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(54) Title: METAL REMOVAL FROM FLUIDS

(57) Abstract: Metals, such as mercury, may be removed from aqueous, hydrocarbon, or mixed oilfield or refinery fluids by: applying a sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group either alone or in combination with or as a blend with at least one demulsifier, a buffering agent, a pour point depressant, and/or a water clarifier to chelate the at least one metal and form a chelate complex of the sulfur compound with the at least one metal and then separating the chelate complex from the fluid.



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METAL REMOVAL FROM FLUIDS

TECHNICAL FIELD

[0001] The present invention relates to additives and methods for removing metals from various oilfield and refinery fluids, and more particularly relates to the removal of metals, such as mercury, from oilfield and refinery fluids by introducing a sulfur compound alone or in combination with at least one demulsifier, a water clarifier, a buffering agent and/or a pour point depressant to the fluids to separate the metals from the fluid.

BACKGROUND

[0002] The removal of metals found in oil and natural gas streams, such as lead, mercury, copper, iron, magnesium, sodium, molybdenum, zinc, cadmium, vanadium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver, calcium, lithium, and arsenic, is an important element to oil and gas production and refining.

[0003] The presence of such metals can cause problems during the processing and refining of hydrocarbon streams and significantly reduce their value and the markets into which hydrocarbons may be sold. Moreover, many of these metals, such as mercury, are toxic and pose an environmental risk, making the treatment and disposal of industrial fluid streams containing them challenging.

[0004] Various technologies and methods have been employed over the years to try to effectively removal of metals from oilfield and refinery fluids. Prior methods of mercury removal from hydrocarbon streams, for example, have utilized dithiocarbamate additives, filtration, thermal processes, and oxidation. However, such removal methods are often hindered by the interference from water, other solids, and oil emulsions and/or interfaces present in the stream. In addition, dithiocarbamate chemistries are known to be toxic and can generate undesirable rag layers during treatment, which increases processing time and expense.

[0005] Therefore, it would be desirable to develop metal removal additives and methods that are less toxic and more efficient in separating metals from oilfield and refinery fluids.

SUMMARY

[0006] There is provided, in one form, a method of removing metals from a fluid comprising: applying a sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group, to an aqueous, hydrocarbon, or mixed fluid containing at least one metal to chelate the at least one metal and form a chelate complex of the sulfur compound with the at least one metal, and separating the chelate complex from the fluid via, for example, solids disposal or water washing. In one non-restrictive embodiment, at least one demulsifier, a buffering agent, a water clarifier, and/or a pour point depressant may be further applied to the fluid with the sulfur compound in a blend or separately.

[0007] There is also provided, in another form, a treated fluid in which a fluid comprising at least one metal is combined with an additive comprising (1) a sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group, and (2) a component selected from the group consisting of at least one demulsifier, a buffering agent, a water clarifier, a pour point depressant, and combinations thereof. The at least one metal to be removed may be lead, mercury, copper, iron, magnesium, sodium, molybdenum, zinc, cadmium, vanadium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver, arsenic, selenium, calcium, lithium, silicon and combinations thereof. The fluid to be treated may be selected from a group consisting of crude oil, an oilfield condensate, liquified petroleum gas, natural gas liquid, propane, butane, a refinery distillate, a residual fuel, storage tank sludge, a coke product, natural gas, refinery fuel gas, wastewater, produced water, a chemical process fluid, and combinations thereof. In one non-limiting embodiment, the treated fluid additionally comprises a chelate complex of the sulfur compound with the at least one metal.

DETAILED DESCRIPTION

[0008] It has been discovered that adding a sulfur compound having the general formula HS-X, either by itself or with at least one demulsifier, a buffering agent, a pour point depressant, and/or a water clarifier, to an oilfield or refinery fluid having at least one metal, such as crude oil, is useful in separating (i.e. removing) the at least one metal from the fluid. More specifically, it has been discovered that a sulfur compound of the kind(s) described herein is useful to chelate the at least one metal present in the fluid and form a chelate complex with the at least one metal so that the at least one metal may be more easily removed or separated from the fluid.

[0009] The sulfur compound is a compound having the general formula HS-X, in which X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkyl-aryl group. The heteroatom may be oxygen, sulfur, phosphorous, and/or nitrogen. The alkyl, cycloalkyl, aryl, or alkylaryl groups may have from 1 independently to 12 carbon atoms; alternatively from 2 independently to 6 carbon atoms. As used herein with respect to a range, "independently" means that any threshold given may be used together with any other threshold given to provide a suitable alternative range. Non-limiting examples of sulfur compounds falling within this formula that are effective in removing (i.e. separating) metals from a fluid when applied to the fluid are, without limitation, 2-mercaptoethanol, bis (2-mercaptoethyl) sulfide, 2-mercaptoethyl disulfide, 1,8-dimercapto-3,6-dioxaoctane, mercaptoacetic acid, glyceryl monothioglycolate, 2-mercaptophenol, 4-mercaptophenol, 1,2 dithioethane, cysteamine, N,N dimethyl cysteamine, N,N'-bis(2-mercaptoethyl) ethylene-diamine, thiolactic acid, 1, 3, 5 triazine, 2,4,6 trithiol. In one non-limiting embodiment, the additive to be applied to the fluid containing at least one metal may be comprised of one or more of these sulfur compounds.

[0010] In another non-limiting embodiment, the additional components may be applied to the fluid containing at least one metal to improve separation or removal. The components that may be applied in addition to the sulfur compound described above comprise a buffering agent, at least one demulsifier, a pour point depressant, and/or a water clarifier. These additional components

may be blended with the sulfur compound or each other before being applied to the fluid or be added to the fluid separately in combination with the sulfur compound or in combination with each other.

[0011] A buffering agent may be applied to change pH of the fluid and enhance the metal removal. Suitable buffering agents include, without limitation, glycolic acid, acetic acid, lactic acid, and combinations thereof.

[0012] Because demulsifiers work to break water-in-oil or oil-in water emulsions in fluid containing hydrocarbons, the application of at least one demulsifier to a hydrocarbon fluid may help release the metal particle complex created by the sulfur compound from the oil phase of the fluid. Suitable demulsifiers include, but are not limited to, oxyalkylated phenolic resins, oxyalkylated alkyl phenol formaldehyde resins, benzenesulfonic acid, 4-C10-13-sec-alkyl derivatives, bis(2-ethylhexyl) sulfosuccinate sodium salt, phenol (para C4–C12 alkyl) bis polymer with (chloromethyl)oxirane methyloxirane and oxirane, methyloxirane polymers with oxirane, propoxylated or ethoxylated polyamines, and combinations thereof. It has also been shown that the at least one demulsifier may be a complex blend of crosslinked polyols, oxyalkylated phenolic resins, alkylarylsulfonic acid, polyol esters, and combinations of these. In the case of treating a hydrocarbon fluid for metal removal, pour point depressants may be applied with the at least one demulsifier to help avoid crystallization of paraffins in the hydrocarbon fluid and aid in separating metals from the hydrocarbon phase of fluid. The pour point depressants that may be applied include, without restriction, ethylene vinyl acetate copolymers, polyacrylamide copolymers and terpolymers, olefin maleic copolymer esters, and/or polyacrylate homopolymers, copolymers, and terpolymers, such as methacrylate homopolymers, copolymers, and terpolymers.

[0013] The water clarifier that may be applied may, without limitation, be one or more of the following: a cationic starch aqueous carbohydrate dispersion, a water-soluble modified starch, chitosan acetate, aluminum chloride hydroxide cationic polyacrylamide, an anionic polysulfonated copolymer, and a quaternized polytriethanolamine polymer.

[0014] In some non-limiting embodiments, certain optional chelants and ionic liquids may also be added to the fluid to help effect precipitation of the metals, especially in the case of removal or separation of mercury. Examples of such chelants include, without limitation, sodium trithiocarbonate, N,N dimethyl dithiocarbamate, polyammonium dithiocarbamate, and/or sodium, potassium or ammonium thiocyanate.

[0015] The fluid to be treated with such an additive is any fluid that contains at least one metal. The metals present in the fluid may be selected from the group consisting of lead, mercury, copper, iron, magnesium, sodium, molybdenum, zinc, cadmium, vanadium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver, arsenic, selenium, calcium, lithium, silicon, and combinations thereof. The fluid may be (1) an aqueous fluid, where the continuous phase is water or brine and where the fluid contains more than 50% by volume of water or brine, (2) a hydrocarbon fluid, where the continuous phase is a hydrocarbon liquid or hydrocarbon gas and where the fluid contains 50% or more by volume of hydrocarbon or (3) a fluid containing a mixture or combination of water and hydrocarbons. Such fluids may be found in oilfield and refinery environments and may include, but are not necessarily limited to, crude oil, an oilfield condensate, liquified petroleum gas, natural gas liquid, propane, butane, a refinery distillate, a residual fuel, storage tank sludge, a coke product, natural gas, refinery fuel gas, wastewater, produced water, a chemical process fluid, and combinations thereof. It will be appreciated that, in the case of treating an aqueous fluid, an additive comprising the sulfur compound alone may be effective in removing metals from the fluid.

[0016] Once the additive has been applied to the fluid, been given time to mix with the fluid, and the treated fluid is allowed to settle, the sulfur compound and the at least one metal may be separated or removed from the fluid. Without being limited to any particular mechanism or explanation, it is believed that the sulfur compound chelates the at least one metal, thereby forming a chelate complex that can be separated or removed from the fluid. For purposes of this disclosure, the terms “separation,” “separating,” “removal,” and “removing” are

synonymous. By “removing” or “separating” a metal from a fluid means any and all partitioning, sequestering, separating, transferring, eliminating, dividing, removing, dropping out of the metal from the fluid to any extent. In one embodiment, this separation and removal can be accomplished by directing the treated fluid to a water wash to have the metal transferred to a water stream for further treatment or disposal. Alternatively, or additionally, this separation may be carried out by directing the treated fluid to a centrifuge or filter for the metal to be removed from the sulfur compound as a disposable solid. That is, separating the chelate complex (*i.e.* the combination of the sulfur compound and the at least one metal) may be carried out by a process selected from the group consisting of centrifuging, filtering, air flotation, gravity separation, distillation, adsorption, electrophoresis, and combinations thereof, and combinations thereof.

[0017] A goal of the method is to separate the metal from the fluid to an acceptable level for the fluid to be properly processed, discharged to the environment, or reused. While complete separation of metals is desirable, it should be appreciated that complete separation is not necessary for the methods and additives discussed herein to be considered effective. Success is obtained if more metals are separated from the fluid using an effective amount of components of the present disclosure than in the absence of an effective amount of them. In a non-limiting embodiment, the amount of the sulfur compound effective for metal removal may range from about 1 ppm to about 500 ppm per ppm of the at least one metal in the fluid, the amount of the optional at least one demulsifier in the additive may range from about 1 ppm to about 500 ppm based on total volume of the fluid, the amount of the optional pour point depressant may range from about 15 ppm to about 2000 ppm based on the total volume of the fluid, and the amount of the optional water clarifier in the additive may range from about 0.1 ppm to about 200 ppm based on the total volume of the fluid.

[0018] The invention will be illustrated further with reference to the following Examples, which are not intended to limit the invention, but instead illuminate it further.

EXAMPLES

[0019] The data in Tables 1, 2, 3, 4, 5, and 6 show the results of bottle testing various metal removal additives of the kinds described herein when they are applied to samples of oilfield condensate, South American Crude Oil Storage Tank Bottoms, crude oil, and raw crude oil to evaluate their performance in removing mercury from the samples tested.

[0020] Table 1 reflect the results from a series of bottle tests of 100 ml samples of oilfield condensates containing no added water. The 100 ml sample of oilfield condensate was placed in a 100 ml centrifuge tube and treated with various doses of the metal removal additives identified in Table 1 below. Each treated sample was shaken by hand 100 times and then allowed to settle at room temperature for 1 hour. After the settling period, an aliquot of oil was taken from the mid-level of the tube for mercury analysis. Additives were then evaluated for how well they removed mercury in the sample prior to and after a water wash procedure.

[0021] For purposes of the Tables below, the “demulsifier” is formaldehyde, polymer with 4-nonylphenol and oxirane, WC1 is a cationic aqueous carbohydrate dispersion, WC2 is a water-soluble modified starch, WC3 is an aluminum chloride hydroxide/acrylamide copolymer, and WC4 is a water-soluble modified starch. Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs. is another demulsifier additive that was evaluated. A clear cell indicates that no measurement was taken for that sample at that point in the evaluation.

Table 1. Hg Removal Test Results
Oilfield Condensate Samples (No Added Water)

Additive(s)	Dosage of additives (ppm-v)	Oil Mercury Content – No Water Wash Procedure (ppb)	Oil Mercury Content – With Water Wash Procedure (ppb)
Untreated hydrocarbon		669	669
2-mercaptoethanol	100	623	86
2-mercaptoethanol + demulsifier	50 + 50		74
2-mercaptoethanol + demulsifier + WC1	50 + 50 + 20		58
2-mercaptoethanol + demulsifier + WC2	50 + 50 + 20		35
2-mercaptoethanol + demulsifier + WC3	84 + 15 + 1		36
Mercaptoacetic acid	100	58	25
Mercaptoacetic acid + demulsifier	50 + 50	167	32
Mercaptoacetic acid + demulsifier + WC4	50 + 50 + 20		66
Mercaptoacetic acid + Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.	50 + 50	172	176
Mercaptoacetic acid + Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs. + demulsifier	50 + 50 + 50		210
Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.	100	409	
1,8-dimercapto-3,6-dioxaoctane	100	528	470
1,8-dimercapto-3,6-dioxaoctane + demulsifier	50 + 50		537

[0022] Table 2 shows the results from a second series of bottle tests in which 5 ml of deionized water is added to 95 ml of the oilfield condensate sample and then treated with various sulfur compounds of the kinds described herein and 50 ppm of the demulsifier. In this evaluation, after addition of all materials to the tube, the tube was shaken by hand 100 times. After shaking the sample, it was placed in a centrifuge set at 1300 rpm for 5 minutes. After the

centrifuge treatment, an oil sample was taken from the mid-level of the tube for mercury analysis.

Table 2. Hg Removal Test Results
Oilfield Condensate Samples (w/ Added Water)

Additive(s)	Dosage of additives (ppm-v)	Hg Content (ppb)
Untreated hydrocarbon		669
2-mercaptoethanol + demulsifier	50 + 50	74
Mercaptoacetic acid + demulsifier	50 + 50	65
1,8-dimercapto-3,6-dioxaoctane + demulsifier	50 + 50	537

[0023] Table 3 shows the bottle test results when samples of South American Crude Oil Storage Tank Bottoms having a wax content of 6%, a water content of 2%, a solids content of 0.8%, and an emulsion content of 0.8% was treated with various mercury removal additives of the kinds described herein. For this set of bottle tests, all of the hydrocarbon fluid samples were placed in a graduated 100 ml centrifuge tube and dosed with 200 ppm of an olefin maleic copolymer ester crude oil pour point additive. The mercury reduction additive was then added and the mixture shaken by hand 100 times. Samples were then placed in a heated (65 °C) oven and sampled at the mid-level of the tube after 1 hour, 2 hours or 14 hours of settling time.

Table 3. Hg Removal Test Results
South American Crude Oil Storage Tank Bottom Samples

Additive(s)	Dosage of additives (ppm-v)	Hg content @ 1 hour settling time (ppb)	Hg content @ 2 hour settling time (ppb)	Hg content @ 14 hour settling time (ppb)
Untreated Hydrocarbon		55,943		
Mercaptoacetic acid	200	55,552		
Mercaptoacetic acid + demulsifier + WC2	200 + 50 + 20	54,054		
2-Mercaptoethanol	200	38,381		
2-Mercaptoethanol	500		31,519	
2-Mercaptoethanol	2000			14,306
2-Mercaptoethanol + demulsifier + WC2	200 + 50 + 20	32,994		
Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.	150	29,147		
Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.	500		38,128	38,601
Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs.	2000			14,306
Benzenesulfonic acid, 4-C10-13-sec-alkyl derivs. + demulsifier + WC2	150+50+20	20,998		

[0024] The results from these bottle tests show that applying an additive containing both a sulfur compound of the kind described herein and a suitable demulsifier performs well in removing mercury from hydrocarbon fluids, and that, in general, the addition of a demulsifier and/or water clarifier to the sulfur compound additive reduces mercury levels even more than when the sulfur compound is introduced alone.

[0025] In addition, several samples of crude oil containing mercury were treated with various combinations of the metal removal additives and then analyzed for their mercury content. Specifically, the crude oil samples were treated with the varying dosages of the additives identified in column 1 of Table 4. The additives were applied to the crude oil, shaken 100 times, and then 5% by volume water was added to the treated samples before being shaken

another 100 times. The hydrocarbon and aqueous phases of the crude oil samples were allowed to separate under ambient conditions. After one (1) hour, a small amount of the oil phase each sample was taken and analyzed for mercury content.

Table 4. Hg Removal Test Results
Crude Oil Samples (w/ Added Water)

Additive(s)	Dosage of additives (ppm-v)	Hg in oil (ppb-w) with no water wash
Untreated Crude Oil	0	699
2 -Mercaptoethanol	100	86
2-Mercaptoethanol+demulsifier	100 + 50	74
2-Mercaptoethanol +demulsifier + Water clarifier	100+50+20	35

[0026] The results in Table 4 indicate that the demulsifier may help release the mercury particle complexes created by the sulfur compound from the oil phase and that the addition of a water clarifier may help to attract the mercury particle complexes formed by the sulfur compound, which allows them to grow bigger and settle faster from the oil.

[0027] Finally, raw crude oil samples were treated with a (1) blended additive comprising mercaptoacetic acid and a glycolic acid buffering agent ("Blend XL 18") in combination with demulsifier and/or an ethylene vinyl acetate copolymer pour point depressant and (2) equal amounts of WC1, WC2, WC3, and WC 4 to evaluate the effectiveness in removing mercury from the raw crude oil samples after a 5% water wash at 150 °F and after 24 hours settling time.

Table 5 – Hg Removal Test Results with 5% water wash
Raw Crude Oil Samples (No Added Water)

Additive(s)	Dosage of additives (ppm-v)	Hg in oil (ppb-w) (Crude oil only)
Raw Crude Oil	0	54,670
Blend XL18	200	4,252
Blend XL18/demulsifier	200/100	3,086
Blend XL18/demulsifier/pour point depressant	200/100/250	2,070

Table 6 - Hg Removal Test Results with 5% water wash
Raw Crude Oil Samples with Water Clarifier only

Water Clarifier	Dosage of Water Clarifier (ppm-v)	Hg in oil (ppb-w) (Crude oil only)
Raw Crude Oil	0	669
Water clarifier 1	100	172
Water clarifier 2	100	140
Water clarifier 3	100	165
Water clarifier 4	100	258

[0028] The results in Table 5 show that an additive comprising Blend XL 18, formaldehyde, polymer with 4-nonylphenol and oxirane, and a pour point depressant performs the best in removing mercury from raw crude oil compared to samples treated only with Blend XL 18 or treated with Blend XL 18 and formaldehyde, polymer with 4-nonylphenol and oxirane. Table 6 shows that WC2 is the best of the four water clarifiers tested in mercury removal.

[0029] In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been described as effective in providing methods, additives, and treatments for removing metals from a fluid. However, it will be evident that various modifications and changes can be made thereto without departing from the broader scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense. For example, fluids, sulfur compounds, demulsifiers, buffering agents, pour point depressants, water clarifiers, functional groups, crosslinkers, mixtures, process conditions and parameters, and the composition and amounts and proportions of additive and components falling within the claimed parameters, but not specifically identified in this disclosure or evaluated in a particular Example, are expected to be within the scope of this invention.

[0030] The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed. For instance, the method or treated fluid may comprise, consist essentially of, or consist of the steps or components recited in

the independent claims, respectively. Specifically, there may be provided a method for removing metals from a fluid, the method consisting essentially of or consisting of applying an additive comprising a sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group, to an aqueous, hydrocarbon, or mixed fluid containing at least one metal to chelate the at least one metal and form a chelate complex of the sulfur compound with the at least one metal, and separating the chelate complex from the fluid. Further there may be provided a treated fluid consisting essentially of or consisting of a fluid comprising at least one metal, and an additive consisting of or consisting essentially of (1) a sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group, and (2) a component selected from the group consisting of at least one demulsifier, a buffering agent, a water clarifier, a pour point depressant, and combinations thereof.

[0031] The words “comprising” and “comprises” as used throughout the claims, are to be interpreted to mean “including but not limited to” and “includes but not limited to”, respectively.

[0032] As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise.

[0033] As used herein, the term “about” in reference to a given parameter is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the given parameter).

[0034] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items

CLAIMS

What is claimed is:

1. A method for removing metals from a fluid, the method comprising:
 - being characterized by applying a sulfur compound to the fluid, the sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group, to a fluid containing at least one metal, the sulfur compound chelating the at least one metal to form a chelate complex; and
 - separating the chelate complex from the fluid.
2. The method of claim 1 further applying a buffering agent to the fluid.
3. The method of claim 1 further applying at least one demulsifier to the fluid.
4. The method of claim 1 further applying a water clarifier to the fluid.
5. The method of claim 1, 2, 3, or 4 wherein the heteroatom is selected from a group consisting of sulfur, oxygen, nitrogen, phosphorus, and combinations thereof.
6. The method of claim 1, 2, 3, or 4 wherein the at least one metal is selected from a group consisting of lead, mercury, copper, iron, magnesium, sodium, molybdenum, zinc, cadmium, vanadium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver, arsenic, selenium, calcium, lithium, silicon, and combinations thereof.
7. The method of claim 1, 2, 3, or 4 wherein the fluid is an aqueous fluid, a hydrocarbon fluid, or a fluid comprising both water and a hydrocarbon.

8. The method of claim 1, 2, 3, or 4 wherein the fluid is a hydrocarbon fluid and a pour point depressant is further applied to the fluid in an amount ranging from 15 ppm to 2000 ppm, based on total volume of the fluid.
9. The method of claim 3, wherein the at least one demulsifier is selected from a group consisting of an oxyalkylated alkyl phenol formaldehyde resin, benzenesulfonic acid, 4-C10-13-sec-alkyl derivs., bis(2-ethylhexyl) sulfosuccinate sodium salt, phenol (para C4–C12 alkyl) bis polymer with (chloromethyl)oxirane methyloxirane and oxirane, methyloxirane polymer with oxirane, a propoxylated or ethoxylated polyamine, and combinations thereof.
10. The method of claim 4, wherein the water clarifier is selected from the group consisting of a cationic starch aqueous carbohydrate dispersion, a water-soluble modified starch, chitosan acetate, aluminum chloride hydroxide cationic polyacrylamide, an anionic polysulfonated copolymer, and a quaternized polytriethanolamine polymer.
11. The method of claim 1, 2, 3, or 4 wherein the fluid is a hydrocarbon fluid or a fluid comprising both water and a hydrocarbon, and where separating the chelate complex from the fluid comprises washing the fluid with water after applying the sulfur compound.
12. The method of claim 1, 2, 3, or 4 wherein separating the chelate complex comprises a process selected from the group consisting of centrifuging, filtering, air flotation, gravity separation, distillation, adsorption, electrophoresis, and combinations thereof.
13. A treated fluid comprising:
 - a fluid comprising at least one metal; and
 - characterized by an additive comprising a sulfur compound having the general formula HS-X, wherein X is a heteroatom substituted alkyl, cycloalkyl, aryl, and/or alkylaryl group, and a component selected

from the group consisting of at least one demulsifier, a buffering agent, a water clarifier, a pour point depressant, and combinations thereof.

14. The treated fluid of claim 13 wherein the fluid comprising at least one metal is selected from the group consisting of crude oil, an oilfield condensate, liquified petroleum gas, natural gas liquid, propane, butane, a refinery distillate, a residual fuel, storage tank sludge, a coke product, natural gas, refinery fuel gas, wastewater, produced water, a chemical process fluid, and combinations thereof.

15. The treated fluid of claim 13 wherein the sulfur compound is selected from the group consisting of 2-mercaptoethanol, bis (2-mercaptoethyl) sulfide, 2-mercaptoethyl disulfide, 1,8-dimercapto-3,6-dioxaoctane, mercaptoacetic acid, glyceryl monothioglycolate, 2-mercaptophenol, 4-mercaptophenol, 1,2 dithioethane, cysteamine, N,N dimethyl cysteamine, N,N'-bis(2-mercaptoethyl) ethylene-diamine, thiolactic acid, 1, 3, 5 triazine, 2,4,6 trithiol, and combinations thereof.

16. The treated fluid of claim 13, 14, or 15 wherein the additive comprises the sulfur compound and a buffering agent selected from a group consisting of glycolic acid, acetic acid, lactic acid, and combinations thereof.

17. The treated fluid of claim 13, 14, or 15 wherein the amount of the sulfur compound in the fluid ranges from 1 ppm to 500 ppm per the amount, in ppm, of the at least one metal in the fluid.

18. The treated fluid of claim 13, 14, or 15 wherein the additive comprises the sulfur compound and at least one demulsifier.

19. The treated fluid of claim 18 wherein the amount of the at least one demulsifier in the additive ranges from 1 ppm to 500 ppm, based on total volume of the fluid.
20. The treated fluid of claim 13, 14, or 15 wherein the additive comprising the sulfur compound and a water clarifier.
21. The treated fluid of claim 20 wherein the amount of the water clarifier in the additive ranges from 0.1 ppm to 200 ppm, based on the total volume of the fluid.
22. The treated fluid of claim 13, 14, or 15 further comprising a chelate complex of the sulfur compound with the at least one metal.

A. CLASSIFICATION OF SUBJECT MATTER**C10G 29/10(2006.01)i, C10G 29/20(2006.01)i, C10G 33/04(2006.01)i, C10L 3/10(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G 29/10; A61K 31/795; C02F 1/58; C07C 323/59; C09K 8/58; C10G 33/04; C10L 1/18; E21B 43/25; C10G 29/20; C10L 3/10

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: sulfur compound, HS-X, metal, chelate complex, fluid, buffering agent, demulsifier, water clarifier, pour point depressant, hydrocarbon fluid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0076246 A1 (HALEY, BOYD E. et al.) 31 March 2011 See paragraphs [0020], [0021], [0061], [0062].	1,5-7,12
Y		2-4,8-11,13-22
Y	US 2011-0172473 A1 (NGUYEN, TRAN M. et al.) 14 July 2011 See paragraphs [0021]-[0039], [0066].	2,3,8,9,11,13-19,22
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Y	US 6117333 A (FRANKIEWICZ, THEODORE C. et al.) 12 September 2000 See columns 1-3.	4,10,13,20-21
Y	MA, LUN et al., "A new Cu-cysteamine complex: structure and optical properties", Journal of Materials Chemistry C, 31 March 2014 (Publication date), Vol. 2, No. 21, pages 4239-4246 See abstract.	15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/047255

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