

Description

Title of Invention: Corrosion Inhibitors and Methods of Use

Technical Field

- 5 The present invention generally relates to corrosion inhibitors and methods of using the same.

Background Art

Corrosion of steel or other metallic alloys occurring during the transport of hydrocarbon fluids is a problem faced by the petrochemical industry in general. Steel corrosion may
10 erode and compromise the structural integrity of transportation piping over a period of time if left unchecked. Additionally, the extent of corrosion may be exacerbated by the presence of acidic or basic compounds in the fluid streams being transported within these steel conduits.

Various technical solutions have been proposed for addressing the issue of corrosion and
15 for improving asset integrity. For instance, surfaces which are susceptible to corrosion may be coated or embedded with a protective or sacrificial metal layer which oxidizes preferentially to the surface material. Alternatively, a protective or chemically inert coating may also be applied to the surface to act as a physical barrier between the surface and the corrosive environment. Another solution involves the use of compounds which act as
20 corrosion inhibitors. Corrosion inhibitors usually act by adsorption to the surface to be protected and may possess one or more functional groups capable of repelling the corrosive elements present in the fluid flow. In some instances, corrosion inhibitors are injected

intermittently or continuously in controlled amounts into a body of flowing fluid. As examples, polyvinyls and polyesters have been demonstrated to provide particularly useful corrosion inhibitors for protecting carbon steel that is exposed to acidic flow conditions.

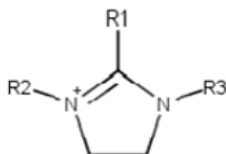
However, currently available solutions may prove inadequate for preventing corrosion of metal, in particular steel surfaces, under harsher or more severe flow conditions, e.g., high pressure conditions wherein one or more gaseous components exists as supercritical fluids. Under such conditions, the rate of corrosion of metal is typically more pronounced, which may render the provision of protective layers or sacrificial layers impractical and costly due to the constant need for replacement and/or re-coating. More importantly, damage caused to the gas transport equipment or piping by corrosive fluids or severe flow conditions may result in flow interruption and operation downtime, which reduces flow assurance. Supercritical fluid environments may also impair the ability of conventional corrosion inhibitors to adsorb onto the surface of the material being protected, in particular, since these interactions are non-covalent interactions.

Accordingly, there is a need to provide a composition for preventing corrosion of metal surfaces that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

In an aspect of the present disclosure, there is provided a composition for use as a corrosion inhibitor in a fluid environment having a CO₂ partial pressure of up to 150 bars, the composition comprising at least one substituted imidazoline of Formula (I) and a thiosulfate salt:

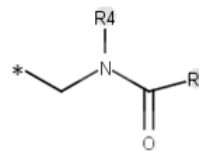
2a



Formula I

wherein

R1 is a hydrophobic group;



R2 is a polar group having the following structural formula , wherein *

- 5 denotes that attachment point, wherein R4 and R5 are independently H, halogen, optionally substituted alkyl, haloalkyl, optionally substituted alkenyl and optionally substituted alkynyl; and
- R3 is H, optionally substituted alkyl, optionally substituted alkenyl, or optionally substituted alkynyl.
- 10 In another aspect of the present disclosure, there is provided a method of inhibiting or reducing corrosion on a metal surface being exposed to a flowing fluid stream, the method comprising a

step of contacting the metal surface with a corrosion inhibitor composition comprising at least one substituted imidazoline of Formula (I) as defined herein and a thiosulfate salt, or a composition as disclosed herein.

5 In a further aspect of the present disclosure, there is provided a use of a corrosion inhibitor composition as disclosed herein for inhibiting or reducing corrosion of a steel surface.

In a further aspect of the present disclosure, there is also provided a system for transporting a fluid, said system comprising at least one metal conduit for conveying said fluid therethrough, and wherein said system comprises at least one inlet means that is fluidly communicated with a source of a corrosion inhibitor composition as disclosed herein, and wherein said inlet means is
10 configured to discharge the corrosion inhibitor composition into the fluid during transport of said fluid.

According to the present disclosure, there is provided a composition comprising at least one substituted imidazoline and a thiosulfate salt. The disclosed composition may be suitable for use as a corrosion inhibitor. In embodiments, the disclosed composition may serve as a corrosion
15 inhibitor for preventing or reducing corrosion of a metal surface that is being exposed to supercritical fluid flow, e.g., supercritical carbon dioxide (CO₂). The disclosed composition may be advantageously suited for use in reducing corrosion rate under fluid environments with CO₂ partial pressure of up to 150 bars. In embodiments disclosed herein, the metal surface may refer to a steel surface, or a carbon steel surface, or other alloys of steel thereof.

The substituted imidazoline may comprise at least one polar moiety and at least one non-polar moiety. The non-polar moiety may be a hydrophobic group or an electron-donating group.

Without being bound by theory, it is postulated that the polar moiety anchors the imidazoline to the metal surface to be protected (e.g., a steel surface), while the imidazoline is sterically
5 arranged or configured to present the non-polar / electron-donating moiety (e.g., long-chain alkyl) in an orientation normal to the surface to which the imidazoline is anchored. Advantageously, the arrangement of the hydrophobic or non-polar moiety helps to repel reactive species from contacting or reacting with the metal surface, thereby preventing electrochemical corrosion. Advantageously, the polar group may allow the imidazoline to form *in situ* a
10 protective film layer that is coupled to the metal surface. The film layer may be substantially uniform in thickness. The film layer may also be electrostatically bound to the metal surface due to the presence of the polar group.

The type of imidazoline is not particularly limited and it is expected that suitable technical variants and derivatives of imidazoline would be known to one ordinarily skilled in the art.
15 Nonetheless, the present disclosure exemplifies at least one corrosion inhibitor composition comprising a substituted imidazoline in combination with the thiosulfate salt.

Advantageously, it has been found that when a substituted imidazoline is combined with a thiosulfate, the resulting composition provides unexpectedly superior corrosion inhibition, even when used under or injected into in a supercritical fluid. In embodiments, the disclosed
20 composition is capable of providing a reduced corrosion rate of the metal surface that has been exposed to or is in contact with a supercritical fluid, e.g., supercritical CO₂ and water. Advantageously, the reduced corrosion rate of the metal surface may be less than 0.5 mm/year, less than 0.4, less than 0.3, less than 0.2, less than 0.1, less than 0.09, less than 0.08, less than 0.07, less than 0.06, or less than 0.05 mm/year. In embodiments, the reduced corrosion rate may
25 be from about 0.01 – 0.2, from about 0.01 to about 0.1, from about 0.01 to about 0.05, from about 0.01 to about 0.025 mm/year. In other embodiments, the corrosion rate may be

advantageously be from 0 to 0.1 mm/year under the above described high CO₂ partial pressure conditions.

In embodiments disclosed herein, the supercritical fluid may comprise supercritical carbon dioxide and water. The supercritical fluid may comprise essentially of supercritical carbon dioxide, that is, the bulk of the fluid is supercritical carbon dioxide and wherein trace amounts of water may be present. In other embodiments disclosed herein, the supercritical fluid may consist essentially of supercritical carbon dioxide. The disclosed corrosion inhibitor comprising the substituted imidazoline and the thiosulfate salt has been found to be particularly effective in preventing or reducing corrosion of steel surfaces that are in contact with water-containing supercritical carbon dioxide.

The present disclosure also relates to a method for inhibiting or reducing corrosion of a metal surface, the method comprising a step of contacting the metal surface with a corrosion inhibitor composition comprising a substituted imidazoline and a thiosulfate salt. In embodiments, the metal surface may be one that is constantly, intermittently or periodically exposed to a supercritical fluid. The method may comprise contacting the metal surface with a corrosion inhibitor composition that is disclosed herein.

Likewise, the disclosed method may be advantageously suited for inhibiting or reducing corrosion of metal surfaces that are exposed to or under high pressure, high temperature or supercritical fluid flow conditions. The disclosed method may be advantageously suited for inhibiting or reducing corrosion of metal surfaces exposed to supercritical carbon dioxide. In embodiments, the disclosed method and composition may inhibit or reduce corrosion rates at fluid flow pressure of up to 150 bars and a fluid flow temperature of up to 100 °C. In particular embodiments, the disclosed method and corrosion inhibitor composition may be capable or inhibiting or reducing corrosion of metal surfaces exposed to fluids having a CO₂ partial pressure of from about greater than 0 bars to about 150 bars, about 10 to about 150 bars, about 20 to about 150 bars, about 30 to about 150 bars, about 40 to about 150 bars, about 50 to about

150 bars, about 60 to about 150 bars, about 70 to about 150 bars, about 80 to about 150 bars, about 90 to about 150 bars, about 100 to about 150 bars, about 110 to about 150 bars, about 120 to about 150 bars, about 130 to about 150 bars, or about 140 to about 150 bars. For brevity, it should be noted that each disclosed pressure range may be subject to a variance of about ± 9 ,
5 ± 8 , ± 7 , ± 6 , ± 5 , ± 4 , ± 3 , ± 2 or ± 1 bar.

Definitions

The following words and terms used herein shall have the meaning indicated:

The term “alkyl”, when used herein, refers to a linear or branched, optionally substituted, saturated hydrocarbon group having from 1 to 40 carbon atoms. Exemplary alkyl groups
10 include but are not limited to methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl,
15 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, undecyl, and dodecyl.

The term “heteroalkyl” when used herein, refers to an alkyl group wherein one or more carbon atoms are replaced by an oxygen-, nitrogen-, phosphorus, boron or sulphur atom.

20 The terms “heteroalkenyl” and “heteroalkynyl” shall be construed accordingly.

The term “alkenyl” when used herein, refers to straight chain or branched chain unsaturated aliphatic groups containing at least one carbon-carbon double bond and having from 2 to 20 carbon atoms. Exemplary alkenyl groups may include but are not limited to ethenyl, propenyl, butenyl, 1-butenyl, 2-butenyl, 2-methylpropenyl, 1-pentenyl, 2-pentenyl, 2-methylbut-1-enyl, 3-methylbut-1-enyl, 2-methylbut-2-enyl, 1-hexenyl, 2-hexenyl, 3-
25 methylbut-1-enyl, 3-methylbut-1-enyl, 2-methylbut-2-enyl, 1-hexenyl, 2-hexenyl, 3-

hexenyl, 2,2-dimethyl-2-butenyl, 2-methyl-2-hexenyl, 3-methyl-1-pentenyl, and 1,5-hexadienyl.

The term "alkynyl" when used herein, refers to a hydrocarbon group having at least 2 to 30 carbon atoms and containing at least one carbon-carbon triple bond.

- 5 The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one, two, three or more groups other than hydrogen provided that the indicated atom's normal valency is not exceeded, and that the substitution results in a stable compound. Such groups may be, for example, halogen, hydroxy, oxo, cyano, nitro, alkyl, alkoxy, haloalkyl, haloalkoxy, aryl alkoxy, alkylthio,
- 10 hydroxyalkyl, alkoxyalkyl, cycloalkyl, cycloalkylalkoxy, alkanoyl, alkoxycarbonyl, alkylsulfonyl, alkylsulfonyloxy, alkylsulfonylalkyl, arylsulfonyl, arylsulfonyloxy, arylsulfonylalkyl, alkylsulfonamido, alkylamido, alkylsulfonamidoalkyl, alkylamidoalkyl, arylsulfonamido, arylcarboxamido, arylsulfonamidoalkyl, arylcarboxamidoalkyl, aroyl, aroyl4alkyl, arylalkanoyl, acyl, aryl, arylalkyl, alkylaminoalkyl.

- 15 The terms "halo-" or "halogen" may refer to fluorine, bromine, chlorine, and iodine.

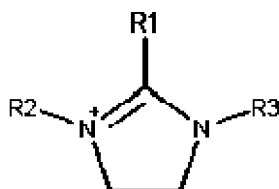
The term 'steel' is to be interpreted broadly to include an alloy of iron, carbon and optionally further including one or more elements selected from manganese, nickel, chromium, molybdenum, vanadium, silicon, boron, aluminium, cobalt, copper, cerium, niobium, titanium, tungsten, tin, zinc, lead, and zirconium. The term "steel" should be

20 taken to broadly include crucible steel, carbon steel, alloy steel, and alloys thereof. In one embodiment, the "steel" surfaces referred to in the present disclosure may be "alloy steel".

The term "carbon steel", as used in the context of the present application, refers to steel in which the primary alloying component is carbon and wherein from 0.1 to 3% by weight of the alloy is carbon.

The term “supercritical fluid” as used in the context of the present application, refers to a fluid that is subjected to or existing under a specific set of pressure and temperature conditions, such that the fluid does not possess distinct liquid and gas phases. The temperature and pressure at which a fluid becomes supercritical is termed “critical temperature” and “critical pressure” respectively. At supercritical conditions, the density possessed by the fluid is also termed its “critical density”. As an example, supercritical CO₂ occurs at 304.1k, 72.8 bar and possesses a critical density of 0.469 gcm⁻³.

The term “substituted imidazoline”, as used in the context of the present application, refers to a five-membered heterocyclic compound having a generic structure expressed by



Formula I

Formula I ; and wherein R1-R3 are as defined herein. The term “substituted imidazoline” may include imidazoline compounds comprising at least one polar moiety and at least one hydrophobic moiety. The polar moiety may be provided on position 3 of the heterocycle (i.e., at R2’s position). The non-polar or hydrophobic moiety may be provided at position 2 of the heterocycle, i.e., at position R1.

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the

stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

In an embodiment of the present disclosure, there is provided a composition comprising at least one substituted imidazoline and a thiosulfate salt, wherein said substituted imidazoline comprises at least one polar moiety and at least one non-polar or hydrophobic moiety. The substituted imidazoline and the thiosulfate salt may be blended in weight ratios as disclosed herein to form an admixture or a ready-to-use corrosion inhibitor ("CI") formulation. Other suitable additives, including but not limited to, excipients, surfactants, solvents, rheological modifiers and carriers may be mixed with the above active ingredients of the disclosed

composition. Such additives would be known to one skilled in the art and would not be further discussed herein.

In embodiments disclosed herein, the CI composition comprises about 1% to about 10% by weight of the thiosulfate salt, such as about 1%, about 2%, about 3%, about 4%, about 5%,
5 about 6%, about 7%, about 8%, about 9% or about 10% by weight of the thiosulfate salt. The CI composition may comprise the thiosulfate salt in a range comprising an upper limit and a lower limit selected from any two percentage values disclosed above.

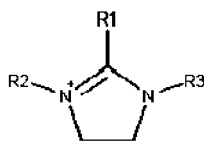
The thiosulfate salt may be selected from lithium thiosulfate, potassium thiosulfate or sodium thiosulfate. In a particular embodiment, the disclosed composition comprises about
10 5% by weight of a sodium thiosulfate.

In embodiments disclosed herein, the CI composition comprises about 10% to about 30% by weight of the substituted imidazoline, for example, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23%, about 24%, about 25%, about 26%, about 27%,
15 about 28%, about 29% or about 30% by weight of the substituted imidazoline. The amount of substituted imidazoline contained within the CI composition may be in a range comprising an upper limit and a lower limit selected from any two percentage values disclosed above. In a particular embodiment, the disclosed composition comprises about 30% by weight of a substituted imidazoline of formula II as further disclosed herein.

20 A particular embodiment of the disclosed CI composition comprises from about 20 wt. % to about 30 wt. % of the substituted imidazoline, about 1 wt. % to about 10 wt. % of the thiosulfate salt and about 40 wt. % to about 89 wt. % of a solvent, wherein the total weight percent is 100 %. A preferred solvent for the disclosed composition is water.

A further embodiment of the disclosed CI composition comprises from about 30 wt. % of
25 said imidazoline derivative, about 5 wt. % thiosulfate and about 65 wt. % of the solvent. The solvent may be water.

The substituted imidazoline may be a compound having the following formula (I):



Formula I

wherein

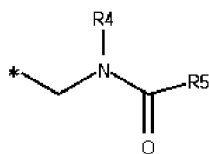
R1 is a hydrophobic group;

5 R2 is a polar group; and

R3 is H, optionally substituted alkyl, optionally substituted alkene, or optionally substituted alkynyl.

R1 may be a non-polar, hydrophobic group. In embodiments, R1 may be optionally substituted alkyl, optionally substituted heteroalkyl, optionally substituted alkene, optionally substituted heteroalkene, or optionally substituted alkynyl. R1 may be a C₁₀₋₄₀ alkyl or a heteroalkyl comprising at least one unsaturated carbon or at least one heteroatom expressing a lone pair of electrons. In embodiments, R1 is a unsubstituted C₁₀₋₂₀ alkenyl group. In other embodiments, R1 may be an unsubstituted C₁₂₋₁₇ alkenyl group. R1 may be selected from an unsaturated C6-20 alkyl group, C7-20 alkyl group, C8-20 alkyl group, C9-20 alkyl group, C10-20 alkyl group, C11-20 alkyl group, C12-20 alkyl group, C13-20 alkyl group, C14-20 alkyl group, C-15-20 alkyl group, C16-20 alkyl group, C17-20 alkyl group, C18-20 alkyl group, or a C19-20 alkyl group.

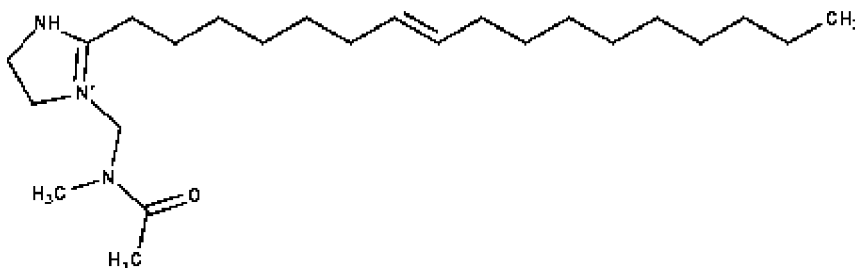
In embodiments, R2 may be a polar moiety comprising at least one polar functional group that expresses electrostatic affinity with a metal surface. For example, R2 may be optionally substituted amino, alkoxy, ether, carbonyl, carboxylate, or optionally substituted alkylacetamide, each group may be optionally attached to the core imidazoline structure via an alkylene bridge. For instance, R2 may be a polar group having the following structural



formula , wherein * denotes that attachment point, wherein R4 and R5 are independently H, halogen, optionally substituted alkyl, haloalkyl, optionally substituted alkenyl and optionally substituted alkynyl. In embodiments, R4 and R5 may be independently selected from methyl, ethyl, propyl, butyl, pentyl or hexyl.

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In one embodiment, the substituted imidazoline for use in the disclosed corrosion inhibitor compositions is a compound having the **formula (II)**:



The present disclosure also relates to a method of inhibiting or reducing corrosion on a metal surface being exposed to a flowing fluid stream, the method comprising a step of contacting the metal surface with a corrosion inhibitor composition comprising at least one substituted imidazoline and a thiosulfate salt, or the compositions as disclosed above.

The fluid stream may comprise carbon dioxide and water. The water may be present in a liquid state e.g., free-flowing water, or may be present as water vapour, or a mixture thereof. In embodiments, the fluid stream may comprise supercritical carbon dioxide containing trace amounts of water or is saturated with water. The water content may exceed 10,000 ppm. In certain embodiments, the water content of the fluid stream may be from about 1,000 ppm to about 10,000 ppm. In embodiments disclosed herein, the water content of the fluid stream may be about 1,000 ppm, 2,000 ppm, 3,000 ppm, 4,000 ppm, 5,000 ppm, 6,000 ppm, 7,000 ppm, 8,000 ppm, 9,000 ppm or 10,000 ppm, subject to a variance of

±250 ppm. Under water-saturation conditions, the water content of the fluid stream may be about 7,000 ppm. Advantageously, it has been found that even at water-saturation conditions, the disclosed corrosion inhibitor is capable to reducing corrosion rates to less than 0.5 to 0.05 mm per year.

- 5 The fluid stream may be characterized by a mixture of carbon dioxide and water, wherein the molar concentration of carbon dioxide may be from about 1 to 99 mol%. The molar concentration (mol %) of CO₂ may be about 1 mol%, 5 mol%, 10 mol%, 15 mol%, 20 mol%, 25 mol%, 30 mol%, 35 mol%, 40 mol%, 45 mol%, 50 mol%, 55 mol%, 60 mol%, 65 mol%, 70 mol%, 75 mol%, 80 mol%, 85 mol%, 90 mol%, 91 mol%, 92 mol%, 93
10 mol%, 94 mol%, 95 mol%, 96 mol%, 97 mol%, 98 mol%, or 99 mol%. The molar concentration of CO₂ may be in a range comprising an upper and lower limit selected from any two of the above disclosed values.

- The fluid stream may be characterized by a partial pressure of CO₂ of from about greater than 0 bar to about 150 bars, and a temperature of about 15 °C to about 100 °C. In
15 embodiments, the fluid stream is subjected to conditions for providing supercritical carbon dioxide, wherein the fluid stream is at critical temperature and critical pressure of carbon dioxide. In embodiments, the flowing fluid stream may be characterized by a CO₂ partial pressure of from about 70±5 – 120±5 bars, and at a temperature of at least 15±5 °C to 80 ±5°C. In embodiments, the flowing fluid stream may be characterized by a CO₂ partial
20 pressure of at least 73 bar, and at a temperature of at least 32 °C. The fluid stream may be one that is substantially free of hydrogen sulfide.

- The contacting step may be accomplished by mixing of the corrosion inhibitor composition with the flowing fluid stream in an amount effective to inhibit or reduce corrosion of the metal surface. In embodiments disclosed herein, the corrosion inhibitor composition may
25 be added to the flowing fluid stream in an amount required to provide a concentration of from about 0.01 ppm to about 500 ppm of the corrosion inhibitor in the fluid flow.

Advantageously, it has been found that a substantially low concentration of the corrosion inhibitor composition is sufficient for achieving the desired reductions in corrosion rates. In embodiments, the concentration of the corrosion inhibitor in the fluid stream may be about 0.01 ppm, 0.1 ppm, 1 ppm, 10 ppm, 20 ppm, 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250
5 ppm, 300 ppm, 350 ppm, 400 ppm, 450 ppm or about 500 ppm.

In this particular embodiment, the substituted imidazoline is found to be effective under conditions wherein the hydrogen sulfide is present in the fluid stream at a concentration of from about 0.01 to about 500 ppm. Likewise, a minimal concentration of the corrosion inhibitor has been advantageously found to be sufficient for inhibiting or reducing
10 corrosion rates to a rate of from lesser than 0.5 to lesser than 0.05 mm per year. In embodiments, it has been found that a concentration of about 0.01 to about 500 ppm, e.g., about 0.01 ppm, about 0.1 ppm, about 1 ppm, about 10 ppm, about 20 ppm, about 50 ppm, about 100 ppm, about 150 ppm, about 200 ppm, about 250 ppm, about 300 ppm, about 350 ppm, about 400 ppm, about 450 ppm or about 500 ppm of the corrosion inhibitor (without
15 thiosulfate salt) is sufficient for achieving the desired protection.

Accordingly, the present disclosure further relates to the use of a corrosion inhibitor composition or a imidazoline-based corrosion inhibitor as described herein for inhibiting or reducing corrosion of a metal surface, in particular, a steel surface that is exposed to a fluid or a supercritical fluid disclosed herein.

20 The present disclosure further provides a system for transporting a fluid, said system comprising at least one metal conduit for conveying said fluid therethrough, and wherein said system comprises at least one inlet means that is fluidly communicated with a source of a corrosion inhibitor composition as defined herein, and wherein said inlet means is configured to discharge the corrosion inhibitor composition into the fluid during transport.

25 The corrosion inhibitor composition used in such a system may comprise a substituted imidazoline and a thiosulfate salt. The inlet means may be fluidly communicated with a

source of a corrosion inhibitor composition as disclosed herein, and wherein said inlet means is configured to discharge the corrosion inhibitor composition into the fluid during transport of said fluid. The transported fluid may consists essentially of supercritical CO₂, or water-containing supercritical CO₂ or water-saturated supercritical CO₂. The disclosed system
5 may be particularly useful for transporting a supercritical fluid, including supercritical carbon dioxide. The disclosed system may be transporting a stream of supercritical CO₂ having a water content in an amount of from 1000 ppm to 7,000 ppm.

The disclosed systems may further comprise metering means acting in cooperation with said inlet means and configured to discharge the required doses of the corrosion inhibitor
10 composition or the substituted imidazoline to achieve a desired concentration of the corrosion inhibitor in the flowing fluid.

In embodiments, the corrosion inhibitor composition may be admixed with a feed fluid stream prior to being conveyed to the steel conduit. This may be accomplished via a flow mixer installed upstream of the metal conduit.

15 In embodiments, the corrosion inhibitor may be introduced via one or more separate inlets, each inlet being fluidly communicated with the steel conduit. The corrosion inhibitor composition may be introduced in a single dose or repeatedly via multiple doses. The corrosion inhibitor may also be introduced to the fluid stream by a plurality of inlets disposed along a length between an upstream section and a downstream section of the metal conduit.

20 **Brief Description of Drawings**

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

25 **Fig.1**

[Fig. 1] is a schematic diagram representing a truncated section of a sub-sea pipe transporting a fluid dosed with a corrosion inhibitor composition as disclosed herein.

Fig. 2

[Fig. 2] is a graph showing the comparative experimental results of the performance of a corrosion inhibitor according to the present invention (Line A) compared to conventional inhibitors (Lines B and C) and a control (Line D).

Detailed Description of Drawings

Referring to Fig. 1, there is depicted a truncated section 10 of a carbon steel pipe 12 transporting a stream of fluid 2. Fluid stream 2 comprises supercritical carbon dioxide that is water-saturated. Water saturation of supercritical carbon dioxide may occur at a water content of around 7,000 ppm H₂O. The fluid stream 2 is otherwise composed essentially of supercritical carbon dioxide.

The pipe 12 may comprise at least an upstream section extending above sea level (denoted by line 8a) and a downstream section submerged below the water surface and disposed in proximity and in parallel to the sea bed (denoted by line 8b). During normal flow operation, the fluid stream 2 flowing through the upstream section may have a temperature of around 80 °C and may also possess a CO₂ partial pressure of around 120 bar. The lower circumference of the pipe 12 may come into contact with water entrained within the fluid 2. The water may be due to carry-over from an earlier process or may be due to condensation. The carry-over water may accumulate at a base region 4a of the pipe 12. Region 4a is therefore at substantial risk of corrosion under normal operating conditions.

Likewise, region 4b denotes a section of the pipe that may be susceptible to bottom of the line corrosion. Such corrosion is typically caused by the accumulation of water due to entrainment at the flow boundaries. The presence of water may also be due to the condensation as the submerged section of the pipe 12 experiences a lower ambient

temperature relative to its upstream section. Corrosion of the pipe 12 is typically negligible at sections which are in contact with the CO₂ rich phase of the fluid 2.

The downstream fluid stream 14 may possess a carbon partial pressure of around 80 bars and a temperature of around 25°C.

- 5 The pipe may be fluidly communicated with a source of the corrosion inhibitor composition as disclosed herein. The corrosion inhibitor composition may be discharged into the fluid stream 2 prior to ingress into the pipe. The dosing may be a batch operation. Optionally, one or more additional inlets (not shown) may be installed along the length of the pipe for injection of plural doses of the corrosion inhibitor composition.
- 10 A pipe transporting fluid that has not been dosed with a corrosion inhibitor disclosed herein may experience corrosion at the corrosion-susceptible regions at a rate of more than 80 mm per year. Conversely, it has been observed that a pipe subjected to similar flow conditions and comparable periods of exposure may exhibit a corrosion rate of 0.5 mm per year or less when the transported fluid has been dosed with a corrosion inhibitor composition as
- 15 disclosed herein.

Examples

A non-limiting example of the invention will be further described in greater detail, which should not be construed as in any way limiting the scope of the invention.

Example 1

- 5 A set of comparative experimental results are shown in Fig. 2. In this Example, the performance (measured by corrosion rate, mm/year) of a corrosion inhibitor composition according to the present invention comprising a substituted imidazoline (Formula II) and sodium thiosulfate (Product A) is being compared against conventional CI compositions product B and product C. Line D of Figure 2 shows the corrosion rate (uninhibited)
- 10 wherein no corrosion inhibitor has been added.

The testing conditions are as follows:

Piping surface material: Carbon steel

Fluid / Gas flow rate: 1m/s superficial liquid velocity

Fluid / Gas flow composition: CO₂ gas with water (70 mol. %)

- 15 Fluid / gas flow conditions: 120 bar, 80 °C

Compositions A-C:

	Composition
Product A	20% corrosion inhibitor of formula (II) with 5% thiosulfate salt
Product B	40% Imidazoline derivative with thioglycolate salt
Product C	20% Imidazoline derivative with thioglycolate salt

The experimental results demonstrate that the use of a CI composition according to an aspect of the present disclosure results in superior corrosion inhibition relative to conventional CI compositions when exposed to the same gas flow conditions. In particular, 5 the disclosed CI composition has been demonstrated to achieve less than 0.1 mm / year rate of corrosion when exposed to supercritical CO₂ conditions even in the presence of significant water content in the fluid flow. Importantly, it can be observed that increasing concentration of imidazoline from Product C to Product B did not improve corrosion resistance and instead resulted in inferior performance. The surprising superior corrosion 10 inhibition in Product A can therefore be attributed to the addition of the thiosulfate salt.

Industrial Applicability

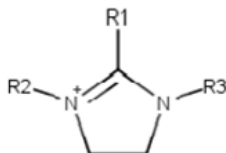
Supercritical carbon dioxide is commonly used as cleaning agents, solvents or as extracting agents in industrial chemical processes. Hence, increasingly, there is a need to provide or install equipment or piping for either the storage or transport of supercritical carbon dioxide. The maintenance of such systems requires a suitable formulation for protecting such equipment and modules from corrosion. This in turn extends the plant life and reduces down time for maintenance and replacement of parts.

Advantageously, the disclosed corrosion inhibitor composition has been shown to possess unique utility in reducing or inhibiting corrosion of metal surfaces, in particular, steel surfaces when exposed to supercritical fluids including water-saturated supercritical fluids. The disclosed compositions may therefore be applied in a wide variety of petrochemical and pharmaceutical processes requiring the transport of supercritical fluids. In a particularly useful embodiment, the disclosed corrosion inhibitor may be advantageously applied in and to subsea piping systems transporting supercritical CO₂.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

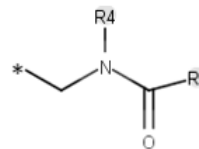
1. A composition for use as a corrosion inhibitor in a fluid environment having a CO₂ partial pressure of up to 150 bars, the composition comprising at least one substituted imidazoline of Formula (I) and a thiosulfate salt:

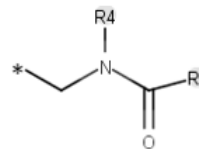


Formula I

wherein

R1 is a hydrophobic group;



R2 is a polar group having the following structural formula , wherein * denotes that attachment point, wherein R4 and R5 are independently H, halogen, optionally substituted alkyl, haloalkyl, optionally substituted alkenyl and optionally substituted alkynyl; and

R3 is H, optionally substituted alkyl, optionally substituted alkenyl, or optionally substituted alkynyl.

2. The composition of claim 1, wherein said substituted imidazoline of Formula (I) and the thiosulfate salt are blended in a mixture.
3. The composition of claims 1 or 2, comprising 1% to 10% by weight of said thiosulfate salt.

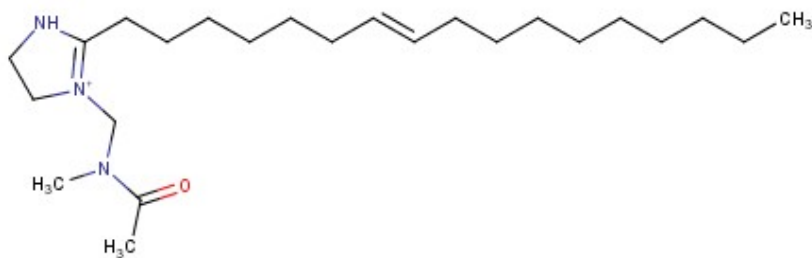
4. The composition of claim 3, comprising 10% to 30% by weight of said substituted imidazoline of Formula (I).
5. The composition of any preceding claim, comprising from 20 wt. % to 30 wt. % of said substituted imidazoline of Formula (I), 1 wt. % to 10 wt. % of said thiosulfate salt and 40 wt. % to 89 wt. % of a solvent, wherein the total weight percent is 100 %.
6. The composition of claim 5, comprising from 30 wt. % of said substituted imidazoline of Formula (I), 5 wt. % sodium thiosulfate and 65 wt. % of water.

7. The composition of any one of claims 1 to 6, wherein

R1 is an optionally substituted alkyl group, an optionally substituted heteroalkyl group, an optionally substituted alkenyl group, an optionally substituted heteroalkenyl group, or an optionally substituted alkynyl group.

8. The composition of claim 7, wherein R1 is a C₁₀₋₄₀ alkyl or a heteroalkyl comprising at least one unsaturated carbon or at least one heteroatom expressing a lone pair of electrons.

9. The composition of any preceding claim, wherein the imidazoline is a compound of **formula (II)**:



10. A method of inhibiting or reducing corrosion on a metal surface being exposed to a flowing fluid stream, the method comprising a step of contacting the metal surface with a

corrosion inhibitor composition comprising at least one substituted imidazoline of Formula (I) as defined in any one of claims 1 to 9 and a thiosulfate salt, or a composition as defined in any one of claims 1 to 9.

11. The method of claim 10, wherein the fluid stream comprises carbon dioxide and water.
12. The method of claim 11, wherein the fluid stream comprises supercritical carbon dioxide.
13. The method of any one of claims 10 to 12, wherein said fluid stream is characterized by a partial pressure of CO₂ of from greater than 0 bar to 150 bars.
14. The method of claim 13, wherein said fluid stream is characterized by a partial pressure of CO₂ of from 60 bars to 150 bars.
15. The method any one of claims 10 to 14, wherein the fluid stream is characterized by a temperature of 15 °C to 100 °C.
16. The method of any one of claims 10 to 15, wherein the fluid stream is at critical temperature and critical pressure of carbon dioxide.
17. The method of any one of claims 10 to 16, wherein the fluid stream is substantially free of hydrogen sulfide.
18. The method of any one of claims 10 to 17, wherein the fluid stream consists essentially of supercritical carbon dioxide.
19. The method of any one of claims 10 to 17, wherein the fluid stream comprises liquid water in an amount of from 0 to 10,000 ppm.
20. The method of claim 19, wherein the fluid stream is supercritical carbon dioxide that is water saturated.
21. The method of any one of claims 10 to 20, wherein the flowing fluid stream is characterized by a CO₂ partial pressure of at least 73 bar, a temperature of at least 32 °C.

22. The method of any one of claims 10 to 21, wherein the contacting step comprises mixing said corrosion inhibitor composition into the flowing fluid stream in an amount effective to inhibit or reduce corrosion of the metal surface.
23. The method of any one of claims 10 to 22, wherein said corrosion inhibitor composition is added in an amount to achieve a concentration of 0.01 ppm to 500 ppm in said flowing fluid stream.
24. The method of claims 20 or 21, wherein the substituted imidazoline is added to said fluid stream in an amount to obtain a concentration from 0.01 ppm to 500 ppm in said fluid stream.
25. Use of a corrosion inhibitor composition as defined in any one of claims 1 to 9 for inhibiting or reducing corrosion of a steel surface.
26. A system for transporting a fluid, said system comprising at least one metal conduit for conveying said fluid therethrough, and wherein said system comprises at least one inlet means that is fluidly communicated with a source of a corrosion inhibitor composition as defined in any one of claims 1 to 9, and wherein said inlet means is configured to discharge the corrosion inhibitor composition into the fluid during transport of said fluid.
27. The system of claim 26, wherein said fluid being transported comprises a supercritical fluid.
28. The system of claim 26 or 27, wherein said fluid being transported comprises supercritical CO₂ and water in an amount of up to 7,000 ppm.