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(54) Title: LOW TOXICITY CORROSION INHIBITOR

(57) Abstract

A water soluble corrosion inhibitor containing a compound having at least one five–membered heterocyclic ring having at least one thione group and at least one other pendant group is described. Such a corrosion inhibiting compound can be made by reacting together a thiourea and a polyalkylene polyamine. A specific example includes preparing 1–(2–aminoethyl)–2–imidazolidinethione by reacting thiourea, *per se*, and diethylenetriamine. These corrosion inhibition compounds have greatly reduced aquatic toxicity, and may be employed as corrosion inhibitors in hydrocarbon streams.

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LOW TOXICITY CORROSION INHIBITOR

Field of the Invention

The present invention relates to corrosion inhibitors for hydrocarbons, and more particularly relates, in one embodiment to water soluble corrosion inhibitors having low aquatic toxicity.

Background of the Invention

It is well known that steel tubulars and equipment used in the production of oil and gas are exposed to corrosive environments. Such environments generally consist of acid gases (CO_2 and H_2S) and brines of various salinities. Under such conditions the steel will corrode, possibly leading to equipment failures, injuries, environmental damage and economic loss. Further in some cases, drilling fluids have acid intentionally added thereto in order to acidize the formations to enhance hydrocarbon recovering. This added acid also causes corrosion problems.

While the rate at which corrosion will occur depends on a number of factors such as metallurgy, chemical nature of the corrodent, salinity, pH, temperature, etc., some sort of corrosion almost inevitably occurs. One way to mitigate this problem consists of using corrosion inhibitors in the hydrocarbon production system.

It would be advantageous if a new corrosion inhibitor were discovered that would be an improvement over the presently known systems. In cases where the corrosion inhibitor may be present in the wastewater of a particular chemical, industrial, or hydrocarbon recovery process, it is further necessary and desirable to provide corrosion inhibitors which are of low toxicity in this era of greater environmental sensitivity.

Summary of the Invention

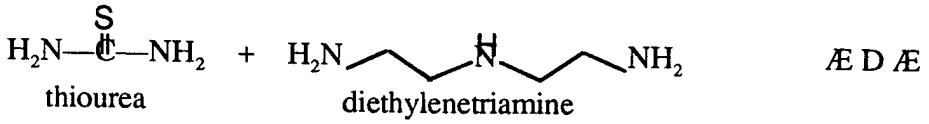
Accordingly, it is an object of the present invention to provide a corrosion inhibitor that is effective in inhibiting the corrosion of steel surfaces in oil field tubing and equipment.

It is another object of the present invention to provide a corrosion inhibitor that has greatly reduced aquatic toxicity.

In carrying out these and other objects of the invention, there is provided, in one form, a water soluble corrosion inhibitor comprising a compound having at least one five-membered heterocyclic ring having at least one thione group and at least one other pendant group, the compound being present in an amount effective to reduce corrosion of a metal.

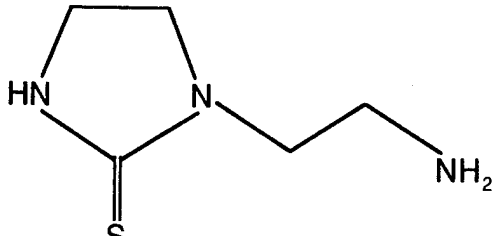
Detailed Description of the Invention

It has been discovered that a water soluble corrosion inhibitor may be formed by the reaction of equimolar amounts of thiourea and diethylenetriamine to give 1-(2-aminoethyl)-2-imidazolidinethione. This reaction is schematically illustrated below:



thiourea diethylenetriamine

Æ D Æ



1-(2-aminoethyl)-2-imidazolidinethione

Ammonia, which is easily removed from the reactor, is a by-product of this process. The 1-(2-aminoethyl)-2-imidazolidinethione is produced with a yield of about 80%, based on the initial charge of the reactants.

The invention involves compounds of at least one five-membered heterocyclic ring having at least one thione group and at least one other pendant group which exhibit corrosion inhibiting properties. This is expected to be particularly true where the heterocyclic atoms in the five-membered ring include at least one nitrogen atom, and/or where the at least one other pendant group is terminated by an amine group or an hydroxyl group. In one embodiment of the invention, the compound preferably contains no hydroxyl groups.

U.S. Pat. No. 2,613,212 discloses 1-(2-aminoethyl)-2-imidazolidinethione, but only suggests it for the treatment of cellulosic materials or pesticides, not for corrosion inhibition.

The reactants used to make this invention include, but are not limited to sulfur-containing compounds such as thiourea, *per se,* and other thioureas, *e.g.* substituted thioureas, for example, alkyl, allyl, benzyl, phenyl, and vinyl thioureas, and mixtures thereof; and polyalkylene polyamines such as diethylenetriamine (DETA), triethylenetetramine, tetraethylenepentamine, and aminoethylethanolamine, and mixtures thereof. The thiourea and polyalkylene polyamine may be reacted at temperatures in the range from about 250°F (121°C) to about 500°F (260°C), preferably from about 300°F (149°C) to about 400°F (204°C). The reaction may be conducted at atmospheric pressures. A catalyst will not normally be required. The molar ratio of sulfur-containing compound to polyalkylene polyamine will vary depending upon the substituents desired in the final product. For example, if more thione groups are desired, the molar proportion

of sulfur-containing compound required would be greater, whereas if more amine functionality is desired, a greater molar and/or equivalent proportion of polyalkylene polyamine would be necessary.

In the process of making the corrosion inhibitors of this invention, it is preferred to use nitrogen not only while cooling the product, but also during the reaction. This is crucial to the process. Further, it has been discovered that the reaction product can be used "as is" as a corrosion inhibitor without recrystallizing the final product. In one non-limiting embodiment of the invention, the molar ratio of thiourea to DETA may range from 1/1.25 to 1.25/1; preferably from 1/1.1 to 1.1/1, and is most preferably 1:1.

The water soluble, alicyclic (nonaromatic) heterocyclic thiones of this invention have greatly reduced aquatic toxicity. This characteristic is particularly important for offshore hydrocarbon recovery operations. Toxicological testing on 1-(2-aminoethyl)-2-imidazolidinethione gave a very high EC_{50} (236 mg/l). Additionally, for Example 1 materials, EC_{50} = 491 mg/l. Both results were obtained on *Skeletonema costatum*. The 1-(2-Aminoethyl)-2-imidazolidinethione prepared in Example 1 showed 100% biodegradability after 28 days (in sea water).

The 1-(2-aminoethyl)-2-imidazolidinethione compound of this invention is a light yellow, waxy solid in pure form. It would be commercialized in solution. Suitable solvent systems for 1-(2-aminoethyl)-2-imidazolidinethione would include, but are not limited to, water, in a non-limiting example, deionized (DI) water; alcohols, in a non-limiting example, methanol; glycols, in non-limiting examples butyl Carbitol™ and triethylene glycol (TEG); esters; ethers; and mixtures thereof. The solution can contain from about 10 to about 90% of the active compound, *e.g.* 1-(2-aminoethyl)-2-imidazolidinethione, with the balance being a solvent or a mixture thereof as described above.

The compounds of this invention should be present in a corrosion inhibitor in an amount effective to reduce corrosion of a metal contacting the fluid. The compounds of this invention will have utility in preventing and/or inhibiting corrosion of metals, particularly of steels, in hydrocarbon recovery environments, such as in the production of petroleum and/or natural gas from subterranean wells. They may be used in hydrocarbon streams, aqueous streams, and in combinations thereof such as emulsion streams including oil/water and water/oil emulsions. It will be appreciated that it is difficult to predict with accuracy what an effective amount will be for a particular application since there are a number of complex, interacting factors to be taken into account including, but not necessarily limited to, nature of the acidic medium, temperature of the medium, the nature of the metal being protected, and the like. It will be appreciated that one of ordinary skill in the art will be able to determine the proportion of corrosion inhibiting compound

from merely routine trial and error. As a mere general and non-limiting indication, it is anticipated that a proportion range of the compounds of this invention in a hydrocarbon stream may range from about 5 to about 250 ppm, preferably from about 25 to about 100 ppm.

The invention will be further described with respect to the following Examples which are not limiting and intended only to further illustrate the invention.

EXAMPLE 1

1-(2-Aminoethyl)-2-imidazolidinethione Preparation

Thiourea, 228.3 g (76.1 molecular weight, 3 moles), and diethylenetriamine (DETA) 309.6 g (103.2 molecular weight, 3 moles) were charged to a 1-liter glass kettle equipped with a condenser, a stirrer and a gas inlet tube. The overhead condenser was turned on and a slow nitrogen sparge was started. Using an electric heating mantle, the mixture was heated to 350°F (177°C) while stirring. The reaction temperature was kept at 350°F (177°C) for 5 hours. The product, a viscous, yellow liquid, was allowed to cool to form a waxy solid. The overall yield was 76%. The following solutions were made up:

TABLE I
Solution Compositions

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
1-(2-aminoethyl)-2-imidazolidinethione	40.9 g	7.5 g	3 g	15.0 g	15.0 g	15.0 g
DI Water	61.35 g	—	12 g	15.0 g	10.0 g	10.0 g
Butyl Carbitol	61.35 g	—	—	—	5.0 g	—
TEG	—	42.5 g	—	—	—	—
Methanol	—	—	—	—	—	5.0 g

The proportions of 1-(2-Aminoethyl)-2-imidazolidinethione compound in these corrosion inhibiting solutions ranges from 15 wt.% (Example 2) to 50 wt.% (Examples 4-6). In one embodiment of the invention, the proportions of effective compound in these corrosion inhibitors ranges from about 5 wt.% to about 75 wt.%, preferably from about 20 wt.% to about 50 wt.%, and most preferably from about 15 wt.% to about 25 wt.%

Corrosion Test Results

Rotating Cylinder Electrode Test — Examples 7-20

A cylindrical steel coupon is rotated at 6000 rpm while immersed in a synthetic brine or a mixture of synthetic brine and kerosene. The fluids temperature is maintained at

150°F (66°C) and CO_2 is bubbled through the fluids for the duration of the test. The corrosion rate is measured by Linear Polarization Resistance and weight loss.

TABLE II

Rotating Cylinder Electrode Test Results

Ex.	Inhibitor	Concentration (ppm)	Steady State Corrosion Rate (mpy)	% Inhibition	Weight Loss (mg)
Brine 90% Kerosene 10%		0	340	—	21
7	Example 1	5	2.6	99.2	1.9
8	Example 1	10	2.4	99.3	1.7
9	Example 1	25	1.7	99.5	1.7
10	Example 1	50	1.4	99.6	1.4
1% NaCl Brine 90% TEG 60%		0	80	—	13.0
11	Example 2	8.3	70	12.5	9.4
12	Example 2	16.7	30	62.5	4.5
13	Example 2	33.3	15	81.3	3.8
14	Example 2	83.3	9	88.8	5.5
15	Example 2	166.7	10	87.5	2.4
16	Example 2	166.7	8	90.0	5.4
17	Example 2	333.3	3	96.3	2.8
Brine 95% Methanol 5%		0	500	—	44.7
18	Example 4	5	20	96.0	5.4
19	Example 5	5	24	95.2	5.7
20	Example 6	5	20	96.0	5.4

Bubble Test — Example 21

Cylindrical steel electrodes are immersed in a mixture of 80% synthetic brine and 20% kerosene. The fluids temperature is maintained at 50°C and CO_2 is bubbled through the fluids for the duration of the test. The inhibitor is added on top of the organic phase. The corrosion rate is measured by Linear Polarization Resistance.

TABLE III

Bubble Test Results — Example 21

	Corrosion Rate (mpy)					
	Blank	1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
Example 3 (10 ppm)	34.9	1.3	1.1	0.8	0.7	0.6

Wheel Test — Examples 22-25

A flat steel coupon is immersed in a mixture of 80% synthetic brine and 20% kerosene inside of a capped soda bottle. The gas space on top of the bottle is CO_2. The bottle is rotated for 24 hours while the temperature is maintained at 180°F (82°C) throughout the test. The corrosion rate is measured by weight loss.

TABLE IV

Wheel Test Results

Ex.	Inhibitor	Concentration (ppm)	Weight Loss (mg)	% Inhibition
22	Blank	0	0.0655	—
23	Example 3	5	0.0091	86.1
24	Example 3	10	0.0091	89.4
25	Example 3	25	0.0058	91.2

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in inhibiting corrosion. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or 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, specific alicyclic, heterocyclic water soluble thione corrosion inhibitors made with sulfur-containing compounds and amines and/or alcohols falling within the claimed parameters, but not specifically identified or tried as reactants to make corrosion inhibitors herein, are anticipated to be within the scope of this invention.

Claims

I Claim:

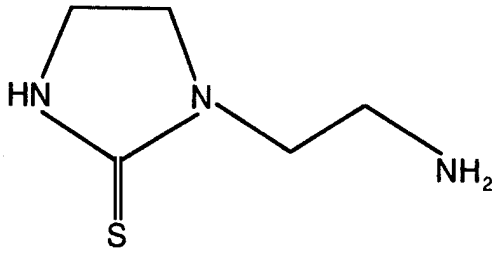
1. A water soluble corrosion inhibitor comprising a compound having at least one five-membered heterocyclic ring having at least one thione group and at least one other pendant group, said compound being present in an amount effective to reduce corrosion of a metal.

2. The water soluble corrosion inhibitor of claim 1 where the heterocyclic atoms in the five-membered ring include at least one nitrogen atom.

3. The water soluble corrosion inhibitor of claim 1 where the at least one other pendant group is terminated by an amine group or an hydroxyl group.

4. The water soluble corrosion inhibitor of claim 1 where the at least one other pendant group is terminated by an amine group.

5. The water soluble corrosion inhibitor of claim 1 where the compound is 1-(2-aminoethyl)-2-imidazolidinethione having the formula:



6. A method of inhibiting corrosion of metal in contact with a fluid comprising adding to the fluid an effective amount of a compound having at least one five-membered heterocyclic ring having at least one thione group and at least one other pendant group.

7. The method of inhibiting corrosion in a fluid of claim 6 where the compound is 1-(2-aminoethyl)-2-imidazolidinethione.

8. The method of inhibiting corrosion in a fluid of claim 6, where the fluid is involved in the production of a hydrocarbon from a subterranean well.

9. A method of preparing of a compound having at least one five-membered heterocyclic ring having at least one thione group and at least one other pendant group, comprising reacting a thiourea and a polyalkylene polyamine.

10. The method of claim 9 where the reaction is conducted at a temperature in the range of about 250°F (121°C) to about 500°F (260°C).

11. The method of claim 9 where the thiourea is thiourea and the polyalkylene polyamine is diethylenetriamine, and the compound prepared is 1-(2-aminoethyl)-2-imidazolidinethione.

12. The method of claim 11 where the molar ratio of thiourea to diethylenetriamine ranges from about 1/1.25 to 1.25/1.

13. The method of claim 11 where the amounts of thiourea and diethylenetriamine are equimolar.

INTERNATIONAL SEARCH REPORT

In tional Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B41/02 C07D233/42 C23F11/16

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)
IPC 6 E21B C07D C23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 926 169 A (W.B. HUGHES) 23 February 1960 see column 5; example 12 ---	1,2,6, 8-10
X	US 2 613 212 A (M.D. HURWITZ) 7 October 1952 cited in the application see column 1, line 35 - column 2, line 2 see column 2; example 2 ---	9-13
X	DATABASE WPI Section Ch, Week 8403 Derwent Publications Ltd., London, GB; Class E13, AN 84-014465 XP002072877 & JP 58 207 377 A (NIPPON SYNTHETIC CHEM IND CO) see abstract --- -/--	1-3,6

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 232 933 A (W. GÜNDEL) 1 February 1966 see column 3, line 55 - column 4, line 1 see column 6, line 25 - line 26 see column 6; example I	1-4,6
X	US 2 895 961 A (W.B. HUGHES) 21 July 1959 see column 2, line 5 - line 18 see column 7; example 10 see column 1, line 15 - line 18	1,2,6, 8-10
X	DATABASE WPI Section Ch, Week 8749 Derwent Publications Ltd., London, GB; Class A18, AN 87-345600 XP002072880 & JP 62 250 043 A (SANSHIN KAGAKU KOGYO CO) see abstract	1,2,6
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