



- (51) **International Patent Classification:**
C23F 11/14 (2006.01)
- (21) **International Application Number:**
PCT/CN2016/086835
- (22) **International Filing Date:**
23 June 2016 (23.06.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
201510362558.9 26 June 2015 (26.06.2015) CN
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(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

(54) **Title:** CORROSION INHIBITOR COMPOSITION AND USE THEREOF

(57) **Abstract:** A corrosion inhibitor composition comprises a water soluble polymer and a compound of formula (I) or a salt thereof. The corrosion inhibitor composition can reduce the rate of corrosion of metals including ferrous metal and galvanized steel.



CORROSION INHIBITOR COMPOSITION AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims the benefit of Chinese Patent Application No. 201510362558.9, filed June 26, 2015, which is incorporated by reference in its entirety.

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TECHNICAL FIELD

[0002] The present application relates to compositions and methods for inhibiting corrosion.

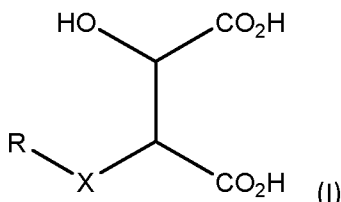
BACKGROUND OF THE INVENTION

[0003] The related art has corrosion inhibitors for inhibiting the corrosion of metal.

10 [0004] There is still a need in the market for further corrosion inhibitors to effectively inhibit the corrosion of metal, especially ferrous metal and/or galvanized steel.

BRIEF SUMMARY OF THE INVENTION

[0005] In an embodiment, the present invention provides a corrosion inhibitor composition. The composition comprises a water soluble polymer and a compound of
15 formula (I) or a salt thereof:



wherein X is NH, NR¹, or O, and

R and R¹ are independently selected from the group consisting of hydrogen, C₁₋₁₀ hydrocarbon, and aryl.

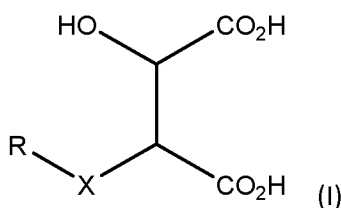
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DETAILED DESCRIPTION OF THE INVENTION

[0006] Applicants have surprisingly and unexpectedly discovered that there is a synergistic effect between a compound of formula (I) or a salt thereof and a water soluble

polymer in reducing the rate of corrosion of ferrous metal and galvanized steel. In certain embodiments, the composition is effective at reducing corrosion of metal in water systems with suspended solids such as silt, oxides of metal ions, and the like. In certain embodiments, the composition is more effective at corrosion inhibition and/or reduction than a phosphorus-based corrosion inhibitor.

[0007] In an embodiment, the present invention provides a corrosion inhibitor composition. The composition comprises a water soluble polymer and a compound of formula (I) or a salt thereof:



wherein X is NH, NR¹, or O, and

R and R¹ are independently selected from the group consisting of hydrogen, C₁₋₁₀ hydrocarbon, and aryl.

[0008] The “C₁₋₁₀ hydrocarbon” may be a substituted or non-substituted C₁₋₁₀ alkyl group, C₁₋₁₀ alkenyl group, C₁₋₁₀ alkynyl group, or the like. For example, the C₁₋₁₀ hydrocarbon group may be selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, hexyl, octyl, ethylhexyl, hydroxyethyl, methoxypropyl, 2-methylpropenyl, and the like.

[0009] The “aryl” may be a phenyl, benzyl, naphthyl, or the like. The aryl may be substituted with one or more of methyl, ethyl, propyl, butyl, methoxy, or a combination thereof.

[0010] In certain embodiments, X is NH and R is a C₁₋₁₀ alkyl.

[0011] In certain embodiments, X is NH and R is n-butyl, i.e., 2-(n-butyl) amino-3-hydroxysuccinic acid.

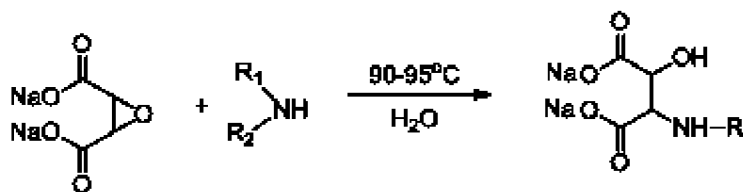
[0012] In certain embodiments, X is NR¹, and R and R¹ are C₁₋₁₀ alkyl.

[0013] In certain embodiments, X is NR¹, and R and R¹ are methyl, i.e., 2-(N,N-dimethyl)amino-3-hydroxysuccinic acid.

[0014] In certain embodiments, a compound of formula (I) may be an alkali metal salt or alkaline-earth metal salt. For example, a compound of formula (I) may be a salt selected

from the group consisting of mono-, di- or tri-salt of sodium, potassium, ammonium, calcium, magnesium, or combinations thereof. In certain embodiments, a compound of formula (I) may be a monosodium salt or disodium salt, such as monosodium 2-(n-butyl) amino-3-hydroxysuccinate, disodium 2-(n-butyl) amino-3-hydroxysuccinate, or disodium 2-(N,N-dimethyl) amino-3-hydroxysuccinate.

[0015] In certain embodiments, a compound of formula (I) or a salt thereof may be prepared through the following method: (1) preparing disodium *cis*-epoxy succinate (ESA) (see *J. Org. Chem.*, 1959, 24 (1), pp 54–55); and (2) reacting an amino compound or alcohol compound with the disodium *cis*-epoxy succinate to obtain a compound of formula (I). An example of the preparation of an N-substituted-2-amino-3-hydroxysuccinic acid is shown below.



[0016] A compound of formula (I) or a salt thereof may be prepared using the above method or using a method in the art.

[0017] In certain embodiments, the water soluble polymer is selected from a group consisting of polymaleic acid, polyacrylic acid, copolymers of acrylic acid and maleic anhydride, copolymers of acrylic acid and 2-acrylamido-2-methylpropylsulfonic acid, and combinations thereof.

[0018] A person skilled in the art will understand that a water soluble polymer used in the present application is not limited to the above listed water soluble polymers. Any water soluble polymer used for corrosion inhibition in the art may be used in the present invention. A water soluble polymer used in the present invention can be prepared by a method known in the art.

[0019] In certain embodiments, the composition may also further comprise an additive selected from a group consisting of a zinc salt, a molybdate, a tungstate, a tin salt, a silicate, and a combination thereof.

[0020] In certain embodiments, the silicate is a water soluble silicate such as sodium silicate, calcium silicate, or the like.

[0021] In certain embodiments, the zinc salt is a water soluble zinc salt such as zinc chloride, zinc sulfate, zinc nitrate, or the like.

[0022] In certain embodiments, the molybdate is a water soluble molybdate such as sodium molybdate, potassium molybdate, or the like.

5 [0023] In certain embodiments, the tungstate is a water soluble tungstate such as sodium tungstate, potassium tungstate, or the like.

[0024] In certain embodiments, the tin salt is a water soluble tin salt such as stannic chloride or the like.

[0025] In certain embodiments, the composition comprises a compound of formula (I)
10 and water soluble polymer at a weight ratio of from about 1:50 to about 50:1. In certain embodiments, the composition comprises a compound of formula (I) and water soluble polymer at a weight ratio of from about 1:5 to about 5:1.

[0026] In certain embodiments, the composition further comprises an additive at a weight ratio between the compound of formula (I) and the additive of from about 50:1 to about 1:50.

15 In certain embodiments, the composition further comprises an additive at a weight ratio between the compound of formula (I) and the additive of from about 20:1 to about 2:1. In certain embodiments, the composition further comprises a zinc salt at a weight ratio between the compound of formula (I) and the zinc salt of from about 15:2 to about 2:1. In certain embodiments, the composition further comprises a molybdate at a weight ratio between the
20 compound of formula (I) and the molybdate of from about 50:1 to about 2:1. In certain embodiments, the composition further comprises a tungstate at a weight ratio between the compound of formula (I) and the tungstate of about 500:1 or less. In certain embodiments, the composition further comprises a tin salt at a weight ratio between the compound of formula (I) and the tin salt of about 10:1 or less. In certain embodiments, the composition
25 further comprises a silicate at a weight ratio between the compound of formula (I) and the silicate of from about 50:1 to about 2:1.

[0027] A person skilled in the art will understand that certain components of the composition may be unstable if mixed together with other components of the composition. Thus, in certain embodiments, the composition of the present application may be formulated
30 by mixing all of the components together, or the components in the composition of the present application may be added to separately to an aqueous solution to inhibit or reduce corrosion. The components of the corrosion inhibitor composition of the present application

may be added directly into an aqueous solution for inhibiting or reducing corrosion simultaneously or separately in any sequence.

[0028] In certain embodiments, the composition does not comprise a phosphorus-containing compound.

5 [0029] In certain embodiments, a compound of formula (I) is added to an aqueous solution used to inhibit and/or reduce corrosion at a concentration of from about 1 ppm to 50 ppm, based on weight of the aqueous solution. In certain embodiments, a water soluble polymer is added to an aqueous solution used to inhibit and/or reduce corrosion at a concentration of from about 1 ppm to 50 ppm, based on weight of the aqueous solution.

10 [0030] In certain embodiments, a zinc salt is added to an aqueous solution used to inhibit corrosion at a concentration of from about 1 ppm to about 5 ppm, based on weight of the aqueous solution. In certain embodiments, a molybdate salt is added to an aqueous solution used to inhibit corrosion at a concentration of from about 5 ppm to 50 ppm, based on weight of the aqueous solution. In certain embodiments, a tungstate is added to an aqueous solution
15 used to inhibit corrosion at a concentration of at least about 500 ppm, based on weight of the aqueous solution. In certain embodiments, a tin salt is added to an aqueous solution used to inhibit corrosion at a concentration of at least about 10 ppm or less, based on weight of the aqueous solution. In certain embodiments, a tin salt is added to an aqueous solution used to inhibit corrosion at a concentration of from about 5 ppm to about 100 ppm, based on weight
20 of the aqueous solution.

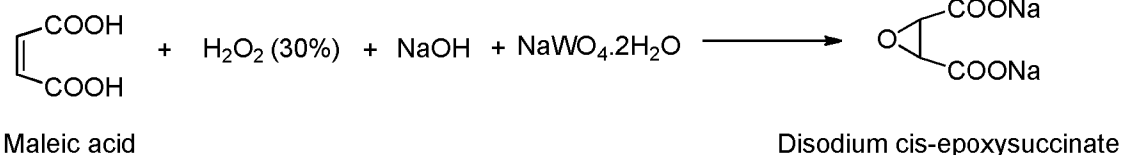
[0031] In another embodiment, the composition is used as a corrosion inhibitor to inhibit corrosion of ferrous metal or galvanized steel. In certain embodiments, the composition is used as a corrosion inhibitor to inhibit corrosion of carbon steel.

EXAMPLE 1

25 PREPARATION OF N-SUBSTITUTED 2-AMINO-3-HYDROXYSUCCINIC ACID DERIVATIVE

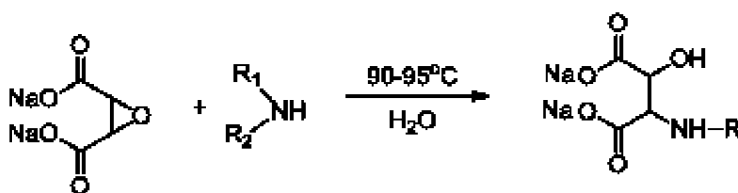
[0032] In the Examples, unless otherwise specifically stated, all chemical agents were purchased. The corrosion rate was determined according to GB/T 18175-2000 (2000 Edition). N-substituted 2-amino-3-hydroxysuccinic acid derivatives were prepared as shown
30 below.

[0033] Preparation of disodium *cis*-epoxy succinate



[0034] To a 1-liter, 5-neck, round bottom flask equipped with stirrer, thermometer, and dropping funnel was charged a filtered solution of 116 g. (1.0 mole) of maleic acid in 300 ml. of distilled water. To this was added a solution of 60 g. (1.5 moles) of sodium hydroxide in 100 ml. of water. The heat of neutralization caused a rise in temperature to about 70°C. To the warm solution was added 6.6 g. (0.02 mole) of sodium tungstate dihydrate. Standard pH electrodes were inserted into the solution and 1.2 moles of 30%, hydrogen peroxide was added in portions. The strongly exothermic reaction was held at 63-65°C by cooling with an ice bath for about 15 min, during which time, the pH fell from about 5.5 to about 4.11. In order to maintain the pH at a minimum of 4, a solution of 0.5 mole of sodium hydroxide in 100 ml. of water was added dropwise as needed throughout the remainder of the reaction. After an additional hour at 65°C, the solution was cooled to 40°C and treated with the remainder of the sodium hydroxide solution. After vacuum concentration at 40°C, 176 g. (100%) of disodium *cis*-epoxy succinate was obtained as product.

[0035] Preparation of N-substituted 2-amino-3-hydroxysuccinic acid derivatives



[0036] To a reaction vessel was added 9.35 g (1 mole) of cis-Epoxy succinate and 1 mole of respective amine and 25 ml of water at room temperature. The reaction vessel was closed. The mixture was refluxed under stirring at 90°C-95°C for 12 hours, and reaction mixture was dried in rotary evaporator to yield the product. The purified product was characterized using NMR spectroscopy.

[0037] As known in the art, the corresponding dicarboxylic acid or monocarboxylic acid compound of the above disodium salt may be obtained through neutralization with an acid.

[0038] The compounds of formula (I) may be synthesized using the above method or a known method.

EXAMPLE 2

ELECTROCHEMICAL METHOD FOR TESTING CORROSION RATE

[0039] Electrochemical test method for corrosion rate was as follows:

A. Specimen

5 1. Metallurgy - C1010 mild steel seamless specimens

2. Dimension – ½” long, ½” O.D.

3. Finishing - Grit #600

(1-3 above are specifications for the specimens)

4. Mounting - The tubular specimen was mounted on the specimen holder with
10 two Teflon Spacers and a Delrin end cap. The specimen was inspected before mounting and the following questions were asked – Is it a seamless specimen (any welding mark on the inside surface)? Is there any major defect/pit/scratch on the metal surface? Do not use the specimen if it is not seamless or if you find any defects.

5. Polishing - The mounted specimen was polished with #600 SiC paper gently
15 again prior to the test.

6. Cleaning - The specimen was cleaned by rinsing with acetone and wiped clean with Kimwipes.

7. After cleaning, white nylon gloves were used to handle the specimen to avoid transferring any fingerprints or oil from the fingers.

20 8. Coating - The edges of the mild steel specimen were then painted with Microstop Lacquer paint to minimize crevice corrosion. A heat gun was used to dry the paint. The specimen holder was then attached to the shaft of the rotator.

9. Specimen Holder - Teflon tape was wrapped around the stainless steel specimen holder to electrically isolate the stainless steel holder from the system, leaving only
25 the mild steel specimen exposed.

10. No pre-passivation was needed.

B. Test Solution

1. Solution with specific water chemistry was prepared and heated to 50°C.

2. Volume - Introduce 800 ml of test solution into the glass cell.

30 3. Temperature/Gas – Turn on the temperature controller to 120° F and purged the solution with air (very low rate).

4. pH - Calibrated the pH meter/probe (two point calibration) before each test. Inserted the calibrated pH probe in the test solution. Adjusted the solution pH to setpoint (with dilute KOH or H₂SO₄ or CO₂) after the system temperature and pH reached steady state values.

5. Dosed in inhibitor at 25 ppm active chemical (prepared 4 gm/L active stock solution of the inhibitor solution and adjusted its pH to setpoint; added 5 mL of the stock solution to the cell)

C. Electrochemical Measurements

1. Rotating Cylinder Electrode – The rotator speed was set to 500 rpm.
2. Polarization Resistance (Rp) – Rp measurements should be conducted at a potential scan rate of 0.1 mV/second within 20 mV of the corrosion potential (E_{corr}) from the cathodic region to the anodic region.
3. Tafel Plots – At the end of each experiment, potentiodynamic polarization measurements were performed to obtain the cathodic and the anodic Tafel plots at a potential scan rate of 0.5 mV/second. The cathodic Tafel scan was conducted first from (E_{corr}- 350 mV) to E_{corr}. The anodic scan was then conducted from E_{corr} to (E_{corr} + 350 mV).
4. Calculations of Corrosion Rate
 - (1) Tafel Extrapolations - The Tafel plots were extrapolated to the corrosion potential to determine the corrosion rate in mpy (Gamry software, E/Log I plot), the cathodic Tafel slope (B_c), and the anodic Tafel slope (B_a).
 - (2) Polarization Resistance – The values of B_a, B_c (obtained in (1) above), and Rp were used to determine the corrosion rate based on the Stern-Geary equation (Gamry software). A corrosion rate (mpy) versus time curve was plotted using the Gamry software. Determined the steady state corrosion rate with this plot.
 - (3) Determined the average corrosion rate calculated from Tafel Extrapolations and Rp measurements.

[0040] Additionally, the water chemistry of the tested water used in the following examples is shown in the following Table 1.

Table 1

Ca hardness (ppm as CaCO ₃)	180
Mg hardness (ppm as CaCO ₃)	66

Alkalinity (ppm as CaCO ₃)	170
Cl ⁻ (ppm by weight as ion)	256
SO ₄ (ppm by weight as ion)	63

EXAMPLE 3

TEST FOR CORROSION RATE

[0041] Another test method for corrosion rate (or effect on slowing down the corrosion)

was as follows:

1. To a 2L beaker, 2L of deionized water was added. In addition to alkalinity, corresponding volume of the solution of mineral salts (such as calcium chloride, magnesium chloride, sodium chloride, sodium sulfate and so on) was added first, so as to formulate the corresponding water quality. The solution was heated to 45°C.

2. After the corresponding products were added (normally add agent containing dispersant first, and then products which need to be dispersed, such as zinc salts, phosphate and so on), the pH value was adjusted to about 6.5 using the diluted sodium hydroxide solution/diluted sulfuric acid solution (to eliminate the acidity/alkalinity brought by the products), and then added corresponding NaHCO₃ to adjust the alkalinity.

3. If pH value of the tested water quality needs to be controlled, the pH value of the solution can be adjusted by diluted sodium hydroxide solution/diluted sulfuric acid solution. After counterbalancing for 1~2 hours at 45°C, the coupon was placed therein after the pH value was determined/adjusted. If there was no need to control pH value of the water quality after counterbalancing for 1~2 hours, the coupon can be placed therein directly. The coupon number and its corresponding weight were recorded before placing it.

4. Due to water evaporation, each beaker should be refilled to the corresponding volume with water 2 times/day.

Steps 1-4 were carried out at a temperature of 45°C and at a rotational speed of 100 to 150 rpm.

5. The test period was three days. The test was stopped three days later. Removed the coupon, used paper to absorb water on its surface, and then dried it in the oven. Photos were taken of both the upper and lower sides before cleaning. The coupon was cleaned as follows: removed the rust floated on the surface by physical method, washed with 0.8%(w/v) of

hexamethylene tetramine in the chlorhydric acid solution (diluted one part of concentrated chlorhydric acid in four parts of water), washed with deionized water, wiped it dry, washed with acetone, and then weighed after drying in the oven. The acid washing duration for each coupon did not exceed 1 min.

- 5 **[0042]** Additionally, the water chemistry of the tested water used in the following Examples is shown in the following Table 2.

Table 2

Ca hardness (ppm by weight as CaCO_3)	100
Mg hardness (ppm by weight as CaCO_3)	50
Alkalinity (ppm by weight as CaCO_3)	100
Cl^- (ppm by weight as ion)	200
SO_4 (ppm by weight as ion)	100

EXAMPLE 4

10

CORROSION INHIBITOR COMPOSITION

[0043] A corrosion inhibitor comprising polymaleic acid, disodium 2-(n-butyl) amino-3-hydroxysuccinate, and ZnCl_2 was prepared. The weight ratio between the polymaleic acid and the disodium 2-(n-butyl) amino-3-hydroxysuccinate was 5:5 and the weight ratio between the disodium 2-(n-butyl) amino-3-hydroxysuccinate and the ZnCl_2 was 5:2.

15

[0044] The corrosion inhibitor was obtained by mixing the three components together.

EXAMPLE 5

TESTING THE CORROSION RATE OF CORROSION INHIBITOR M AND COMPARATIVE COMPOSITIONS E-F

[0045] In this Example, the components of composition M and comparative compositions E-F were added directly to the tested aqueous solution with the concentration shown in Table 3. Composition M and comparative compositions E-F were tested according to the method recited in Example 2.

20

[0046] The constitutions of the composition M and the comparative compositions E-F and the test results are shown in Table 3.

Table 3

composition	disodium 2-(n-butyl) amino-3-hydroxysuccinate (ppm by weight)	polymaleic acid (ppm by weight)	Corrosion rate (mpy)
M	20	10	0.1
Comparative E	30	0	0.2
Comparative F	0	30	0.3

[disodium 2-(n-butyl) amino-3-hydroxysuccinate: X=NH, R=n-butyl, disodium salt]

[0047] The disodium 2-(n-butyl) amino-3-hydroxysuccinate was produced according to Example 1 and the polymaleic acid was purchased from Wujin Fine Chemical Factory.

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EXAMPLE 6

TESTING THE CORROSION RATE OF CORROSION INHIBITORS A-D AND COMPARATIVE COMPOSITIONS G-J

[0048] In this Example, all the components of compositions A-D and comparative compositions G-J were added directly to the tested aqueous solution with the concentrations showed in Table 4. Compositions A-D and comparative compositions G-J were tested according to the method recited in Example 3.

10

[0049] The constitutions of compositions A-D and comparative compositions G-J and the test results are shown in Table 4.

Table 4

composition	ZnCl ₂ (ppm by weight)	disodium 2-(n-butyl) amino-3-hydroxysuccinate (ppm by weight)	polymaleic acid (ppm by weight)	Corrosion rate (mpy)
A	2	15	4	0.56
Comparative G	2	15	0	2.7
B	2	10	4	0.80
Comparative H	2	10	0	14
C	2	5	4	1.0
Comparative I	2	5	0	16
Comparative J	2	0	5	16
D	0	5	4	3.2

[disodium 2-(n-butyl) amino-3-hydroxysuccinate: X=NH, R=n-butyl, disodium salt]

[0050] Disodium 2-(n-butyl) amino-3-hydroxysuccinate was produced according to Example 1 and the polymaleic acid was purchased from Wujin Fine Chemical Factory.

[0051] In this embodiment, the polymaleic acid acts as a scaling inhibitor, and the zinc salt acts as a corrosion inhibitor.

[0052] Table 4 shows that the corrosion inhibition effects of the combination of zinc salt and the compound of formula (I) or the water soluble polymer are less than to those of the combination of zinc salt, the compound of formula (I), and the water soluble polymer. From the data for comparative composition I and comparative composition J in Table 4, it can be seen that the significant enhancement of the corrosion inhibition effect does not result from the combination of additive zinc salt and the compound of formula (I) or the water soluble polymer, but results from a synergistic effect between the compound of formula (I) and the water soluble polymer.

[0053] From the data for compositions A, B and C in Table 4, it can be seen that the corrosion inhibition effect was enhanced with the increase of the amount of the compound of formula (I). The addition of zinc salt would significantly enhance the synergistic effect between the compound of formula (I) and the water soluble polymer as indicated by the comparison between the test results of C and D in Table 4.

[0054] Table 3 shows that the use of a combination of compound of formula (I) and the water soluble polymer was significantly superior to that of the compound of formula (I) or the water soluble polymer alone, which shows that there was a synergistic technical effect between the compound of formula (I) and the water soluble polymer.

EXAMPLE 7

TESTING THE CORROSION RATE OF CORROSION INHIBITOR N AND COMPARATIVE COMPOSITIONS K-L

[0055] In this Example, the components of composition N and comparative compositions K-L were added directly to the tested aqueous solution with the concentrations shown in Table 5. Composition N and comparative compositions K-L were tested according to the method recited in Example 3.

[0056] The constitutions of composition N and comparative compositions K-L and the test results are shown in Table 5.

Table 5

Composition	ZnCl ₂ (ppm by weight)	disodium 2-(n-butyl) amino-3-hydroxysuccinate (ppm by weight)	polyacrylic acid (ppm by weight)	Corrosion rate (mpy)
Comparative K	2	0	5	20
Comparative L	2	5	0	16
N	2	5	5	3.0

[disodium 2-(n-butyl) amino-3-hydroxysuccinate: X=NH, R=n-butyl, disodium salt]

[0057] Disodium 2-(n-butyl) amino-3-hydroxysuccinate was produced according to Example 1 and the polyacrylic acid was purchased from Nalco.

5 **[0058]** Table 5 shows that a significant enhancement of corrosion inhibition does not result from the combination of dzinc salt and the compound of formula (I) or water soluble polymer, but results from the synergistic effect between the compound of formula (I) and the water soluble polymer.

[0059] The present disclosure is an exemplification of the principles of the embodiments of the present application, which is not intended to make any formal or essential limitation to the present application or limit the present application to the particular embodiments illustrated. It is apparent to a person skilled in the art that elements of technical schemes, the compounds, polymers, components, compositions, preparations, processes of the embodiments of the present application could vary, change, modify and evolve without departing the principle, spirit and scope of the embodiments and technical schemes of the present application as disclosed above, for example, as defined in the claims. These varied, changed, modified and evolved embodiments are included in equivalent embodiments of the present application, which are included in the scope of claims in the present application. While embodiments of the present application may be embodied in many different forms, there are described in detail herein some embodiments of the present invention. Additionally
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 embodiments of the present application include any and all possible combinations of any, some and all elements of various embodiments described herein. Any and all patents, patent applications and other references recited in the present application or in any recited patent, any recited patent application or other cited data are hereby incorporated herein by reference in their entirety.

[0060] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

5 **[0061]** The above disclosure is intended to be illustrative and not exhaustive. This description will suggest many variations and alternatives to a person skilled in the art. All these alternatives and variations are intended to be included within the scope of the claims where the term "comprising" means "including, but not limited to".

[0062] The use of the terms "a" and "an" and "the" and "at least one" and similar
10 referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The use of the term "at least one" followed by a list of one or more items (for example, "at least one of A and B") is to be construed to mean one item selected from the listed items (A or B) or any combination of two
15 or more of the listed items (A and B), unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (i.e., meaning "including, but not limited to,") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range,
20 unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a
25 limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

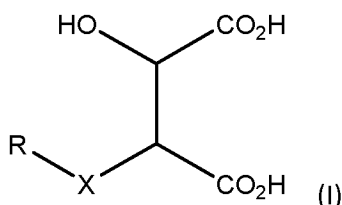
[0063] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred
30 embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as

specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or

5 otherwise clearly contradicted by context.

CLAIMS:

1. A corrosion inhibitor composition comprising a water soluble polymer and a compound of formula (I) or a salt thereof:



5 wherein X is NH, NR¹, or O, and

R and R¹ are independently selected from the group consisting of hydrogen, C₁₋₁₀ hydrocarbon, and aryl.

2. The composition of claim 1, wherein X is NH and R is C₁₋₁₀ alkyl group.

3. The composition of claim 1, wherein X is NH and R is n-butyl group.

10 4. The composition of claim 1, wherein X is NR¹ and R and R¹ are C₁₋₁₀ alkyl.

5. The composition of claim 1, wherein X is NR¹ and R and R¹ are methyl.

6. The composition of any one of claims 1-5, wherein the compound of formula (I) is a salt selected from the group consisting of a mono-, di-, or tri-salt of sodium, potassium, ammonium, calcium, magnesium, and combinations thereof.

15 7. The composition of any one of claims 1-6, wherein the water soluble polymer is selected from the group consisting of polymaleic acid, polyacrylic acid, copolymers of acrylic acid and maleic anhydride, copolymers of acrylic acid and 2-acrylamido-2-methylpropyl sulfonic acid, and a combination thereof.

8. The composition of claim 1, wherein the composition comprises polymaleic acid and wherein X is NH and R is n-butyl.

9. The composition of any one of claims 1-8, wherein the composition further comprises an additive selected from the group consisting of a zinc salt, a molybdate, a tungstate, a tin salt, a silicate, and combinations thereof.

10. The composition of any one of claims 1-9, wherein the composition does not comprise a phosphorus-containing compound.

11. The composition of any one of claims 1-9, wherein the weight ratio between the compound of formula (I) and the water soluble polymer is from about 1:5 to about 5:1.

5 12. The composition of claim 9, wherein the weight ratio between the compound of formula (I) and the additive is from about 20:1 to about 2:1.

13. Use of the composition of any one of claims 1-12 as a corrosion inhibitor for inhibiting the corrosion of ferrous metal or galvanized steel.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/086835

A. CLASSIFICATION OF SUBJECT MATTER

C23F 11/14(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNXTT;CNABS;EPODOC;WPI;ECOLAB, TONG,Yinyin, GILL Jasbir S, REED Peter E, BANERJEE Santanu, SAVCHENKO Julia, HARBINDU Anand, corrosion, inhibitor, water soluble polymer, HSA, hydroxysuccinic acids, hydrogen, hydrocarbon, aryl, alkyl, butyl, methyl, polymaleic acid, polyacrylic acid, acrylic acid, maleic anhydride, 2-acrylamido-2-methylpropyl sulfonic acid, phosphorus, ferrous, galvanized steel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010051141 A1 (GENERAL ELECTRIC COMPANY) 06 May 2010 (2010-05-06) paragraphs [0009]-[0010]	1-13
A	WO 0066810 A1 (BETZDEARBORN INC.) 09 November 2000 (2000-11-09) claims 1-306	1-13
A	WO 2010062461 A1 (GENERAL ELECTRIC COMPANY) 03 June 2010 (2010-06-03) claims 1-29	1-13
A	WO 2012076887 A1 (RHODIA OPERATIONS) 14 June 2012 (2012-06-14) claims 1-26	1-13
A	US 2003063998 A1 (GHOSH,TIRTHANKAR ET AL.) 03 April 2003 (2003-04-03) claims 1-10	1-13
A	US 5183590 A (CARTER, CHARLES G. ET AL.) 02 February 1993 (1993-02-02) claims 1-11	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance
 “E” earlier application or patent but published on or after the international filing date
 “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 “O” document referring to an oral disclosure, use, exhibition or other means
 “P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 “&” document member of the same patent family

Date of the actual completion of the international search

11 August 2016

Date of mailing of the international search report

08 September 2016

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/086835

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2010051141	A1	06 May 2010	CA	2740692	A1	06 May 2010
				CN	102203323	B	18 December 2013
				CN	102203323	A	28 September 2011
				BR	PI0914358	A2	20 October 2015
				MX	2011004605	A	25 May 2011
				KR	20110083683	A	20 July 2011
				US	8021607	B2	20 September 2011
				JP	2012507628	A	29 March 2012
				MY	155080	A	28 August 2015
				EP	2347035	A1	27 July 2011
				US	2010111757	A1	06 May 2010
WO	0066810	A1	09 November 2000	HU	0201012	A2	29 July 2002
				NO	20015307	D0	30 October 2001
				HU	0201012	A3	28 August 2003
				CN	1359430	A	17 July 2002
				AR	023836	A1	04 September 2002
				BR	0010592	A	05 February 2002
				CA	2369954	A1	09 November 2000
				CZ	20013966	A3	15 May 2002
				MX	PA01011087	A	04 June 2002
				PL	352994	A1	22 September 2003
				NO	20015307	A	02 January 2001
				JP	2002543294	A	17 December 2002
				EP	1177331	A1	06 February 2002
				AU	4972700	A	17 November 2000
WO	2010062461	A1	03 June 2010	KR	20110081324	A	13 July 2011
				EP	2347034	A1	27 July 2011
				US	8025840	B2	27 September 2011
				BR	PI0914532	A2	15 December 2015
				CA	2740635	A1	03 June 2010
				CN	102203322	A	28 September 2011
				JP	2012507627	A	29 March 2012
				US	2010111756	A1	06 May 2010
WO	2012076887	A1	14 June 2012	MX	2011004609	A	24 June 2011
				US	2014135239	A1	15 May 2014
				GB	2486241	A	13 June 2012
				CA	2818744	A1	14 June 2012
				EP	2649220	A1	16 October 2013
				GB	201020798	D0	19 January 2011
				AU	2011340268	A1	20 June 2013
				CN	103314137	B	27 January 2016
				CN	103314137	A	18 September 2013
US	2003063998	A1	03 April 2003	KR	20030020827	A	10 March 2003
				CN	1407058	A	02 April 2003
				CA	2398425	A1	04 March 2003
				MX	PA02008469	A	26 August 2005
				EP	1288338	A1	05 March 2003
				JP	2003183863	A	03 July 2003
US	5183590	A	02 February 1993	CA	2074460	A1	25 April 1993

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2016/086835

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
		AU 648907 B2	05 May 1994
		JP H05214567 A	24 August 1993
		AU 1933592 A	29 April 1993
		CA 2074460 C	06 May 2003
		ZA 9205051 A	08 March 1996
		ZA 9205051 B	08 March 1996