Dimercaptothiadiazoles to Prevent Corrosion of Mild Steel by Acid Gases in Oil and Gas Products

Abstract: Corrosion inhibitor compositions containing at least one sulfur compound and/or at least one aqueous-soluble salt of a sulfur compound inhibit or prevent mild steel corrosion by an acid gas such as carbon dioxide (CO2) and/or hydrogen sulfide (H2S) in oil and gas production processes. The sulfur compound may be a compound comprising at least three sulfur atoms, at least one of which is a thioether functional group. One suitable, but non-limiting, sulfur compound having at least three carbon atoms is 2,5-dimercapto-1,3,4-thiadiazole and salts thereof. The pH of the corrosion inhibitor composition may be optionally adjusted to be within about 5 to about 10 using an alkali metal hydroxide and/or an amine.
DIMERCAPTOTHIADIAZOLEs TO PREVENT CORROSION OF MILD STEEL BY ACID GASES IN OIL AND GAS PRODUCTS

TECHNICAL FIELD

[0001] The invention relates to methods and compositions for inhibiting and/or preventing the corrosion of metals, and, in one aspect, more particularly relates to methods and compositions for inhibiting and/or preventing the corrosion of mild steel in environments containing an acid gas such as carbon dioxide and/or hydrogen sulfide.

TECHNICAL BACKGROUND

[0002] It is well known that iron and steel surfaces will corrode in the presence of brines in equilibrium with acid gases such as carbon dioxide and hydrogen sulfide. While the rate at which corrosion will occur depends on a number of factors, such as the steel alloy itself, the fugacities of acid gases, the temperature of the environment, the length of contact, etc., some sort of corrosion invariably occurs. Attention has turned toward providing corrosion inhibitors in an upstream production stream to prevent corrosion of the steel surfaces that it must come into contact with, and in particular weak acids formed by acid gases.

[0003] Specific environments in which an improved corrosion inhibitor would be appreciated include high-temperature, high-shear wells where carbon steel is used as the tubing material. With respect to oil and gas production, it is well known that during the production life of an oil or gas well, the production zone within the well may be chemically treated to prolong the life of both well tubing and carbon steel pipelines.

[0004] In earlier years of producing subterranean wells, the vast majority of production and workover conduits comprised carbon steels. These steels were utilized either temporarily or permanently in the well, and treatment and/or stimulation fluids were introduced through them into the well. Due primarily to the drilling and completion of many subterranean wells through formations which contain high concentrations of corrosive fluids such as hydrogen sulfide,
carbon dioxide, brine, and combinations of these constituents, the production
and workover conduits for use in the wells are sometimes made of high alloy
steels, however they are normally made of low alloy carbon steels. The high
alloy steels include, but are not necessarily limited to, chrome steels, duplex
steels, stainless steels, martensitic alloy steels, ferritic alloy steels, austenitic
stainless steels, precipitation-hardened stainless steels, high nickel content
steels, and the like. However, corrosion inhibition of mild steel, also known as
plain-carbon steel, is still necessary. Mild steel is the most common form of
steel because its price is relatively low while it provides material properties that
are acceptable for many applications, more so than iron. Low-carbon steel or
mild steel is defined herein as that which contains approximately 0.05 - 0.3
wt% carbon, making it malleable and ductile. Mild steel has a relatively low
tensile strength, but it is inexpensive and malleable.

[0005] The use of monosodium, monopotassium or monooctanolamine salts
of 2,5-dimercapto-1,3,4-thiadiazole (DMcT) for the inhibition of the corrosion of
brass and steel plated with tin, nickel or chromium is known. U.S. Pat. No.
2,836,564 is directed to condensation products of alpha-halogenated aliphatic
mono-carboxylic acids and 2,5-dimercapto-1,3,4-thiadiazole as new composi-
tions of matter, to make the DMcT oil soluble, and to lubricants containing the
same, which lubricants possess corrosion and/or rust inhibiting properties.

Compositions which form homogeneous blends with lubricating oils and the like
are produced by preparing a mixture of an oil-soluble dispersant (preferably a
substantially neutral or acidic carboxylic dispersant) and a dimercaptothia-
diazole, preferably 2,5-dimercapto-1,3,4-thiadiazole, usually with a diluent,
especially a lubricant base liquid, and heating said mixture above about 100°C.
according to U.S. Pat. No. 4,136,043. The compositions often contain dimer-
captothiadiazole moieties in amounts substantially greater than stoichiometric.
They are useful for suppression of copper activity and "lead paint" deposition in
lubricants.

[0006] U.S. Pat. No. 4,193,882 concerns lubricant compositions containing,
in an amount sufficient to inhibit metal corrosion, the reaction product of oleic
acid and 2,5-dimercapto-1,3,4-thiadiazole. U.S. Pat. No. 5,137,649 concerns
mixed alcohol/dimercaptothiadiazole-derived hydroxy borates having been
found to be effective antiwear/antioxidant multifunctional additives for lubricants.

[0007] It would be advantageous if new corrosion inhibitors were discovered that would be an improvement over the presently known systems for mild steel, especially for oil and gas streams that contain carbon dioxide and/or hydrogen sulfide.

SUMMARY

[0008] There is provided, in one non-limiting embodiment, a method of inhibiting or preventing mild steel corrosion in the presence of a fluid comprising water, a hydrocarbon selected from the group consisting of oil, natural gas, products therefrom, and combinations thereof, and an acid gas selected from the group consisting of carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S), and combinations thereof. The method involves adding to a fluid in contact with mild steel an effective amount of a corrosion inhibitor composition to inhibit or prevent corrosion of the mild steel. The corrosion inhibitor composition includes at least one aqueous-soluble sulfur-containing compound including, but not necessarily limited to, a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, a salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, and combinations thereof.

[0009] Further in another non-restrictive version, there is provided an acidic fluid inhibited against mild steel corrosion, where the acidic composition includes water; a hydrocarbon selected from the group consisting of oil, natural gas, products therefrom, and combinations thereof; an acid gas selected from the group consisting of CO$_2$, H$_2$S, and combinations thereof; and a corrosion inhibitor composition including at least one aqueous-soluble sulfur compound including, but not necessarily limited to, a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, a salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, and combinations thereof, where the amount of corrosion inhibitor composition in the acidic fluid is effective to inhibit...
or prevent corrosion of the mild steel when the acidic fluid is in physical contact with mild steel.

BRIEF DESCRIPTION OF THE DRAWING

[0010] FIG. 1 is a graph of the corrosion rate of mild steel at 150°F (66°C) in kettle tests at atmospheric CO₂ with two different concentrations of 2,5-dimercapto-1,3,4-thiadiazole in a brine fluid.

DETAILED DESCRIPTION

[0011] It has been discovered that aqueous-soluble disulfides, including, but not necessarily limited to, dimercaptothiadiazoles such as 2,5-dimercapto-1,3,4 thiadiazole (DMcT) and its aqueous-soluble salts inhibit and prevent mild steel corrosion by acid gases such carbon dioxide (CO₂) and/or hydrogen sulfide (H₂S) with slight amounts of oxygen in oil and gas production processes.

[0012] The methods and compositions herein do not include the oil soluble reaction product of a carboxylic acid with 2,5-dimercapto-1,3,4 thiadiazole disclosed previously in prior art for lubricating oils; see H. Tadashi, K., Ueda, "Anticorrosive effect of dimercaptothiadiazoles", Jpn. Assoc. Corros. Control, Tokyo, Japan 105) Bosei Kanri 1990, 34(12) 538-42 (Japan). These authors examined the anticorrosive effect of sodium, potassium and monoethanol amine salts on ferrous and nonferrous metals. They found anticorrosive effects of the monoethanol amine salts on tin-, nickel- and chromium-plated steels but found no effect on cast iron FC20 and steel SS41. They also noted that dimercaptothiadiazole has poor solubility in water (0.01 wt% in water). In contrast, the methods and compositions herein relate to inhibiting corrosion in fluids that are predominantly water, that is, more than 50 wt% water, alternatively more than 60 wt% water, even more than 70 wt% water, and in other non-limiting embodiments more than 80 wt% water. A large number of oil production systems especially in older fields have liquid streams than often contain more than 90 wt% water. The minimum amount of water is 3 wt%.

[0013] In one non-limiting embodiment it has been surprisingly found that a formulation of 10 wt% 2,5-dimercapto-1,3,4 thiadiazole in water was able to
inhibit the corrosion of mild steel due to carbon dioxide. This discovery is expected to permit development of new high-temperature, high-shear water soluble corrosion inhibitors.

[0014] In more detail, at least one aqueous-soluble sulfur compound that contains at least three sulfur atoms in the structure at least one of which is present in a thioether functional group and more specifically includes, but is not necessarily limited to, 2,5-dimercapto-1,3,4-thiadiazole; 2,5-bis(oclyldithio)-1,3,4-thiadiazole; 1,3,4 thiadiazole-2,5 dithiol; 1,3,4-thiadiazole; 2,5 -bis (tert-nonyldithio); poly(1,3,4-thiadiazole-2,5-diylidithio); poly(1,3,4-thiadiazole-2,5-diylidithio) polymer with sulfur chloride; and combinations thereof. Alkyi groups attached to the thiadiazole may each independently range from about 1 to about 10 carbon atoms; alternatively from 1 to 8 carbon atoms, and in another non-limiting embodiment from 1 to 4 carbon atoms. All of these alkyi groups may independently be straight, branched and/or cyclic. As defined herein with respect to these alkyi groups, "independent" means that each alkyi group on the same molecule may have different carbon atoms, so long as the carbon atoms in each alkyi group falls within the given range, and that each alkyi group on the same molecule may be differently straight, branched and/or cyclic. Other non-limiting examples of suitable disulfides include, but are not necessarily limited to, 2,5-bis(octyldithio)-1,3,4-thiadiazole; 2,5-dimercapto-1,3,4-thiadiazole disodium salt; 2,5-dimercapto-1,3,4-thiadiazole monosodium salt; 2,5-dimercapto-1,3,4-thiadiazole dipotassium salt; 2,5-dimercapto-1,3,4-thiadiazole monopotassium salt; 2,5-dimercapto-1,3,4-thiadiazole dilithium salt; 2,5-dimercapto-1,3,4-thiadiazole zinc salt; 2,5-dimercapto-1,3,4-thiadiazole monobenzoate ester; poly(1,3,4-thiadiazole-2,5-diylidithio); 1,3,4-thiadiazolidine-2,5-dithione, polymer with sulfur chloride; and the like and mixtures thereof.

[0015] In the case where the corrosion inhibitor is one aqueous-soluble salt of the above 1,3,4 thiadiazole compounds, the one aqueous-soluble salt includes, but is not necessarily limited to, metal salts of the above disulfide compounds, amine salts of the above disulfide compounds, and carboxylic acid salts of the above disulfide compounds, where the metal is selected from the group consisting of alkali metal salts (including, but not necessarily limited to, lithium, sodium, potassium, cesium, and combinations thereof), zinc, and
combinations thereof, the amine is selected from the group consisting of primary amines, secondary amines, and tertiary amines, and combinations thereof, and the carboxylic acid is selected from the group consisting of benzoic acid, acetic acid, citric acid, and glycolic acid, and combinations thereof. However, in one non-limiting embodiment, the corrosion inhibitor does not include and has an absence of monoethanolamine salts of the suitable aqueous-soluble sulfur compounds.

[0016] The amount of the corrosion inhibitor composition added to a fluid in contact with mild steel, on a weight basis, ranges from about 0.01 ppm independently to about 10,000 ppm (1 wt%); alternatively from about 0.1 ppm independently to about 5,000 ppm; and in another non-limiting embodiment from about 1 ppm independently to about 1,000 ppm. As used herein with respect to ranges, the word "independently" means that any lower threshold may be used together with any upper threshold to give a suitable alternative range.

[0017] In one optional embodiment of the corrosion inhibiting composition and method described herein, the pH of the corrosion inhibitor composition may be adjusted or raised to be within about 5 independently to about 10; alternatively to from about 6 independently to about 9. The pH may be raised by addition of an effective amount of an alkali metal hydroxide including, but not necessarily limited to, sodium hydroxide and potassium hydroxide, and/or an amine including, but not necessarily limited to, monoethanolamine (MEA), diethylenetriamine (DETA), ethylenediaminetetraacetic acid (EDTA), methyl amine, and combinations of all of these.

[0018] Broadly, the fluid treated may be any fluid that involves the exploration, production and processing of oil and gas, and which contains water, a hydrocarbon and an acid gas (either CO₂ and/or H₂S). As defined herein, the fluids treated and products therefrom may contain oil and/or natural gas, and/or products from oil and/or natural gas. Again, in one non-limiting embodiment, the fluid is predominantly water, defined as greater than 50 wt% water. In this sense, "hydrocarbon" does not refer exclusively to compounds that only contain hydrogen and carbon atoms (although these are certainly included), but instead
refers to the broader sense in which "hydrocarbon" is used with respect to the exploration, production and processing of oil and gas, in the oil field and in refineries. The hydrocarbons in this sense may include, but are not necessarily limited to, those substituted with nitrogen, oxygen and sulfur, oligomers thereof, polymers thereof and the like.

[0019] The water in the fluid may be relatively pure, but is more likely to be brine, meaning that it has a salt content. The water in the fluid may also include any sea water, fresh water (including but not necessarily limited to river water, lake water, well/aquifer water and the like), condensed water, and the like, etc. The water may also include any water that could be used for secondary recovery, e.g. reservoir pressure maintenance. The salt in the brine may be any of those commonly found in the oil field, including, but not necessarily limited to, brines containing naturally occurring salts, or salts introduced via the process of exploration and production of hydrocarbons, including, but not necessarily limited to petroleum (also known as crude oil) and natural gas. The salts in the brine may include, but are not necessarily limited to, sodium chloride, potassium chloride, calcium bromide, calcium chloride, sodium bromide, other bromide salts, zinc salts, formate salts, and the like and combinations thereof. In one non-limiting embodiment of the invention, the brine is in equilibrium with the acid gas present.

[0020] The compositions and methods described herein are not limited to any particular proportion of acid gas. In one non-limiting embodiment, the method is practiced in systems without oxygen or in the absence of oxygen; more specifically without molecular oxygen or in the absence of molecular oxygen, O₂. Alternatively, the acidic fluid is without molecular oxygen or has an absence of molecular oxygen, O₂. Additionally, the fluids described and treated herein to inhibit and/or prevent mild steel corrosion in the presence of an acid gas are not lubricants and/or have an absence of lubricant.

[0021] In an oilfield context, the corrosion inhibitor formulation may be pumped or otherwise introduced into the fluid at a sufficient concentration to coat the mild steel well tubulars and other equipment, for instance to form a thin film.
In one non-restrictive version, an objective of the compositions and methods described herein is to inhibit or prevent corrosion of mild steel contacted by the fluid. It will also be appreciated that it is not necessary that corrosion be entirely prevented for the methods described herein to be considered successful, although corrosion prevention is certainly an acceptable goal. The methods may be considered successful if corrosion of mild steel contacting the fluid is inhibited or decreased as compared with an identical fluid which does not have a corrosion inhibitor, as described herein.

Organic sulfur containing molecules such as dimercaptothiadiazoles, including 2,5-dimercapto-1,3,4-thiadiazole, and its aqueous-soluble salts are potential high-shear water soluble high-temperature corrosion inhibitors. By "high-temperature" is meant a temperature between about 100°C independently to about 300°C; alternatively from about 125°C independently to about 275°C, and in a different non-limiting embodiment from about 150°C independently to about 250°C; and in a different non-restrictive embodiment from about 175°C independently to about 225°C. They potentially could be blended with scale inhibitors and may work better than 2-mercaptoethanol and/or 2-mercaptopoethanol sulfide.

Optional additional corrosion inhibitors which may be used with the thiadiazoles include, but are not necessarily limited to Mannich reaction products, imidazolines, amidoamines, phosphate esters, quaternary amine compounds, and combinations thereof. In one non-limiting embodiment, useful corrosion inhibitor bases are the Mannich reaction products, which may include, but are not necessarily limited to, the materials of U.S. Pat. Nos. 3,077,454; 5,366,643; and 5,591,381. The products of U.S. Pat. No. 3,077,454 can be made with approximately a 50% yield, and they require the presence of a fatty acid, such as a tall oil fatty acid, in one non-limiting embodiment. More specifically, the Mannich reaction product may be the product of reaction of:

(i) one mole of an ammonia derivative having at least one hydrogen attached to nitrogen and having no groups reactive under the conditions of reaction other than hydrogen,
(ii) from 1.5 to 10 moles of a carbonyl compound having at least one hydrogen atom on the carbon atom adjacent to the carbonyl group,

(iii) from 2 to 10 moles of an aldehyde different from the carbonyl compound selected from the group consisting of aliphatic aldehydes having from 1 to 16 carbon atoms and aromatic aldehydes of the benzene series and having no functional groups other than aldehyde groups, and

(iv) from 0.6 to 24 parts by weight based on (1), (2), and (3) of an organic acid having from 1 to 20 carbon atoms,

at a temperature from about 150°F (66°C) to about 250°F (121 °C) for from about 1 to 16 hours.

[0025] One suitable non-limiting Mannich reaction based acid corrosion inhibitor is comprised of the condensation reaction product of 1,3-dibutyl thiourea and acetophenone. Baker Hughes CI 200 is a corrosion inhibitor of this type. They contain acetylenic alcohols as well as oxyalkylated alcohol surfactant dispersants, in a co-solvent system containing methanol and fatty acid derivatives.

[0026] Baker Hughes CI 300 is a suitable quinoline quaternary amine-based acid corrosion inhibitor containing cinnamic aldehyde, as well as oxyalkylated linear alcohol dispersants in a mixed solvent system containing primary alcohols and aromatic naphtha.

[0027] Suitable quaternary amine compounds may include, but are not necessarily limited to, the nitrogen-substituted heterocycles of 6 to 10 members quaternized with alkyl halides, also commonly referred to as coal tar based quats. These materials are typically quinolines, pyridines and the like quaternized with alkyl and/or aryl halides, where the alkyl or aryl group may range from methyl to benzyl (C₁ to C₉). Naphthyl quinoline quats are included in this group. Further information may be found with reference to U.S. Pat. No. 2,814,593 which discusses benzyl chloride quats of quinoline.

[0028] Other optional ingredients may be used with the corrosion inhibitor herein, and may include, but are not necessarily limited to, nitrogen compounds, such as a quarternary ammonium compounds, amines amidoamines, phosphate esters solvents such as alcohols or ketones; and aromatic hydrocar-
bons or mixtures thereof, as are known to those skilled in the art. For example, teachings from acid corrosion inhibitors as made and described in U.S. Pat. Nos. 3,514,410; 3,404,094; 3,107,221; 2,993,863; and 3,382,179; may be utilized herein. In one non-restrictive embodiment, the corrosion inhibitor contains at least one acetylenic alcohol having from 3 to 10 carbon atoms. In another non-limiting embodiment herein however, the corrosion inhibitor excludes and/or has an absence of acetylenic alcohol.

[0029] The nitrogen or ammonia compounds that can be optionally employed herein, may include, but are not limited to, those amines having from 1 to 24 carbon atoms in each alkyl moiety as well as the six-membered heterocyclic amines, for example, alkyl pyridines, crude quinolines and mixtures thereof. This includes such amines as ethylamine, diethylamine, triethylamine, propylamine, dipropylamine, tripropylamine, mono-, di- and tripentylamine, mono-, di- and trihexylamine and isomers of these such as isoproplamine, tertiary-butylamine, etc. This also includes alkyl pyridines having from one to five nuclear alkyl substituents per pyridine moiety, such alkyl substituents having from one to 12 carbon atoms, and preferably those having an average of six carbon atoms per pyridine moiety, such as a mixture of high boiling tertiary-nitrogen-heterocyclic compounds, such as HAP (high alkyl pyridines), Reilly 10-20 base and alkyl pyridines H3. Other nitrogen compounds include the crude quinolines having a variety of substituents.

[0030] The corrosion inhibitor may also contain a number of other constituents, such as fatty alcohol adducts, nonyl phenol adducts and tallow amine adducts, tall oil adducts, such as surfactants. Oil wetting components, such as heavy aromatic solvents, may also be present. In another non-limiting embodiment, the corrosion inhibitor contains at least one saturated alcohol having from 1 to 5 carbon atoms, and at least one alkyl phenol or alkoxyolated alkyl phenol having from 15 to 24 carbon atoms.

[0031] The corrosion inhibitor composition also contemplates incorporation of these other corrosion inhibitors, which typically will be provided in treatment concentrations of from about 0.1 ppm, based upon the weight of the entire treatment fluid independently to about 1,000 ppm of such weight. Most often,
the total amount of corrosion inhibitors will range from about 10 independently to 200 ppm.

[0032] It will be appreciated that the compositions and methods herein will have applicability to other industries besides petroleum recovery, including, but not necessarily limited to, well tubing, well casing, pipelines and other conduits, and other applications where it is desirable to decrease corrosion, such as chemical processes that necessarily require the contact of acid gases etc. While the specific implementation of the methods and compositions herein is described in the context of the oil patch, they may certainly find uses in conduits, fittings, and other equipment in hard to reach locations, such as industrial cleaning applications. It will be appreciated that one of ordinary skill in the art of corrosion inhibition will be able to adapt the teachings herein to applications outside the realm of oil and gas recovery, such as the area of chemical processing, with only routine experimentation.

[0033] In the implementation of the methods and corrosion inhibitors herein in the production of fluids from subterranean reservoirs, a fluid may be introduced through a mild steel member or conduit positioned within a well or other equipment. The corrosion inhibitor herein is introduced, added, or injected into the fluid. As noted, the fluid may contain one or more of an acid gas, such as carbon dioxide and/or hydrogen sulfide. Also included herein are methods of treating a well for enhancement of production within a production zone by introduction or addition into a fluid, particularly one containing an acid gas, of the corrosion inhibitor composition herein.

[0034] The invention will be described further in the following illustrative Example, which is non-limiting and serves only to further illuminate the invention.

EXAMPLE 1

[0035] A formulation of 10% 2,5-dimercapto-1,3,4 thiadiazole (DMTDA) in water with KOH added to adjust the pH to 8.1 was made. The corrosion inhibition of this formulation was tested in a kettle test at 150°F (66°C), atmos-
pheric CO₂ in a 90% NACE (National Association of Corrosion Engineers) brine and 10% ISOPAR™-M mixture. The results are shown in FIG. 1.

[0036] The blank corrosion rates range from 140 to 190 mpy (mils per year). Immediately with the injection of the corrosion inhibitor, the corrosion rate lowered to below 40 mpy in the test with the addition of 2.5 or 5 ppm of 2,5-dimercapto-1,3,4-thiadiazole.

[0037] Many modifications may be made in the present invention without departing from the scope thereof that are defined only by the appended claims. For example, certain components perse, or combinations of components thereof other than those specifically set out herein may be found by one of routine skill in the art to be particularly advantageous, different aqueous-soluble disulfide compounds, with certain optional solvents and/or other corrosion inhibitors, surfactants, etc. other than those mentioned or exemplified are expected to be useful.

[0038] The words "comprising" and "comprises" as used throughout the claims is interpreted "including but not limited to".

[0039] 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, in one non-limiting embodiment, there is provided a method of inhibiting or preventing mild steel corrosion in the presence of an acid gas selected from the group consisting of carbon dioxide (CO₂), hydrogen sulfide (H₂S), and combinations thereof, where the method consists essentially of or consists of adding to a fluid in contact with mild steel an effective amount of a corrosion inhibitor composition to inhibit or prevent corrosion of the mild steel. The fluid may consist essentially of or consist of water, a hydrocarbon selected from the group consisting of oil, natural gas, products therefrom, and combinations thereof, and an acid gas selected from the group consisting of CO₂, H₂S, and combinations thereof. The corrosion inhibitor composition may consist essentially of or consist of at least one aqueous-soluble sulfur compound selected from the group consisting of a compound comprising at least three sulfur atoms, at least one of which is
present in a thioether functional group (in a non-limiting example, a thiadiazole), a salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, and combinations thereof.

[0040] Alternatively, there may be provided an acidic fluid inhibited against mild steel corrosion, where the acidic composition consists essentially of or consists of brine; a hydrocarbon selected from the group consisting of oil, natural gas, products therefrom, and combinations thereof; an acid gas selected from the group consisting of CO$_2$, H$_2$S, and combinations thereof in equilibrium with the brine; and a corrosion inhibitor composition comprising, consisting essentially of, or consisting of at least one aqueous-soluble sulfur compound selected from the group consisting of aqueous-soluble a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group (such as a thiadiazole), a salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group (such as a thiadiazole), and combinations thereof, where the amount of corrosion inhibitor composition in brines in equilibrium with acid gases such as carbon dioxide and hydrogen sulfide is effective to inhibit or prevent corrosion of the mild steel when the brine in equilibrium with acid gases such as carbon dioxide and hydrogen sulfide is in physical contact with mild steel.
What is claimed is:

1. A method of inhibiting or preventing mild steel corrosion in the presence of a fluid comprising water, a hydrocarbon selected from the group consisting of oil, natural gas, products therefrom, and combinations thereof, and an acid gas selected from the group consisting of carbon dioxide (CO₂), hydrogen sulfide (H₂S), and combinations thereof, the method comprising:
   - adding to the fluid in contact with mild steel an effective amount of a corrosion inhibitor composition to inhibit or prevent corrosion of the mild steel, where the corrosion inhibitor composition comprises at least one aqueous-soluble sulfur compound selected from the group consisting of:
     - a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group,
     - a salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, and combinations thereof.

2. The method of claim 1 where the effective amount of the corrosion inhibitor composition ranges from 0.01 ppm to 10,000 ppm.

3. The method of claim 1 where in the corrosion inhibitor composition:
   - the aqueous-soluble sulfur compound comprising at least three sulfur compounds at least one of which is present in a thioether functional group is a thiadiazole, and
   - the salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group is selected from the group of metal salts, amine salts, and carboxylic acid salts thereof:
a metal of the metal salts is selected from the group consisting of alkali metals, zinc, and combinations thereof,
an amine of the amine salts is selected from the group consisting of primary amines, secondary amines, tertiary amines, and combinations thereof, and
a carboxylic acid of the carboxylic acid salts is selected from the group consisting of benzoic acid, acetic acid, citric acid, glycolic acid, and combinations thereof.

4. The method of claim 1, 2, or 3 further comprising adjusting the pH of the corrosion inhibitor composition to be within 5 to 10.

5. The method of claim 4 where the pH of the corrosion inhibitor composition is adjusted using a pH adjuster selected from the group consisting of:
   alkali metal hydroxides selected from the group consisting of sodium hydroxide and potassium hydroxide;
   amines selected from the group consisting of monoethanolamine (MEA), diethylenetriamine (DETA), ethylenediaminetetraacetic acid (EDTA), methyl amine; and
   combinations of the above.

6. The method of claim 1, 2, or 3 where the at least one aqueous-soluble sulfur compound is selected from the group consisting of 2,5-dimercapto-1,3,4-thiadiazole; 2,5-bis(octyldithio)-1,3,4-thiadiazole; 1,3,4-thiadiazole-2,5 dithiol; 1,3,4-thiadiazole; 2,5 -bis (tert-nonyldithio); poly(1,3,4-thiadiazole-2,5-diyldithio); poly(1,3,4-thiadiazole-2,5-diyldithio) polymer with sulfur chloride; 2,5-bis(octyldithio)-1,3,4-thiadiazole; 2,5-dimercapto-1,3,4-thiadiazole disodium salt; 2,5-dimercapto-1,3,4-thiadiazole monosodium salt; 2,5-dimercapto-1,3,4-thiadiazole dipotassium salt; 2,5-dimercapto-1,3,4-thiadiazole monopotassium salt; 2,5-dimercapto-1,3,4-thiadiazole dilithium salt; 2,5-dimercapto-1,3,4-
thiadiazole zinc salt; 2,5-dimercapto-1,3,4-thiadiazole monobenzoate ester; poly(1,3,4-thiadiazole-2,5-diyldithiol); 1,3,4-thiadiazolidine-2,5-dithione, polymer with sulfur chloride; and combinations thereof.

7. The method of claim 1, 2 or 3 where the fluid comprises more than 50 wt% water.

8. The method of claim 1, 2 or 3 where the acid gas is CO₂ and where the corrosion inhibitor composition comprises at least 10 wt% 2,5-dimercapto-1,3,4-thidiazole and/or salts thereof in water.

9. The method of claim 1, 2, or 3 where the method is practiced in the absence of molecular oxygen.

10. An acidic fluid inhibited against mild steel corrosion, the acidic composition comprising:
    water;
    a hydrocarbon selected from the group consisting of oil, natural gas, products therefrom, and combinations thereof;
    an acid gas selected from the group consisting of CO₂, H₂S, and combinations thereof; and
    a corrosion inhibitor composition comprising at least one aqueous-soluble sulfur compound selected from the group consisting of
    a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group,
    a salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group, and
    combinations thereof;
where the amount of corrosion inhibitor composition in the acidic fluid is effective to inhibit or prevent corrosion of the mild steel when the acidic fluid is in physical contact with mild steel.
11. The acidic fluid of claim 10 where the amount of the corrosion inhibitor composition in the acidic fluid ranges from 0.1 ppm to 1,000 ppm.

12. The acidic fluid of claim 10 where in the corrosion inhibitor composition: the aqueous-soluble thia diazole containing at least three sulfur compounds at least one of which is present in a thioether functional group, and where in the aqueous-soluble salt of a compound comprising at least three sulfur atoms, at least one of which is present in a thioether functional group is selected from the group of metal salts, amine salts, and carboxylic acid salts:
   a metal of the metal salts is selected from the group consisting of alkali metals, zinc, and combinations thereof,
   an amine of the amine salts is selected from the group consisting of primary amines, secondary amines, tertiary amines, and combinations thereof, and
   a carboxylic acid of the carboxylic acid salts is selected from the group consisting of benzoic acid, acetic acid, citric acid, glycolic acid, and combinations thereof.

13. The acidic fluid of claim 10, 11, or 12 where the pH of the corrosion inhibitor composition is adjusted to be within 5 to 10 using a pH adjuster selected from the group consisting of:
   alkali metal hydroxides selected from the group consisting of sodium hydroxide and potassium hydroxide;
   amines selected from the group consisting of monoethanolamine (MEA), diethylenetriamine (DETA), ethylenediaminetetraacetic acid (EDTA), methylamine; and combinations of the above.
14. The acidic fluid of claim 10, 11, or 12 where the acidic fluid has an absence of molecular oxygen.

15. The acidic fluid of claim 10, 11, or 12 where the at least one aqueous-soluble sulfur compound is selected from the group consisting of 2,5-dimercapto-1,3,4-thiadiazole; 2,5-bis(octylthio)-1,3,4-thiadiazole; 1,3,4-thiadiazole-2,5 dithiol; 1,3,4-thiadiazole; 2,5-bis(tert-nonyldithio); poly(1,3,4-thiadiazole-2,5-diyl)dithio); poly(1,3,4-thiadiazole-2,5-diyl)dithio) polymer with sulfur chloride; 2,5-bis(octylthio)-1,3,4-thiadiazole; 2,5-dimercapto-1,3,4-thiadiazole disodium salt; 2,5-dimercapto-1,3,4-thiadiazole monosodium salt; 2,5-dimercapto-1,3,4-thiadiazole dipotassium salt; 2,5-dimercapto-1,3,4-thiadiazole monopotassium salt; 2,5-dimercapto-1,3,4-thiadiazole dilithium salt; 2,5-dimercapto-1,3,4-thiadiazole zinc salt; 2,5-dimercapto-1,3,4-thiadiazole monobenzoate ester; poly(1,3,4-thiadiazole-2,5-diyl)dithio); 1,3,4-thiadiazolidine-2,5-dithione, polymer with sulfur chloride; and combinations thereof.

16. The acidic fluid of claim 10, 11, or 12 where the fluid comprises more than 50 wt% water.

17. The method of claim 10, 11, or 12 where the acid gas is C0_2 and where the corrosion inhibitor composition comprises at least 10 wt% 2,5-dimercapto-1,3,4-thiadiazole and/or salts thereof in water.
**Kettle Test**

90% NACE Brine/10% Isopar M

DMTDA

- 2.5 ppm
- 5 ppm

**FIG. 1**
INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/020351

A. CLASSIFICATION OF SUBJECT MATTER

C23F 11/00; C07C 140/26; C09D 5/08; C07C 145/00; C23F 11/04; C09K 3/00; E21B 41/02; C09K 8/54

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)
C23F 11/00; C07C 140/26; C09D 5/08; C07C 145/00; C23F 11/04; C09K 3/00; E21B 41/02; C09K 8/54

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: corrosion inhibitor, mild steel, composition, thioether, thiadiazole, sulfur and acid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search
24 June 2015 (24.06.2015)

Date of mailing of the international search report
24 June 2015 (24.06.2015)

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