]$ , wherein  $[\text{Cat}^+]$  represents one or more cationic species and  $[\text{X}^-]$  represents one or more alkyl carboxylic acid species, with a sulfur source. The formation of the active organic salt composition can be determined by a change in colour of the composition to dark greenish-blue. This colour change is believed to be due to the formation of trisulfide radical anions ( $[\text{S}_3]^{-\cdot}$ ).

In the present examples, five types of ionic liquid (PTA-1 to PTA-5) (indicated in Table 1 below) were contacted with elemental sulfur to produce a concentration of 1000 ppm wt elemental sulphur in the ionic liquid. The mixtures were then mixed at a rate of from 200 to 400 rpm and heated to 70 °C until a dark-greenish blue mixture was obtained (indicating the formation of the active salt composition).

20

Table 1

<b>Ionic Liquid</b>	<b>Formulations</b>
PTA-1	$[\text{N}_{4444}][2\text{-ethylhexanoate}]$
PTA-2	$[\text{N}_{4444}][\text{heptanoate}]$
PTA-3	$[\text{N}_{4444}][\text{hexanoate}]$
PTA-4	$[\text{N}_{4444}][\text{octanoate}]$
PTA-5	$[\text{N}_{4444}][\text{decanoate}]$

25

As can be clearly observed in Figure 2a, prior to contact with a sulfur source, the colour of the above ionic liquids varies from clear to yellow. Following addition of the sulfur source and heating to 70 °C, a colour change to a dark-greenish blue is observed for each of the examples (Figure 2b) indicating the presence of trisulfide radical anions ( $[\text{S}_3]^{-\cdot}$ ).

30

The formation of sulfur radical anions, trisulfide radical anions ( $[S_3]^{-\cdot}$ ) and (poly)sulfide anions ( $[S_6]^{2-}$ ), was verified using Ultraviolet-visible (UV-vis) spectroscopy. Research by Boros *et al.* 2010, reported the observation of a broad absorption band at 616 nm indicating the presence of ( $[S_3]^{-\cdot}$ ) in tributylethylphosphonium diethylphosphate (~1 wt%) and a further adsorption band at 485 nm representing the presence of ( $[S_6]^{2-}$ ) anions. Figure 3 clearly illustrates that each of the active organic salt compositions (PTA-1 +S to PTA-5+S) produce spectra comprising absorption bands around 470 nm and 615 nm, which correlates with earlier research. Without being bound by theory, it is believed that the slight shifts in the measured absorption peaks is due to the use of a different solvent (*i.e.* an ionic liquid) compared to the earlier research of Boros *et al.* 2010.

## Example 2

### Removal of mercury from an onshore natural gas condensate

In the present examples, the effectiveness of three types of mercury extracting agent, in particular aqueous  $Na_2S$ , aqueous  $K_2S$ , TMT15 ( $C_3N_3S_3Na_3$ ) (all known in the art) and active organic salt compositions in accordance with the present invention, were compared. The mercury extracting agent in each example was added to an onshore condensate in a mass ratio of 1:1 with regards to the amount of mercury present within the condensate. The selected onshore condensate feedstock comprised approximately 1000  $\mu g/kg$  of  $Hg^0$  or approximately 1000  $\mu g/kg$  of  $HgCl_2$ .

The active organic salt compositions of the present invention that were analysed are provided in Table 2 below. The sulfur source added in each example was elemental sulfur. The samples were prepared by adding sulfur to the ionic liquid whilst stirring at 200 to 400 rpm until the concentration of sulfur in the ionic liquid reached 1000 ppb wt. and heating the mixture to up to 70°C until a dark-greenish blue mixture was obtained (the active salt composition).

Table 2

5

Active Organic Salt Composition	Formulations
PTA-1 + S	[N <sub>4444</sub> ][2-ethylhexanoate]
PTA-2 + S	[N <sub>4444</sub> ][heptanoate]
PTA-3 + S	[N <sub>4444</sub> ][hexanoate]
PTA-4 + S	[N <sub>4444</sub> ][octanoate]
PTA-5 + S	[N <sub>4444</sub> ][decanoate]
PTA-6 + S	[P <sub>66614</sub> ][2-ethylhexanoate]

In each example the mercury extracting agent and onshore condensate were combined before shaking for 15 to 20 seconds at room temperature (25 °C). The shaking was then stopped, and the precipitated mercury salt separated from the condensate and ionic liquid by gravimetric settling. The majority of the ionic liquid and condensate was then decanted from the samples leaving only a small volume containing the precipitated mercury salt suspended therein. The suspension was then air dried to remove any remaining liquid.

15

The amount of Hg<sup>0</sup> (µg/kg) remaining in the onshore condensate following treatment with each of the mercury extracting agents is illustrated in Figure 4 and Table 3 below.

Table 3

Mercury Extracting Agent	Remaining [Hg <sup>0</sup> ] in onshore condensate post treatment / µg kg <sup>-1</sup> , (n ≥ 2)								
	Na <sub>2</sub> S	K <sub>2</sub> S	C <sub>3</sub> N <sub>3</sub> S <sub>3</sub> Na <sub>3</sub>	[N <sub>4444</sub> ][2-eh]+S	[N <sub>4444</sub> ][hep]+S	[N <sub>4444</sub> ][hex]+S	[N <sub>4444</sub> ][oct]+S	[N <sub>4444</sub> ][dec]+S	[P <sub>66614</sub> ][2-eh]+S
<b>Average</b>	381.82	398.83	262.29	71.30	48.34	45.53	0.32	10.79	15.17
<b>Std. Dev.</b>	24.97	68.48	12.76	8.37	5.36	1.84	0.36	8.47	3.21

20

It is immediately apparent that the active organic salt compositions falling within the scope of the present invention provide superior extraction of elemental mercury from the onshore condensate. In particular, following treatment with the comparative extracting agents, the amount of Hg<sup>0</sup> remaining in the condensate ranged from 262.29 to 398.83 µg/kg. In

complete contrast, use of the active organic salt compositions reduced the amount of Hg<sup>0</sup> present in the onshore condensate to between 0.32 and 71.30 µg/kg.

Similarly, the amount of HgCl<sub>2</sub> (µg/kg) remaining in the onshore condensate following treatment with each of the mercury extracting agents is illustrated in Figure 5 and Table 4 below.

Table 4

	Remaining [HgCl <sub>2</sub> ] in onshore condensate post treatment / µg kg <sup>-1</sup> , (n ≥ 2)								
Mercury Extracting Agent	Na <sub>2</sub> S	K <sub>2</sub> S	C <sub>3</sub> N <sub>3</sub> S <sub>3</sub> Na <sub>3</sub>	[N <sub>4444</sub> ][2-eh]+S	[N <sub>4444</sub> ][hep]+S	[N <sub>4444</sub> ][hex]+S	[N <sub>4444</sub> ][oct]+S	[N <sub>4444</sub> ][dec]+S	[P <sub>66614</sub> ][2-eh]+S
<b>Average</b>	643.42	701.79	404.67	0.00	0.00	0.29	0.00	0.01	0.00
<b>Std. Dev.</b>	59.42	69.16	22.49	0.00	0.00	0.37	0.00	0.01	0.00

10 Once again, the amount of HgCl<sub>2</sub> present in the onshore condensate was notably lower following treatment with the active organic salt composition, compared with Na<sub>2</sub>S, K<sub>2</sub>S and TMT15.

**Example 3**

15 Removal of mercury from an offshore natural gas condensate

In the present examples an offshore condensate comprising approximately 1000 µg/kg of Hg<sup>0</sup> or approximately 1000 µg/kg of HgCl<sub>2</sub> was treated with mercury extracting agents as defined in Example 2.

20 The amount of Hg<sup>0</sup> (µg/kg) remaining in the offshore condensate following treatment with each of the mercury extracting agents is illustrated in Figure 6 and Table 5 below.

Table 5

	Remaining [Hg <sup>0</sup> ] in offshore condensate post treatment / $\mu\text{g kg}^{-1}$ , (n ≥ 2)								
Mercury Extracting Agent	Na <sub>2</sub> S	K <sub>2</sub> S	C <sub>3</sub> N <sub>3</sub> S <sub>3</sub> Na <sub>3</sub>	[N <sub>4444</sub> ][2-eh]+S	[N <sub>4444</sub> ][hep]+S	[N <sub>4444</sub> ][hex]+S	[N <sub>4444</sub> ][oct]+S	[N <sub>4444</sub> ][dec]+S	[P <sub>66614</sub> ][2-eh]+S
<b>Average</b>	229.96	403.89	529.55	42.78	24.17	22.76	3.15	5.39	4.55
<b>Std. Dev.</b>	33.54	61.11	21.28	5.02	2.68	0.92	3.64	4.24	0.96

With regards to treating offshore condensates, use of the active organic salt composition of the present invention was significantly more effective at reducing elemental mercury present (3.15 to 42.78  $\mu\text{g/kg}$ ) compared to Na<sub>2</sub>S, K<sub>2</sub>S and TMT15 (229.96 to 529.55  $\mu\text{g/kg}$ ).

The amount of HgCl<sub>2</sub> ( $\mu\text{g/kg}$ ) remaining in the offshore condensate following treatment with each of the mercury extracting agents is illustrated in Figure 7 and Table 6 below.

10

Table 6

	Remaining [HgCl <sub>2</sub> ] in offshore condensate post treatment / $\mu\text{g kg}^{-1}$ , (n ≥ 2)								
Mercury Extracting Agent	Na <sub>2</sub> S	K <sub>2</sub> S	C <sub>3</sub> N <sub>3</sub> S <sub>3</sub> Na <sub>3</sub>	[N <sub>4444</sub> ][2-eh]+S	[N <sub>4444</sub> ][hep]+S	[N <sub>4444</sub> ][hex]+S	[N <sub>4444</sub> ][oct]+S	[N <sub>4444</sub> ][dec]+S	[P <sub>66614</sub> ][2-eh]+S
<b>Average</b>	544.19	595.50	631.36	0.00	0.00	0.32	0.00	0.00	0.00
<b>Std. Dev.</b>	50.16	52.60	26.39	0.00	0.00	0.41	0.00	0.00	0.00

The use of an active organic salt composition as defined in the present claims was again significantly more effective in reducing the amount of HgCl<sub>2</sub> present in the offshore condensate. In particular, with regards to PTA-1 + S, PTA-2 + S, PTA-4 + S, PTA-5 + S and PTA-6 + S no measurable amount of HgCl<sub>2</sub> was detected and only trace amounts

15

(0.41  $\mu\text{g}/\text{kg}$ ) of  $\text{HgCl}_2$  were detected in the offshore condensate following treatment with PTA-3 + S.

#### Example 4

##### 5 Controlling the formation of $\beta$ -HgS solids

As discussed above, as a result of the process of the present invention, mercury is removed from the hydrocarbon fluid feed in the form of a mercury sulfide precipitate, preferably as beta-mercury (II) sulfide (metacinnabar).

10 Following contact with the active organic salt composition, the mercury salt precipitate formed may be at least partially separated from the hydrocarbon fluid product by filtration means (such as the use of a membrane or ceramic filter), centrifugation, cyclone or gravity separation. Accordingly, increasing the particle size of the  $\beta$ -HgS solids formed could facilitate the removal of these compounds from the reduced mercury hydrocarbon feed.

15

In this regard, it has surprisingly been found that the ionic liquid present in the active organic salt composition at least partially affects the volume mean particle size of the  $\beta$ -HgS precipitate produced.

20 It is considered readily apparent that the amount of  $\beta$ -HgS solids formed (as a black precipitate) is dependent, at least in part, on the concentration of active organic salt composition added and the initial concentration of mercury in the hydrocarbon fluid feed. For example, Figure 8a clearly illustrates that increased amounts of  $\beta$ -HgS precipitate are formed when a higher concentration of an active organic salt composition in accordance  
25 with the present invention (PTA-4 + S) is added compared to examples using lower concentrations of the active organic salt composition (Figure 8b).

The formation of  $\beta$ -HgS precipitates in each sample was observed.

The precipitate comprised irregular shaped aggregates of various sizes. In order to determine the effect of the ionic liquid on the particle size distribution of the precipitate, active organic salt compositions (PTA-1+S to PTA-4+S, defined above) were added to a synthetic produced water in a mass ratio of 1:1 with regards to the amount of mercury present within the produced water. The active organic salt compositions were added to the produced water in the concentration defined above before shaking for 15 to 20 seconds at room temperature (25 °C) . The resulting precipitate formed was analysed using laser diffraction (LD) and compared to standard  $\beta$ -HgS particles. The results of this analysis are illustrated in Figure 9.

10

As can clearly be observed, the volume mean particle size of the  $\beta$ -HgS precipitate varies from 8.26  $\mu\text{m}$  (PTA-2+S) to 16.55  $\mu\text{m}$  (PTA-1+S). Without being bound by theory, it is believed that the different particle size distributions in the examples is a result of different rates of particle growth (aggregation) via Ostwald ripening. Accordingly, the present invention can be tailored to increase the particle size of the mercury precipitate formed and thereby facilitate the removal of mercury from a mercury-containing hydrocarbon fluid feed.

15

Accordingly, the present invention provides an improved method of extracting mercury from mercury-containing hydrocarbon fluid feeds. As the defined active organic salt compositions are more adept at extracting mercury, the use of such compositions is more effective and reliable at producing hydrocarbon products which meet industry implemented regulations when the concentration of mercury in the feed varies. Furthermore, given that the use of active organic salt compositions as defined herein further reduces the amount of mercury present in the treated hydrocarbon feed compared to other known extracting methods/agents, the requirement of multiple or repeated extraction steps in order to meet the required mercury concentration is avoided. In this way, use of organic salt compositions as defined herein provides a more time and cost-effective method of processing hydrocarbon feedstocks.

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25

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**CLAIMS**

1. A process for removing mercury from a mercury-containing hydrocarbon fluid feed, the process comprising the steps of:

5

- (i) contacting the mercury containing hydrocarbon feed with an active organic salt composition comprising a mixture of an ionic liquid and sulfur, the ionic liquid having the formula:

10



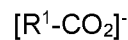
wherein:  $[\text{Cat}^+]$  represents one or more cationic species; and  
 $[\text{X}^-]$  represents one or more alkyl carboxylic acid species;  
and

15

- (ii) separating a hydrocarbon fluid product having a reduced mercury content compared to the mercury containing hydrocarbon feed.

2. A process according to Claim 1, wherein  $[\text{X}^-]$  represents one or more carboxylic acid species of formula:

20



wherein  $\text{R}^1$  is selected from  $\text{C}_1$  to  $\text{C}_{20}$  branched or linear chain alkyl.

25

3. A process according to Claim 2, wherein  $\text{R}^1$  is selected from  $\text{C}_2$  to  $\text{C}_{14}$  linear or branched alkyl, preferably  $\text{C}_2$  to  $\text{C}_{12}$  linear or branched alkyl.

4. A process according to Claim 2 or Claim 3, wherein  $\text{R}^1$  is selected from hexyl, heptyl, octyl, 2-ethylhexyl and decyl, and combinations thereof.

30

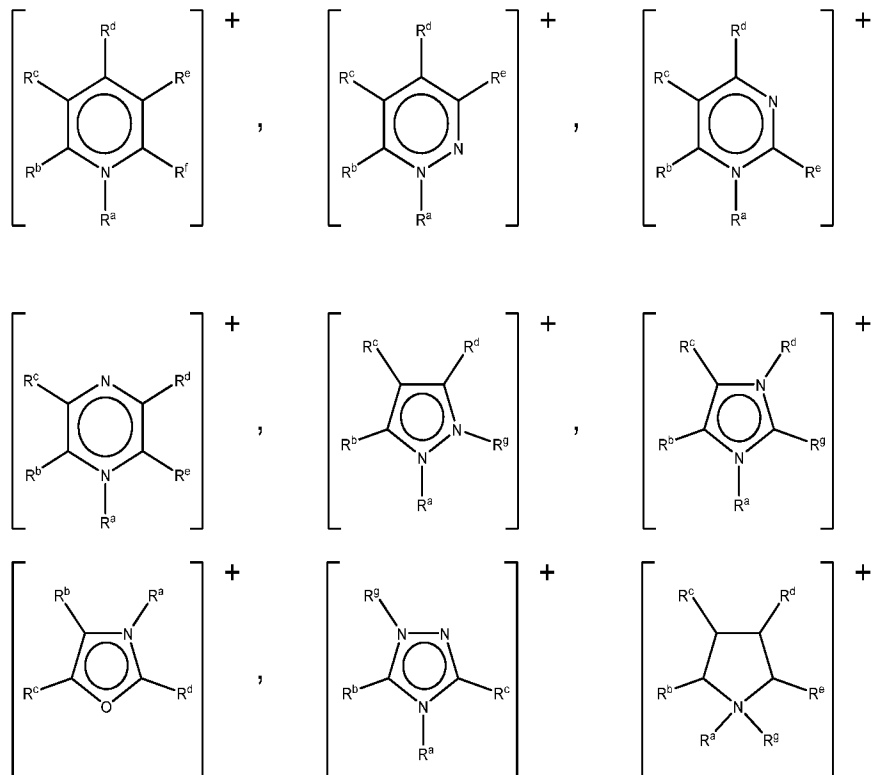
5. A process according to any one of the preceding claims, wherein  $[\text{Cat}^+]$  comprises a cation selected from the group consisting of: ammonium, azaannulenium,

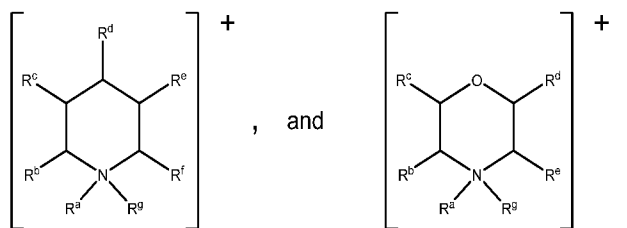
azathiazolium, benzimidazolium, benzofuranium, benzotriazolium, borolium, cinnolinium, diazabicyclodecenium, diazabicyclononenium, diazabicyclo-  
 undecenium, dithiazolium, furanium, imidazolium, indazolium, indolinium, indolium,  
 morpholinium, oxaborolium, oxaphospholium, oxazinium, oxazolium, *iso*-  
 5 oxazolium, oxothiazolium, pentazolium, phospholium, phosphonium, phthalazinium, piperazinium, piperidinium, pyranium, pyrazinium, pyrazolium, pyridazinium, pyridinium, pyrimidinium, pyrrolidinium, pyrrolium, quinazolinium, quinolinium, *iso*-quinolinium, quinoxalinium, selenozolium, sulfonium, tetrazolium, *iso*-thiadiazolium, thiazinium, thiazolium, thiophenium, triazadecenium, triazinium, triazolium, and *iso*-triazolium.

10

6. A process according to Claim 5 wherein [Cat<sup>+</sup>] is selected from the group consisting of:

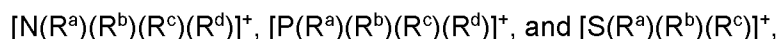
15





wherein:  $\text{R}^a, \text{R}^b, \text{R}^c, \text{R}^d, \text{R}^e, \text{R}^f$  and  $\text{R}^g$  are each independently selected from hydrogen, a  $\text{C}_1$  to  $\text{C}_{30}$ , straight chain or branched alkyl group, a  $\text{C}_3$  to  $\text{C}_8$  cycloalkyl group, or a  $\text{C}_6$  to  $\text{C}_{10}$  aryl group, wherein said alkyl, cycloalkyl or aryl groups are unsubstituted or may be substituted by one to three groups selected from:  $\text{C}_1$  to  $\text{C}_6$  alkoxy,  $\text{C}_2$  to  $\text{C}_{12}$  alkoxyalkoxy,  $\text{C}_3$  to  $\text{C}_8$  cycloalkyl,  $\text{C}_6$  to  $\text{C}_{10}$  aryl,  $-\text{CN}$ ,  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{NO}_2$ ,  $\text{C}_6$  to  $\text{C}_{10}$  aryl and  $\text{C}_7$  to  $\text{C}_{10}$  alkaryl,  $-\text{CO}_2(\text{C}_1$  to  $\text{C}_6)$ alkyl,  $-\text{OC}(\text{O})(\text{C}_1$  to  $\text{C}_6)$ alkyl, or any two of  $\text{R}^b, \text{R}^c, \text{R}^d, \text{R}^e$  and  $\text{R}^f$  attached to adjacent carbon atoms form a methylene chain  $-(\text{CH}_2)_q-$  wherein  $q$  is from 3 to 6.

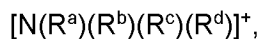
7. A process according to any one of Claims 1 to 5, wherein the cation is selected from the group consisting of:



wherein:  $\text{R}^a, \text{R}^b, \text{R}^c$  and  $\text{R}^d$  are as defined in Claim 6.

20

8. A process according to Claim 7, wherein  $[\text{Cat}^+]$  is selected from:



wherein  $\text{R}^a, \text{R}^b, \text{R}^c$  and  $\text{R}^d$  are each independently selected from  $\text{C}_1$  to  $\text{C}_8$ , straight or branched chain, alkyl.

25

9. A process according to Claims 7 and 8, wherein  $\text{R}^a, \text{R}^b, \text{R}^c$  and  $\text{R}^d$  are the same, and optionally selected from  $\text{C}_1$  to  $\text{C}_8$  straight chain alkyl (methyl, ethyl, n-propyl,

n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl), such as C<sub>2</sub> to C<sub>6</sub> alkyl (ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl).

- 5 10. A process according to any one of Claims 1 to 5 and 7 to 9, wherein [Cat<sup>+</sup>] is tetrabutylammonium.
- 10 11. A process according to any one of Claims 1 to 5 and 7 to 10, wherein the ionic liquid [Cat<sup>+</sup>][X<sup>-</sup>] is selected from one or more of tetrabutylammonium 2-ethylhexanoate, tetrabutylammonium heptanoate, tetrabutylammonium hexanoate, tetrabutylammonium octanoate and tetrabutylammonium decanoate, or combinations thereof; preferably wherein the ionic liquid is tetrabutylammonium hexanoate.
- 15 12. A process according to any one of Claims 1 to 11, wherein the ionic liquid has a melting point of 250°C or less, preferably 100°C or less, and more preferably 30°C or less.
- 20 13. A process according to any one of Claims 1 to 12, wherein the ionic liquid is formed via an acid-base neutralization reaction.
14. A process according to any one of Claim 1 to 13, wherein the ionic liquid is free of halide ions.
- 25 15. A process according to any one of Claims 1 to 14, wherein the sulfur is added as elemental sulfur.
16. A process according to any one of Claims 1 to 15, wherein the active organic salt composition is formed by pre-mixing the ionic liquid and sulfur.
- 30 17. A process according to Claim 16, wherein the pre-mixed ionic liquid and sulfur is heated to a temperature of 60 to 80°C, such as 65 to 75°C.
18. A process according to Claim 16 or Claim 17, wherein the pre-mixed ionic liquid and sulfur is mixed at 100 to 1000 rpm, preferably 200 to 400 rpm.

19. A process according to any one of Claims 1 to 18, wherein the active organic salt composition comprises sulfur in an amount of up to 2000 ppm weight; and preferably from 750 ppm to 1250 ppm weight.
- 5 20. A process according to any one of Claims 1 to 19, wherein the sulfur is present in the form of ions selected from  $[S_6]^{2-}$  and  $[S_3]^\circ$ , and combinations thereof.
21. A process according to any one of Claims 1 to 20, wherein the active organic salt composition is free of halide ions.
- 10 22. A process according to any one of Claims 1 to 21, wherein the mercury-containing hydrocarbon fluid feed comprises one or more of:
- (i) a liquefied natural gas;
  - (ii) a light distillate comprising liquid petroleum gas, gasoline, and/or naphtha;
  - 15 (iii) a natural gas condensate;
  - (iv) a middle distillate comprising kerosene and/or diesel;
  - (v) a heavy distillate; and
  - (vi) a crude oil.
- 20 23. A process according to any one of Claims 1 to 22, wherein the mercury concentration in the mercury-containing hydrocarbon fluid feed is in the range of from 1 to 1,000,000 parts per billion weight; such as from 1 to 250,000 parts per billion weight.
- 25 24. A process according to any one of Claims 1 to 23, wherein the mercury-containing hydrocarbon fluid feed comprises at least one of elemental mercury, particulate mercury, organic mercury, inorganic mercury, or ionic mercury.
- 30 25. A process according to any one of Claims 1 to 24, wherein the active organic salt composition and the liquid mercury-containing hydrocarbon feed are contacted in a volume ratio of from 1:1 to 1:10,000, preferably 1:500 to 1:3000, more preferably 1:1500 to 1:2500.

26. A process according to any one of Claims 1 to 25, wherein the active organic salt composition is contacted with the mercury-containing hydrocarbon feed at a temperature of from 0°C to 250°C, preferably from 0°C to 150°C; more preferably from 25°C to 150°C and most preferably from 25 to 80°C.
- 5
27. A process according to any one of Claims 1 to 26, wherein the active organic salt composition is contacted with the mercury-containing hydrocarbon feed upstream of a mercury removal unit.
- 10
28. A process according to any one of Claims 1 to 26, wherein the process does not comprise a mercury removal unit.
29. A process according to any one of Claims 1 to 28, wherein the mercury is removed as a mercury sulfide precipitate; and preferably beta-mercury (II) sulfide (metacinnabar).
- 15
30. A process according to Claim 29, wherein the mercury sulfide precipitate is removed by way of one or more of gravity separation, centrifuging, filtering, air flotation and electrophoresis.
- 20
31. A process according to Claim 29 or Claim 30 wherein a flocculent is used to aid in removal of the mercury sulfide precipitate; preferably wherein the flocculant comprises a polymeric flocculant and more preferably wherein the polymeric flocculant comprises a cationic or anionic polymer flocculant.
- 25
32. A process for producing an active organic salt composition for use in the process according to any one of Claims 1 to 31, the process comprising the steps of:
- 30
- (i) providing a basic ionic liquid having a neutral cation and a basic anion of formula  $[\text{Cat}^+][\text{Bas}^-]$ ;
  - (ii) providing a carboxylic acid of formula  $\text{R}^1\text{-CO}_2\text{H}$ , wherein R is  $\text{C}_1$  to  $\text{C}_{20}$  branched or linear chain alkyl;
  - (iii) combining the basic ionic liquid and carboxylic acid to produce an ionic liquid of formula  $[\text{Cat}^+][\text{R}^1\text{-CO}_2^-]$  and water;

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- (iv) providing a source of sulfur and adding to the ionic liquid formed in step (iii); and
- (v) obtaining an active organic salt composition.

- 5 33. A process according to Claim 32, wherein in step (iii), the acid is added in excess, such as a ratio of 1:1.5, preferably 1:1.2 and even 1:1.1.
34. A process according to Claim 32 or Claim 33, wherein step (iii) is performed at a temperature of 10 to 50°C, such as 15 to 30°C, for example 20 to 25°C.
- 10 35. A process according to any one of Claims 32 to 34, where step (iii) is performed whilst stirring, such as at a rate of 50 to 500 rpm, more preferably 100 to 300 rpm.
36. A process according to any one of Claims 32 to 35, wherein the water is removed after step (iii) and prior to step (iv).
- 15 37. A process according to any one of Claims 32 to 36, wherein the source of sulfur is elemental sulfur.
- 20 38. A process according to any one of Claims 32 to 37, wherein step (iv) is performed at a temperature of 25 to 100°C, such as 40 to 90°C, for example 60 to 80°C.
39. A process according to any one of Claims 32 to 38, where step (iv) is performed whilst mixing, such as at a rate of 100 to 500 rpm, more preferably 200 to 400 rpm.
- 25 40. Use of an active organic salt composition as described in any one of Claims 1 to 39 for the removal of mercury from a mercury-containing hydrocarbon fluid.
41. Use of an active organic salt composition as described in any one of Claims 1 to 39 as a replacement for a mercury removal unit.
- 30 42. Use of an active organic salt composition as described in any one of Claims 1 to 39 to reduce operating damage to a mercury removal unit.

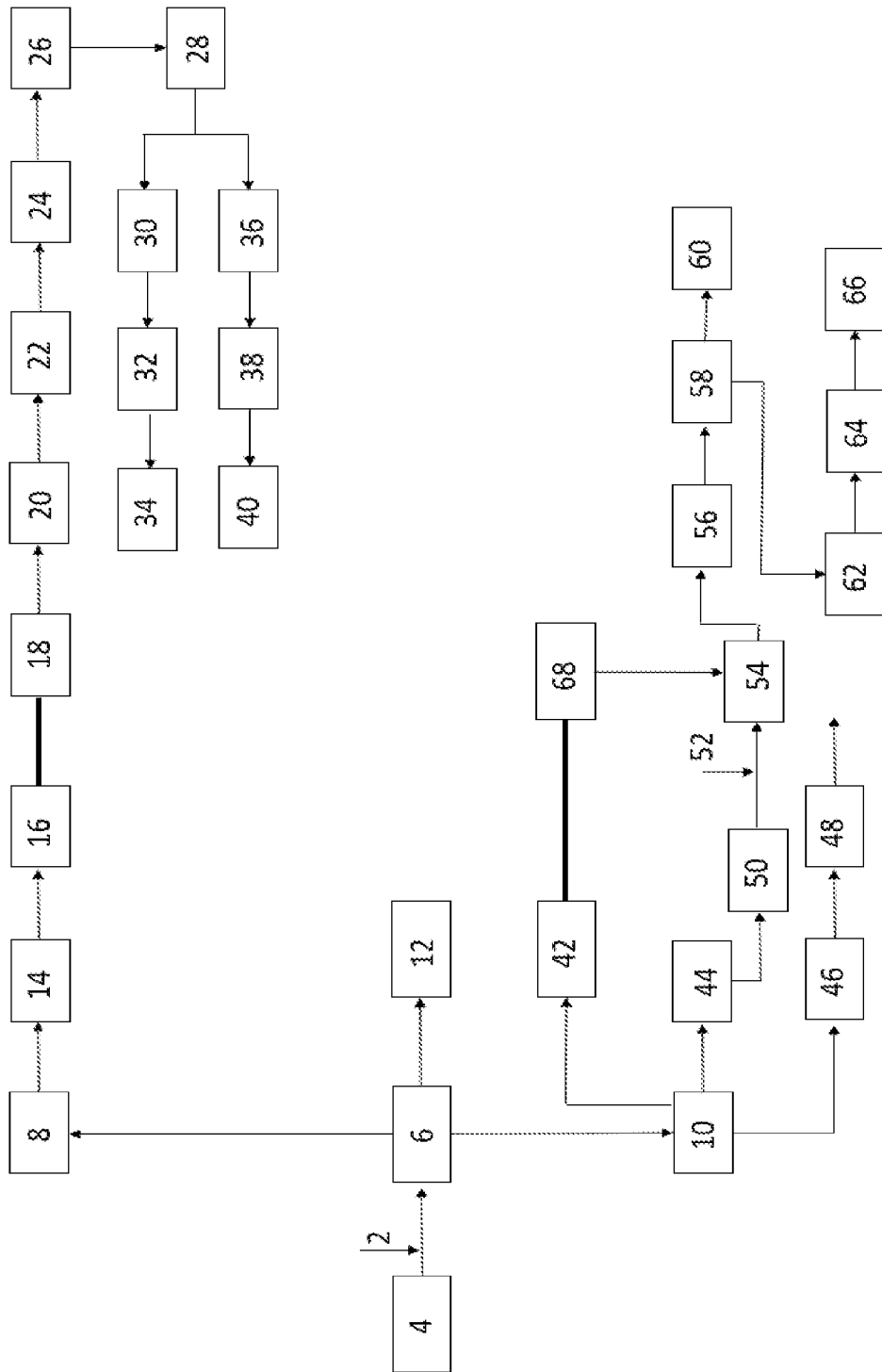


Figure 1

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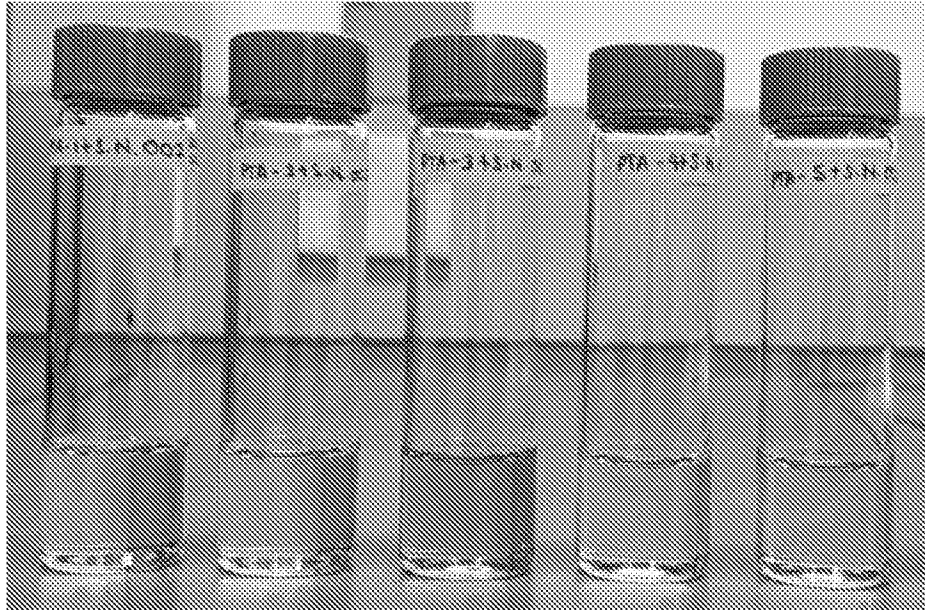


Figure 2a

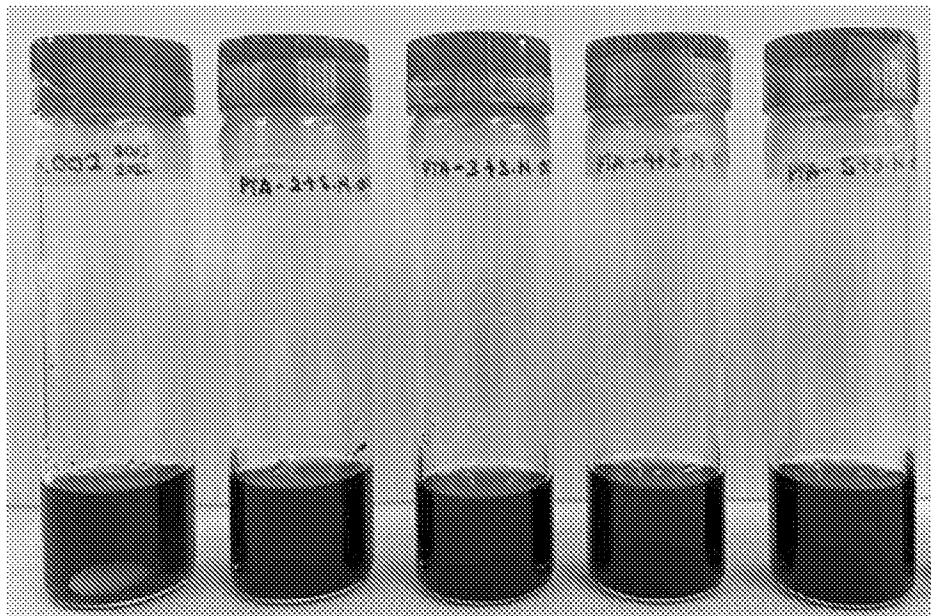


Figure 2b

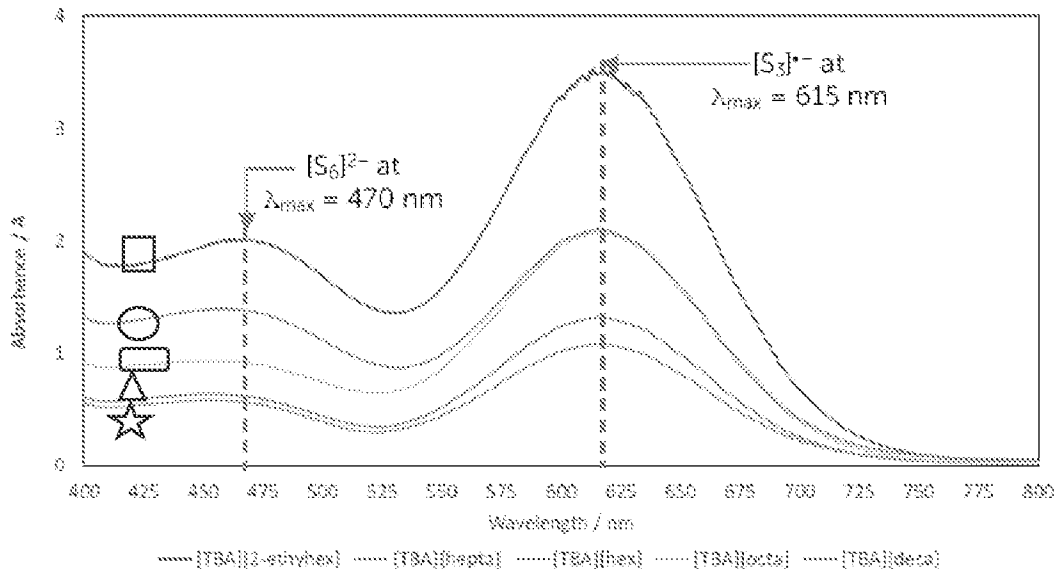


Figure 3

- [TBA][2-ethyhex]
- [TBA][hepta]
- ▭ [TBA][hex]
- △ [TBA][octa]
- ☆ [TBA][deca]



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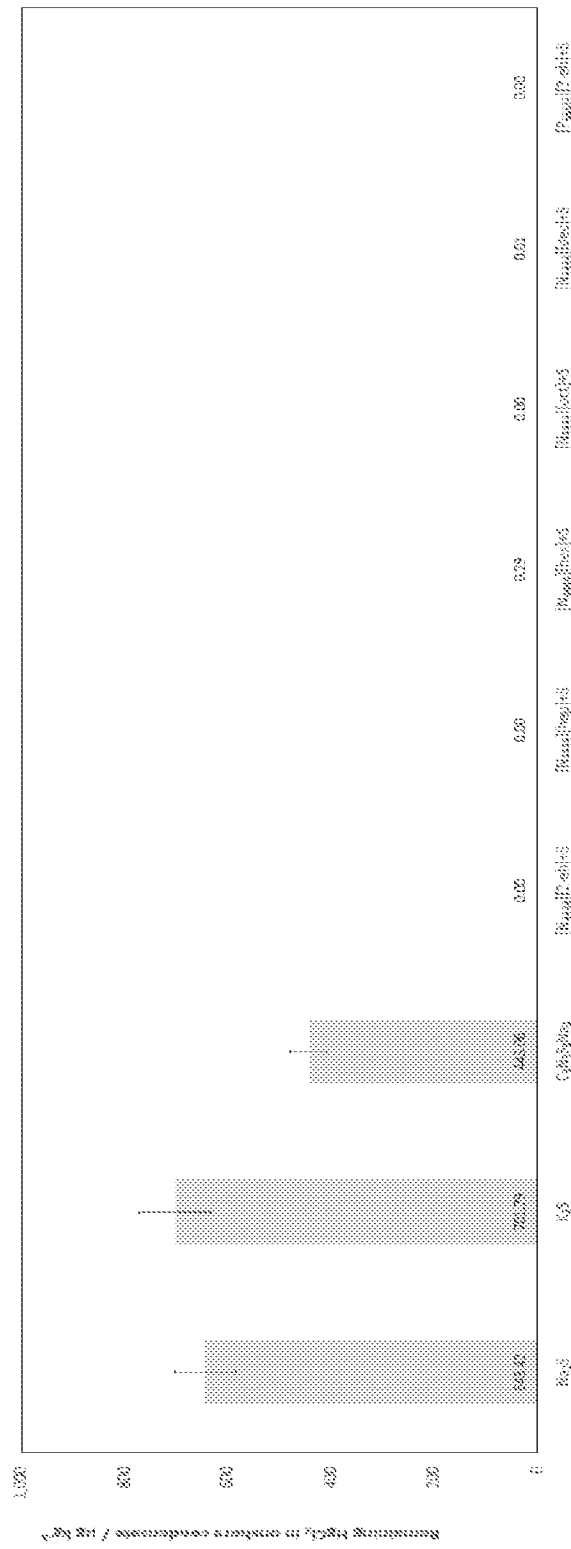


Figure 5

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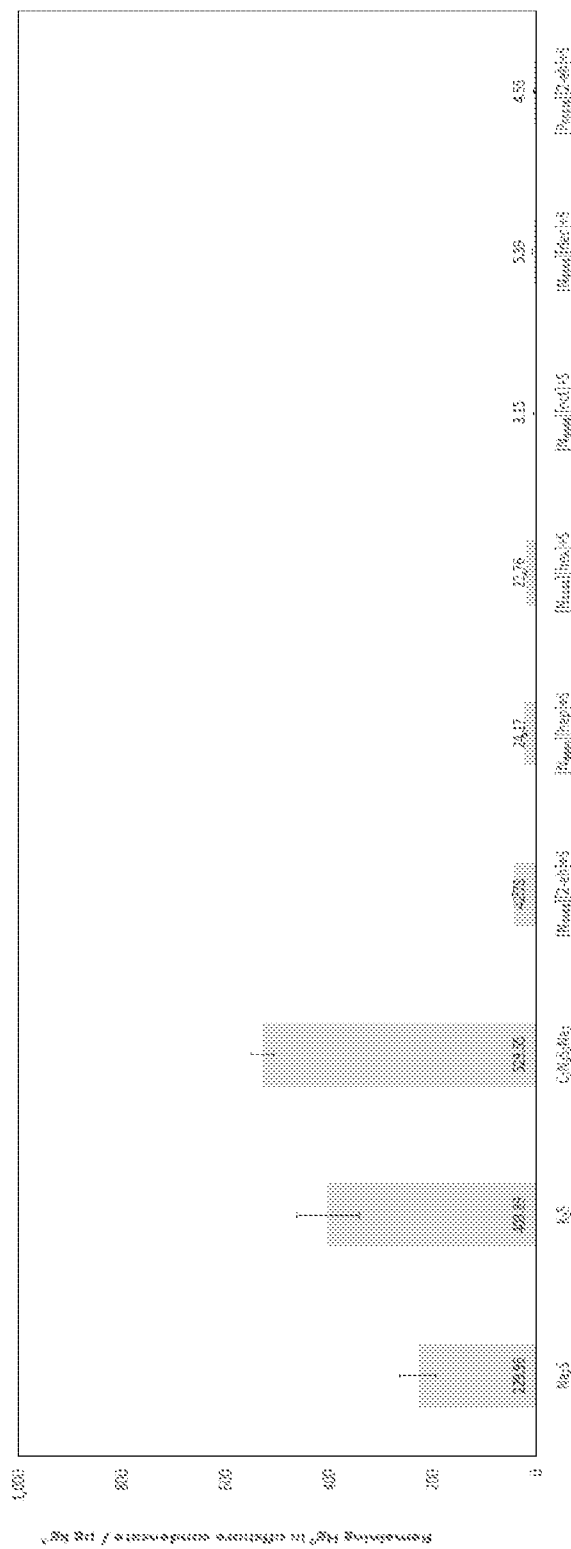


Figure 6

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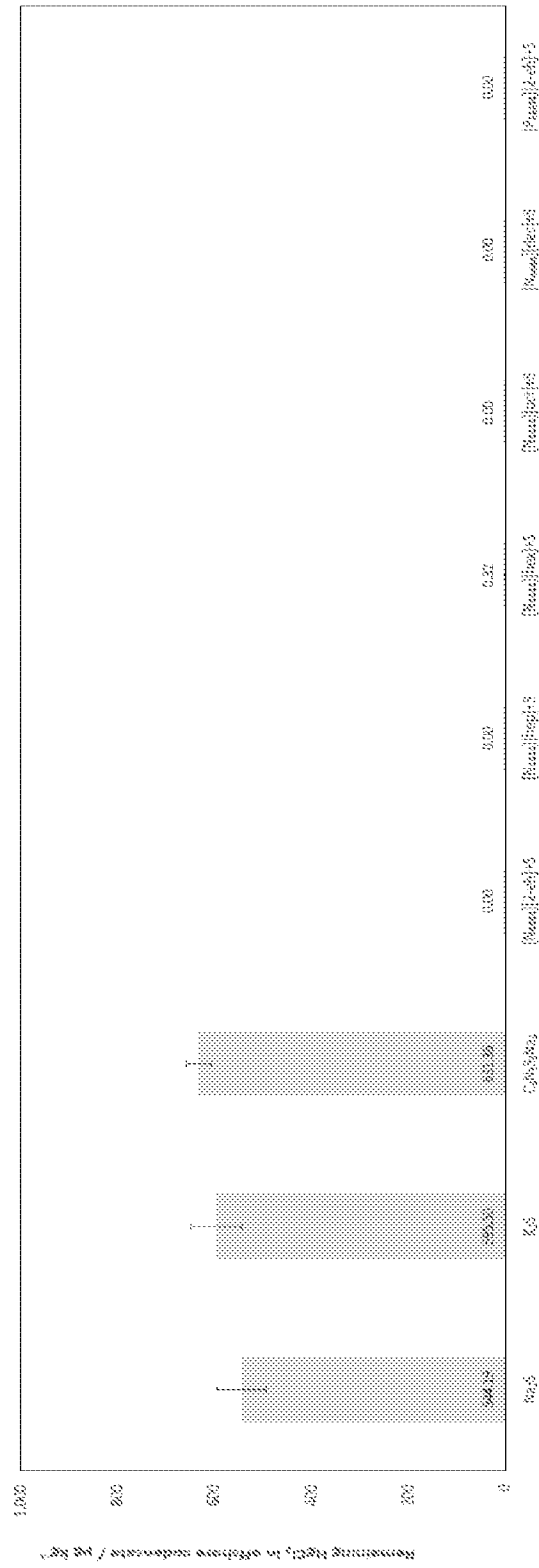
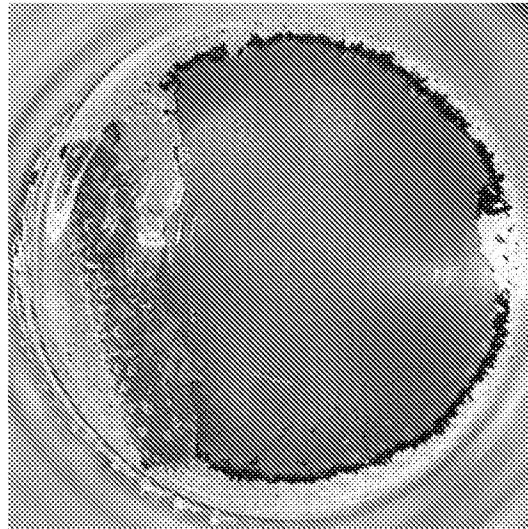
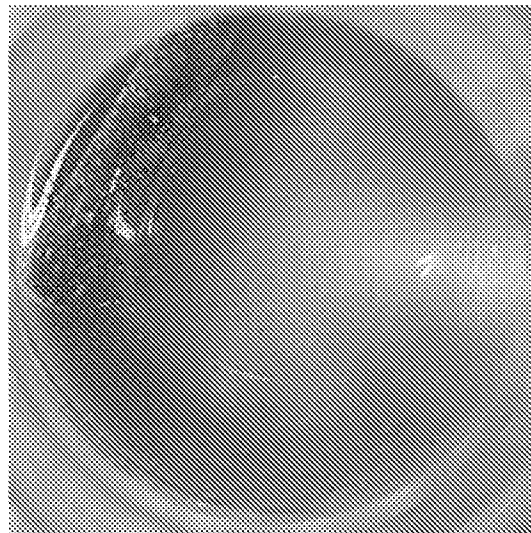


Figure 7

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**Figure 8a**



**Figure 8b**

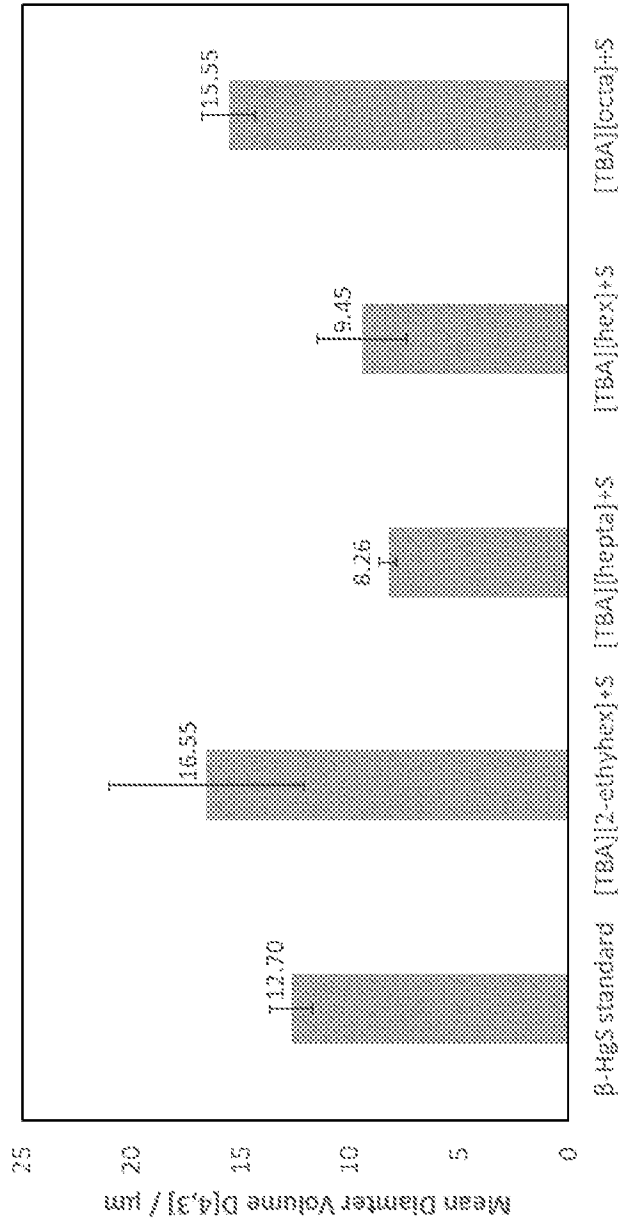


Figure 9

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2024/055606

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> C10G 21/27(2006.01)  According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C10G 21/27(2006.01); B01D 15/04(2006.01); B01D 53/64(2006.01); C07C 7/152(2006.01); C07F 19/00(2006.01); C10G 21/20(2006.01); C10G 25/00(2006.01); C10G 29/06(2006.01)  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: mercury, hydrocarbon, cation, anion, ionic liquid, sulfur		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0121485 A1 (ROBIN D. R. et al.) 17 May 2012 (2012-05-17) claim 1; paragraphs [0005], [0062], [0084], [0087]	1-4
A	US 2017-0037323 A1 (THE QUEEN'S UNIVERSITY OF BELFAST) 09 February 2017 (2017-02-09) claims 72, 87	1-4
A	US 2018-0051216 A1 (PETROLIAM NASIONAL BERHAD (PETRONAS)) 22 February 2018 (2018-02-22) claims 1, 12, 20	1-4
A	US 5989506 A (MARKOV, J.) 23 November 1999 (1999-11-23) claim 1	1-4
A	US 5082569 A (HOMEIER, E. H. et al.) 21 January 1992 (1992-01-21) claim 1	1-4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search <b>11 September 2024</b>		Date of mailing of the international search report <b>13 September 2024</b>
Name and mailing address of the ISA/KR <b>Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea</b> Facsimile No. +82-42-481-8578		Authorized officer <b>HEO, Joo Hyung</b> Telephone No. +82-42-481-5373

**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.: **6, 8, 17, 30, 33**  
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:  
  
Claims 6, 8, 17, 30, 33 are regarded to be unclear because the claims refer to multiple dependent claims which do not comply with PCT Rule 6.4(a).
  
3.  Claims Nos.: **5, 7, 9-16, 18-29, 31, 32, 34-42**  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/IB2024/055606**

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