

Process, Method, and System for Removing Heavy Metals from Fluids

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims benefit under 35 USC 119 of US Patent Application
5 Serial No. 12/883,921, with a filing date of September 16, 2010. This application claims
priority to and benefits from the foregoing, the disclosures of which are incorporated herein
by reference.

TECHNICAL FIELD

10 [002] The invention relates generally to a process, method, and system for removing
heavy metals such as mercury and the like from hydrocarbon fluids such as crude oil.

BACKGROUND

15 [003] Heavy metals such as lead, zinc, mercury, silver, arsenic and the like can be
present in trace amounts in all types of fuels such as crude oils. The amount can range from
below the analytical detection limit (0.5 µg/kg) to several thousand ppb depending on the
feed source. It is desirable to remove the trace elements of these metals from crude oils.

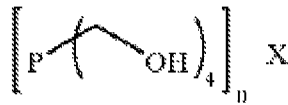
[004] Various methods for removing trace metal contaminants in liquid hydrocarbon
feed prior to fractional distillation have been developed. U.S. Pat. No. 6,350,372 B1
20 discloses utilizing a solubilized sulfur compound in combination with an absorbent carrier.
U.S. Pat. No. 4,474,896 claims the use of absorbent compositions, mainly polysulfide based,
for removal of elemental mercury from gaseous and liquid hydrocarbon streams. The use of
absorbent includes a number of less than desirable attributes. Absorbent beds tend to get
clogged by solid particulates in the crude, thus impeding the flow of the feed. Absorbents
25 can also be very costly due to the large quantity needed. In U.S. Pat. No. 4,915,818, removal
of mercury from liquid hydrocarbon condensate is disclosed. In this method, the liquid
hydrocarbons are treated with a dilute aqueous solution of alkali metal sulfide salt.

[005] There is still a need for improved methods for trace elements extraction from
hydrocarbons.

SUMMARY OF THE INVENTION

[006] In one embodiment, the invention relates to a method to reduce or remove
trace elements such as mercury from a crude oil, comprising mixing the crude oil having a
first concentration of the trace element with a composition comprising a compound of

Formula (I) in an aqueous solvent for a sufficient amount of time to form an oil-water emulsion with the water containing a complex formed by the compound of Formula (I) chemically reacting with the trace elements



[007] (I).

[008] The water containing the heavy metal complex is separated from the crude oil in a phase separation device, for a crude oil having reduced concentration of the trace element.

[009] In yet another embodiment, the composition further includes a complexing additive selected from the group of amine or ammonium derivatives.

BRIEF DESCRIPTION OF THE DRAWINGS

[010] Figure 1 is a graph correlating the mercury concentrations in oil and water at different THPS concentrations at different periods for Example 4.

[011] Figure 2 correlates the mercury concentrations in oil and water at different THPCl concentrations at different periods for Example 5.

DETAILED DESCRIPTION

[012] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[013] “Crude oil” refers to natural and synthetic liquid hydrocarbon products including but not limited to petroleum products, intermediate petroleum streams such as residue, naphtha, cracked stock; refined petroleum products including gasoline, other fuels, and solvents. The liquid hydrocarbon products can be directly from oil wells or after the products have been further processed or derived. The term “petroleum products” refer to crude oil, solid, and semi-solid hydrocarbon products including but not limited to tar sand, bitumen, etc. The term “petroleum products” also refer to petroleum products derived from coal.

[014] “Trace element” refers to the heavy metals such as mercury, lead, zinc, silver, etc. to be removed from the crude oil or for the concentration to be significantly reduced.

[015] Mercury sulfide may be used interchangeably with HgS, referring to mercurous sulfide, mercuric sulfide, or mixtures thereof. Normally, mercury sulfide is

present as mercuric sulfide with a stoichiometric equivalent of one mole of sulfide ion per mole of mercury ion.

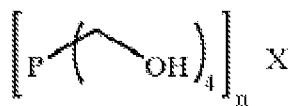
[016] “Mercury salt” or “mercury complex” means a chemical compound formed by replacing all or part of hydrogen ions of an acid with one or more mercury ions.

5 [017] “Oil-water” as used herein means any mixture containing a crude oil with water, inclusive of both oil-in-water emulsions and water-in-oil emulsions. In one embodiment, the emulsion particles are of droplet sizes. In another embodiment, the emulsion particles are of micron or nano particle sizes. In one embodiment, oil is present as fine droplets contained in water in the form of an emulsion, i.e., emulsified hydrocarbons, or
10 in the form of undissolved, yet non-emulsified hydrocarbons.

[018] Crudes and crude blends are used interchangeably and each is intended to include both a single crude and blends of crudes. Crudes may contain small amounts of heavy metals such as mercury, which may be present as elemental mercury Hg^0 , ionic Hg, inorganic mercury compounds, and / or organic mercury compounds. Examples include but
15 are not limited to: mercuric halides (e.g., HgXY , X and Y could be halides, oxygen, or halogen-oxides), mercurous halides (e.g., Hg_2XY , X and Y could be halides, oxygen, or halogen-oxides), mercuric oxides (e.g., HgO), mercuric sulfide (e.g., HgS , meta-cinnabar and/or cinnabar), mercuric sulfate (HgSO_4), mercurous sulfate (Hg_2SO_4), mercury selenide (e.g., HgSe_2 , HgSe_8 , HgSe), mercury hydroxides, and organo-mercury compounds (e.g., alkyl
20 mercury compounds) and mixtures of thereof. Mercury can be present in various forms, e.g., in dissolved form, as particles, and / or adsorbed onto the surfaces such as clay minerals, inorganic mineral scale, sand, and asphaltenes.

[019] The crude oil is brought into contact with a composition wherein the heavy metals form water soluble complexes with the composition, with the water soluble complexes
25 being removable / separated from the crude oil. In one embodiment for removing mercury (Hg) from crude oil, the composition not only dissolves solid forms of Hg, but also forms complexes with Hg^{2+} . The composition can be used in treating crude oil containing heavy metals such as mercury, and in another embodiment, for treating seawater used in the secondary recovery of crude oil containing a high level of mercury.

30 [020] The Composition: The composition for forming complexes with the heavy metals is selected from compounds of Formula (I):



[021]

[022] wherein X is an anion, e.g., a monoanion, dianion, or trianion, and n is the number of phosphonium cations present. In one embodiment, X is chosen such that compounds of Formula (I) are soluble in water, alcohols, or in mixtures thereof. In one embodiment, X is a monoanion selected from the group of halides such as chloride, bromide, and iodide. In another embodiment, X is selected from the group of lower alkyl carboxylates, wherein the term "lower alkyl" refers to a straight or branched C1-C6 alkyl group, e.g., methyl carboxylate (i.e., acetate), ethyl carboxylate, and propyl and iso-propyl carboxylates. In another embodiment, X is selected from sulfur-based anions such as bisulfite, bisulfate, and hydrocarbyl sulfonates. Examples of hydrocarbyl sulfonates include, but are not limited to, methylsulfonate, benzenesulfonate, para-toluenesulfonate, and the isomers of xylenesulfonate. In yet another embodiment, X is selected from monoanions such as nitrate and hexafluorophosphate.

[023] In one embodiment, X is a dianion selected from sulfate, sulfite, and monohydrogenphosphate. In another embodiment, X is a trianion such as phosphate. Without wishing to be bound by any particular theory or principle, it is believed that compounds of Formula (I), particularly when exposed to aqueous solutions having elevated pH, furnish tris(hydroxymethyl)phosphine (TRIS) to dissolve compounds such as HgS and HgO.

[024] Compounds of Formula (I) are commercially available or can be obtained routinely by known syntheses. Two examples are tetrakis(hydroxymethyl)-phosphonium sulfate (THPS) and tetrakis(hydroxymethyl)phosphonium chloride (THPCl), both of which are available commercially, for example, from Rhodia (Cranberry, N.J.), Nippon Industries (Tokyo, Japan), and Cytec Industries (Mobile, Ala.). Tetrakis(hydroxymethyl)phosphonium sulfate (THPS) is normally available as an aqueous acidic solution having a pH of between 1 and 4. Other compounds of Formula (I) bearing different anions X can be prepared straightforwardly by the well-known reaction between phosphine and formaldehyde in the presence of an aqueous acid HX as described in U.S. Pat. No. 4,044,055 to Katz et al, incorporated herein by reference.

[025] The compounds of Formula (I) upon contact with the crude oil, will form water soluble complexes with the trace element of heavy metals in the crude oil. Examples

of heavy metals include solids such as HgS, HgO, as well as water soluble Hg^{+2} , etc. In one embodiment, the composition further includes a complexing additive, which is an amine or its ammonium derivative, and can be selected from a variety of amines and their conjugate acids. Ammonium derivative is the conjugate acid of an amine. The complexing additive is combined with one or more compounds of Formula (I), resulting in effective scavengers of heavy metal compounds such as HgS, HgO, etc. in the crude oil.

[026] In one embodiment wherein the complexing additive is a solid, then it should be soluble in the solvent as Formula (I). In another embodiment, if the amine or its conjugate acid is a liquid, then it is miscible with the solvent for use as Formula (I). One example of a complexing additive is ammonia. In another embodiment, the complexing additive is a primary amine, such as alkylamines. Exemplary alkylamines include, but are not limited to, methylamine, ethylamine, normal- and iso-propylamines, and normal- and tert-butylamines. Other primary amines include alkylenediamines, such as 1,2-diaminoethane and 1,3-diaminopropane. Still other primary amines are cycloalkylamines, such as cyclopropylamine, cyclobutylamine, cyclopentylamine, and cyclohexylamine. In yet another embodiment, the complexing agent is selected from ammonium derivatives of these amines. Examples include but are not limited to ammonium chloride, methylammonium chloride, ammonium nitrate, and ethylammonium chloride.

[027] In one embodiment, the composition is prepared with at least a Formula (I) compound by itself, or a mixture of the Formula (I) compound with at least a complexing additive, for a pH value between 4.5 to 10. In one embodiment, the pH is maintained in the range from 6 to 9. In another embodiment, the pH is maintained at a level of 8.

[028] In one embodiment, additives for crude oil treatment known in the art other than complexing agents can be optionally added to the composition. Examples include surfactants, biocides, water dispersants, demulsifiers, scale inhibitors, corrosion inhibitors, anti-foaming agents, oxygen scavengers, flocculants, and the like. The additives can be added as pure compounds or as commercially available preparations thereof, such as aqueous solutions.

[029] The use of any amount of the composition is effective in removing or reducing the level of heavy metals such as mercury, lead, zinc, etc. from crude oil. In one embodiment, the optimum molar ratio depends somewhat upon the amine or ammonium derivative added to the composition.

[030] In one embodiment, the composition of Formula (I) compound is employed in a molar ratio range of phosphorus to the heavy metal for removal, e.g., mercury, of 1:1 to

50:1. In one embodiment, the ratio is greater than 10:1. In another embodiment, it is less than 100:1. In a third embodiment, it is greater than 20:1. In another embodiment with the use of a complexing additive, the molar ratio varies somewhat upon the amine or ammonium derivative added, and can be determined by routine experimentation. In yet another
5 embodiment for mercury removal / reduction, the molar ratio of phosphorus to mercury is in the range of 1.5:1 to 7:1. In a third embodiment, the ratio is in the range of 2:1 to 5:1.

[031] Method for Removing / Decreasing Levels of Heavy Metals in Crude Oil: In one embodiment, a composition of Formula (I) is first prepared or obtained. In one embodiment with an optional complexing agent, the composition is made by combining
10 suitable amounts of at least one compound of Formula (I) and at least one amine or ammonium derivative in the presence of an aqueous solvent. The order of addition of the reagents can be varied. In one embodiment, the amine or ammonium derivative is added to a compound of Formula (I) wherein the pH has been adjusted as described below. Exemplary solvents include water and an alcohol. In one embodiment, the added reagents make up from
15 0.5 to 50 volume percent of the total mixture of crude oil and reagents. In a second embodiment, the added reagents make up less than 40 vol. % of the mixture. In a third embodiment, less than 30 vol. %. In a fourth embodiment, less than 10 vol. % percent. In a fifth embodiment, less than 5 vol. %.

[032] In another embodiment wherein commercially available aqueous solutions of
20 tetrakis(hydroxymethyl)phosphonium sulfate are used, the pH of the composition is raised by adding a suitable base to the mixture. The pH can be maintained by the use of a buffer. Exemplary buffers, such as phosphate and citrate, are serviceable in the prescribed pH range. Additionally, nitriloacetic acids can be used as buffers. Exemplary acids include nitrilotriacetic acid (NTA) and ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA).

[033] In the next step, the composition is brought in contact with the crude oil
25 containing heavy metals, e.g., trace elements of mercury, and the like, by means known in the art. The composition can be introduced continuously or intermittently, i.e., batch-wise, into operating gas or fluid pipelines, for example. Alternatively, batch introduction is effective for offline pipelines. The contact can be at any temperature that is sufficiently high enough
30 for the crude oil to be completely liquid. In one embodiment, the contact is at room temperature. In another embodiment, the contact is at a sufficiently elevated temperature, e.g., at least 50°C.

[034] The contact is for a sufficient amount of time for the trace elements to be sufficiently removed from the crude oil. The sufficient amount of time is dependent on the

mixing of the crude oil with the composition. If vigorous mixing is provided, the contact time can be as little as less than a minute. In one embodiment, the contact time is at least a minute. In another embodiment, the contact time is at least 5 minutes. In a third embodiment, at least 1 hr. In a fourth embodiment, the contact is continuous for at least 2 hrs.

[035] Upon contact with the crude oil, the composition reacts with the trace elements in the crude oil forming water soluble complexes. Once an oil-water emulsion is formed, the water phase containing the heavy metal complexes can be separated from the crude oil in a phase separation device known in the art, e.g., a cyclone device, electrostatic coalescent device, gravitational oil-water separator, centrifugal separator, etc., resulting in a crude oil with a significantly reduced level of heavy metals. The heavy metal complexes can be isolated / extracted out of the effluent and subsequently disposed.

[036] In one embodiment with mercury as the heavy metal for trace element removal or reduction, the mercury level in the crude oil is reduced to 100 ppb or less. In another embodiment, the level is brought down to 50 ppb or less. In a third embodiment, the level is 20 ppb or less. In a fourth embodiment, the level is 10 ppb or less. In a fifth embodiment, the level is 5 ppb or less. In yet another embodiment, the removal or reduction is at least 50% from the original level of heavy metals such as mercury. In a fifth embodiment, at least 75% of a heavy metal such as mercury is removed. In a seventh embodiment, the removal or the reduction is at least 90%.

[037] In one embodiment, mercury is the heavy metal targeted to be removed / reduced in concentration with the compound of Formula (I) forming a mercury salt complex. The mercury salt complex can be subsequently removed through techniques such as filtration, coagulation, flotation, co-precipitation, ion exchange, reverse osmosis, ultra-filtration using membranes and other treatment processes known in the art.

[038] EXAMPLES: The following examples are given to illustrate the present invention. It should be understood, however, that the invention is not to be limited to the specific conditions or details described in these examples. In examples calling for mercury vapor feed prep, a sufficient amount of mercury (e.g., one or two drops of elemental mercury in a bottle) was sparged by using nitrogen (N₂) gas into another bottle containing white mineral oil overnight.

[039] Example 1 - Scanning UV for complex formation of heavy metals with THPS and THPCl: Samples of mercuric chloride (HgCl₂) were prepared in water according to recipe: 21.3 mg of HgCl₂ in 10 mL of diluents (0.008 moles/mL) and 61.2 mg of HgCl₂ in 25

mL of diluents (0.009 moles/mL). A sample of mercury oxide (HgO) dissolved in nitric acid was provided. The mercury samples were spiked with 75% THPS or 80% THPCl at different molar ratio concentrations: 1:0, 1:1, 1:2, 1:3, 1:4, 1:6, and 1:9. Treated mercury solutions were scanned by UV and compared with untreated solutions. The results from UV scanning showed that HgCl₂ and HgO formed complexes with THPS and THPCl.

[040] Example 2: The experiment showed that THPS is a complexing agent for mercury after iodine (I₂) oxidation in Hg vapor feed prep. Mercury level in 50 mL of distilled water in a 250 mL glass reactor was measured using LUMEX mercury analyzer equipped with PYRO-915+. 50 mL of mercury vapor feed prep containing approximately 1,400 ppb Hg was added to the water. A pre-determined volume of iodine stock prepared in methanol (3% I₂ by weight) was added to the reactor for a final iodine concentration of 50 ppm. The oil-water mixture was stirred up for 1 minute with an overhead agitator at 600 rpm. THPS stock (50 wt.%) was added to the reactor for samples with predetermined concentrations. Mixing resumed for another minute at 600 rpm. Aliquots of both oil and water were analyzed for mercury concentration.

[041] Example 3 – THPS dissolving HgS and HgO to form soluble complexes: Samples of 27±3mg of HgO yellow, HgO red and β-HgS; or 30±10mg of α-HgS were added into 50mL glass bottles. For each glass bottle, 10mL of THPS was added for three different concentrations of THPS. The samples were stirred with a magnetic bar for 18 hrs. The samples were filtered with a 0.45 μm filter to separate liquid from mercury solids. Mercury levels in the filtrates were measured using LUMEX mercury analyzer equipped with PYRO-915+.

[042] Table 1 shows the solubility of HgS and HgO by THPS with the extracted Hg concentration as mg Hg/ kg HgO or HgS:

[043] Table 1

	HgO, yellow	HgO, red	α-HgS	β-HgS
Deionized distill water	545	506	209	143
THPS (10-30 wt. %)	9,428	9,642	1,198	2,204
THPS (10-30 wt. %)	4,597	18,707	1,178	1,597
THPS (70-80 wt. %)	66,976	59,884	4,927	18,031

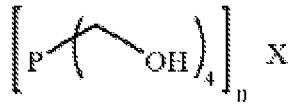
[044] As shown, sulfides and oxides of heavy metals are soluble in THPS solutions, with examples showing that mercury sulfides and oxides can be easily dissolved by using the composition of Formula (I).

[045] Example 4: Example 2 was repeated, except that the oil-water mixture was stirred up for 2 minutes with an overhead agitator at 600 rpm, and THPS stock (50 wt.%) was added to the reactor for samples with concentrations of 1250, 625, 313, and 125 ppm THPS. Aliquots of both oil and water were collected and analyzed for mercury concentration after mixing at 600 ppm, and at intervals of 2, 5, 10, 15 and 30 minutes. Figure 1 illustrates the mercury concentrations in oil and water at different THPS concentrations at different periods.

[046] Example 5: Example 4 was repeated, except that THPCl stock at 80 wt.% was added to the reactor for samples with concentrations of 1064, 532, and 213ppm THPCl. Figure 2 shows the mercury concentrations in oil and water at different THPCl concentrations at different periods.

CLAIMS

1. A method for reducing a trace element of a heavy metal in a crude oil, comprising:
 a) mixing the crude oil containing the heavy metal with a composition
 comprising a compound of Formula (I) in an aqueous solvent for a sufficient amount of time
 5 for the compound to form a heavy metal complex in an oil-water emulsion;



(I)

wherein X is an anion of valency n;

- b) separating the water containing the heavy metal complex from the crude oil in
 a phase separation device for the crude oil to have a reduced concentration of the heavy
 10 metal.

2. The method of claim 1, wherein X is selected from the group consisting of chloride,
 bromide, iodide, lower alkyl carboxylates, bisulfite, bisulfate, hydrocarbyl sulfonates,
 dihydrogenphosphate, nitrate, hexafluorophosphate, sulfate, sulfite, monohydrogenphosphate,
 15 and phosphate.

3. The method of any of claims 1-2, wherein the compound of Formula (I) is selected
 from tetrakis(hydroxymethyl)phosphonium sulfate and tetrakis(hydroxymethyl)phosphonium
 chloride.

4. The method of any of claims 1-2, wherein the compound of Formula (I) is
 tetrakis(hydroxymethyl)phosphonium sulfate.

5. The method of any of claims 1-2, wherein the compound of Formula (I) is
 25 tetrakis(hydroxymethyl)phosphonium chloride.

6. The method of any of claims 1-2, wherein the heavy metal is selected from the group
 of lead, arsenic, zinc, and mercury.

7. The method of any of claims 1-2, wherein the heavy metal is mercury.

8. The method of any of claims 1-2, wherein the molar ratio of the compound having Formula (I) to the trace element of a heavy metal in the crude oil is in the range of 1:1 to 50:1.

5 9. The method of claim 8, wherein the molar ratio is in the range of 1.5:1 to 10:1.

10. The method of claim 9, wherein the molar ratio is in the range of 2:1 to 5:1.

11. A method for reducing a trace element of mercury in a crude oil, comprising:

10 a) mixing the crude oil containing mercury with a composition comprising an amine or ammonium derivative with tetrakis(hydroxymethyl)phosphonium sulfate for a sufficient amount of time to form a mercury complex in an oil-water emulsion;

b) separating the water containing the mercury complex from the crude oil in a phase separation device for the crude oil to have a reduced concentration of mercury.

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12. A method for reducing a trace element of mercury in a crude oil, comprising:

a) mixing the crude oil containing mercury with a composition comprising an amine or ammonium derivative with tetrakis(hydroxymethyl)phosphonium chloride for a sufficient amount of time to form a mercury complex in an oil-water emulsion;

20 b) separating the water containing the mercury complex from the crude oil in a phase separation device for the crude oil to have a reduced concentration of mercury.

13. The method of any of claims 1-2, and 11- 12, wherein the reduced concentration is less than 100 ppb in mercury.

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14. The method of any of claims 13, wherein the reduced concentration is less than 50 ppb in mercury.

15. The method of any of claims 1-2, and 11- 12, wherein the composition further
30 comprises an amine or ammonium derivative.

16. The method of claim 15, wherein the amine or ammonium derivative is selected from the group consisting of alkylamines and their conjugate acids thereof.

17. The method of claim 16, wherein the alkylamine and conjugate acids thereof is selected from the group consisting of methylamine, ethylamine, propylamine, isopropylamine, butylamine, tertbutylamine, and conjugate acids thereof.