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CORROSION INHIBITION

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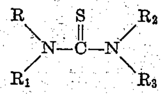
This invention relates to the inhibition of corrosion of metals which come into contact with water as, for example, in water circulation systems, particularly industrial water systems such as utilize heat exchangers, cooling towers and like installations. While it is especially concerned with the protection against corrosion of ferrous metals such as iron and steel, it is also useful for inhibiting corrosion of other metals in contact with water, particularly flowing water, as, for example, copper, copper alloys such as brass and bronze, aluminum and aluminum base alloys, couples of such metals with ferrous metals, and other metals and alloys commonly used in industrial water systems or water circulation systems.

A great deal of work has been done in the field of corrosion inhibition of metals used in water systems where circulating water comes into contact with such metal surfaces. Among the materials utilized as additives to the water to effect corrosion inhibition of the aforesaid types of metals are water-soluble phosphates of various types including monosodium phosphate and sodium polyphosphates; water-soluble hexavalent chromium compounds such as sodium and potassium chromates and dichromates; and various combinations of ingredients as, for instance, mixtures of water-soluble trivalent and hexavalent chromium compounds; mixtures of certain thiols, water-soluble zinc compounds, and water-soluble polyphosphates; and mixtures of water-soluble polyphosphates, water-soluble ferricyanides, and water-soluble chromates. Typical of such approaches are disclosed in U.S. Patents Nos. 2,793,932; 2,887,085 and 2,901,437. While improvement in corrosion inhibition is obtained by following such and other practices of the prior art, nevertheless not infrequently problems of scaling and pitting arise and, in addition, the matter of cost of the corrosion inhibiting compositions is a factor of material consideration.

The present invention is based upon discoveries which result in new and useful corrosion inhibition compositions and significant improvements in regard to inhibition of corrosion of ferrous and other metals through the utilization of such compositions.

It has been discovered that the employment, in conjunction with water-soluble hexavalent chromium compounds, of certain chemical compounds, hereafter described, brings about marked improvement in the corrosion inhibition properties of said hexavalent chromium compounds when dissolved in water and said water is in contact with or is circulated in contact with ferrous metals and other metals in water systems such as have been mentioned above. These improvements manifest themselves particularly in regard to very substantially reduced scaling, which is one of the serious objections, for example, of the use of polyphosphates and various other materials heretofore suggested as corrosion inhibiting materials, and in regard to substantial absence of pitting. Another important advantage resides in the fact that the invention makes possible the utilization of reduced concentrations of hexavalent chromium compounds, thereby resulting in savings in cost.

The chemical compounds which are used in conjunction with the water-soluble hexavalent chromium compounds pursuant to the present invention are water-soluble thiocyanates, and/or water-soluble thiourea compounds of the type represented by the formula



where R, R_1, R_2 and R_3 are each selected from the group consisting of hydrogen, alkali metal, and alkyl radicals containing from 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl and isobutyl. It also has been found that water-soluble thiocarboxylic acids and salts thereof can be utilized as, for example, thioglycolic acid, thiodiglycolic acid and thiomalic acid and the ammonium and sodium salts thereof.

Among the water-soluble thiocyanates are thiocyanic acid and the inorganic salts of thiocyanic acid, particularly the alkali metal thiocyanates, namely, sodium, potassium, ammonium and lithium thiocyanates. Other water-soluble thiocyanate compounds which, in aqueous solution, ionize to produce thiocyanate ions can be utilized. Particularly preferred is ammonium thiocyanate. Mixtures of two or more of such thiocyanate compounds can, of course, be employed.

Of the thiourea compounds, it is particularly preferred to utilize thiourea. Again, it will be understood that mixtures of two or more of said thiourea compounds can be employed, as well as mixtures of the thiocyanate and thiourea compounds.

It has also been found to be particularly desirable to employ, in conjunction with the water-soluble hexavalent chromium compound, one or more water-soluble zinc compounds, particularly zinc compounds such as zinc sulfate, zinc chloride, sodium zincate, and zinc oxide and zinc carbonate in acid solutions in which they are soluble. Other water-soluble zinc compounds which, in aqueous solution, ionize to produce zinc ions can be utilized. Where the zinc compounds are used, it will be understood that such will be selected, in relation to the hexavalent chromium compound or compounds and thiocyanate or thiourea compound, as to be compatible therewith.

With water-soluble hexavalent chromium compounds are, as indicated above, well known in the art. They include particularly the alkali metal chromates and dichromates such as sodium chromate, potassium dichromate, ammonium dichromate, and chromium trioxide in their anhydrous and hydrate forms.

The ranges of concentration in the water of the ingredients utilized pursuant to the present invention are quite variable. Thus, in the case of the hexavalent chromium compound, the concentration may range from about 1 to 10,000 p.p.m., better still from 2 to 100 p.p.m., and particularly desirably from 5 to 30 p.p.m., all calculated as Na_2CrO_4. In the case of the thiocyanates, the thiourea compounds and the thiocarboxylic acid compounds, the concentration may range from about 0.01 to 100 p.p.m., better still from 0.01 to 25 p.p.m., and particularly desirably from 0.02 to 10 p.p.m. In the case of the zinc compounds, where the same are used, the concentration may range from about 0.5 to 25 p.p.m., better still from 0.5 to 15 p.p.m., and particularly desirably from 1 to 8 p.p.m. calculated as zinc.

It will be understood that, if desired, supplemental ingredients can be added to the compositions of the present invention or to water containing the compositions of the invention, so long as the amounts or character of such supplemental ingredients are not such as unduly adversely affect the desired properties of said compositions or water containing the same. Thus, for example, trivalent chromium compounds, phosphates and polyphosphates, and thiols can be added in relatively minor amounts. It is preferred, however, not to utilize said or other supplemental ingredients.

The following examples are illustrative of corrosion inhibiting compositions falling within the scope of the invention. It will be appreciated that other compositions can readily be prepared in the light of the guiding principles and teachings provided herein. All parts listed are by weight.

Example 1

Ammonium dichromate	100
Ammonium thiocyanate	0.3

Example 2

Potassium dichromate	100
Ammonium thiocyanate	0.2
Zinc sulfate	25

Example 3

Potassium dichromate	100
Thiourea	0.2

Example 4

Potassium dichromate	100
Thiourea	0.2
Zinc sulfate	40

Example 5

Sodium dichromate	100
Ammonium thiocyanate	0.2
Thiourea	0.2
Sodium polyphosphate	10
Zinc sulfate	5

Example 6

Sodium dichromate	100
Ammonium thiocyanate	0.2

Example 7

Ammonium dichromate	100
Ammonium thioglycolate	0.3

Example 8

Ammonium dichromate	100
Ammonium thiomalate	0.3

Example 9

Sodium dichromate	100
Chromic acid (as Cr_2O_3)	15.6
Zinc oxide	6.5
Ammonium thiocyanate	0.2

Example 10

Sodium dichromate	100
Chromic acid (as Cr_2O_3)	65
Zinc sulfate	25
Ammonium thiocyanate	0.2

Example 11

Sodium dichromate	100
Chromic acid (as Cr_2O_3)	20
Zinc sulfate	6
Thiourea	0.3

The following table shows the unusual results and synergistic coaction of the ingredients in compositions made in accordance with the present invention.

RECIRCULATING COOLING TOWER

Duration of test, days		28
pH range		6.0–8.0
Chloride as NaCl	p.p.m.	10–1000
Total hardness	p.p.m.	10–1000
Heat exchanger temperature	° F.	70–400
Sulfate as Na_2SO_4	p.p.m.	10–1500

Test No.	VI+ Cr ion, p.p.m.	III+ Cr ion, p.p.m.	II+ Zn ion, p.p.m.	Water soluble phosphate, p.p.m.	Type of organic compound, p.p.m.	Type of Attack	Corrosion rate, MPY*
1	20					Extensive pitting	10
2	8					do	20
3	8	0.3				Moderate pitting	12
4	8	0.1				do	7
5	8	0.02				do	7
6	8		2			Extensive pitting	10
7	8		2	15 (Poly)		Some pitting	5
8	8		2		Sulfonate, 1	do	4
9	8		1		Citrate, 0.05	do	6
10	8		1		Ethylene diamine tetracetic acid, 0.5.	Moderate pitting	7
11	8		2		Thiocyanate, 0.02	Negligible	<1
12	8		1		Thiourea, 0.02	do	<1
13	8				Thiocyanate, 0.05	do	<1
14	8			15 (Ortho)		Some pitting	4

*Mils per year.

It will be seen, from the foregoing table, that hexavalent chromium alone in the amount of 20 p.p.m. as hexavalent chromium ion caused extensive pitting and showed a corrosion rate of 10 mils per year. Hexavalent chromium in admixture with trivalent chromium showed moderate pitting and a corrosion rate in the range of 12 to 7 mils per year. Hexavalent chromium and zinc ions with and without certain supplemental agents showed from extensive to some pitting and a corrosion rate of from 10 to 4 mils per year. In sharp contrast to the above, the addition of as little as 0.02 to 0.05 p.p.m. of thiocyanate (in this case sodium thiocyanate) or thiourea to 8 p.p.m. of hexavalent chromium ion, with and without from 2 to 1 p.p.m. of zinc ion, showed no pitting and a corrosion rate of less than 1 mil per year. The coaction between the hexavalent chromium and the thiocyanate or thiourea, in the presence as well as without the presence of the zinc ion, demonstrates a highly surprising and effective synergistic-like action.

What is claimed as new and desired to be protected by Letters Patent of the United States is:

1. A corrosion inhibiting composition useful upon addition to water to inhibit corrosion of ferrous metals in contact with said water, said composition consisting essentially of the following ingredients in substantially the following parts by weight in relation to each other:

A member selected from the group consisting of water-soluble chromates and dichromates	1 to 10,000 (calculated as Na_2CrO_4).
Water-soluble thiocyanate compound	0.01 to 100.

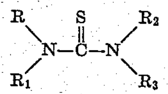
2. A corrosion inhibiting composition useful upon addition to water to inhibit corrosion of ferrous metals in contact with said water, said composition consisting es-

sentially of the following ingredients in substantially the following parts by weight in relation to each other:

A member selected from the group consisting of water-soluble chromates and dichromates	2 to 100 (calculated as Na_2CrO_4).
Water-soluble thiocyanate compound	0.01 to 25.

3. A composition in accordance with claim 2, including from 1 to 8 parts of a water-soluble zinc compound calculated as zinc.

4. A corrosion inhibiting composition useful upon addition to water to inhibit corrosion of ferrous metals in contact with said water, said composition consisting essentially of the following ingredients in substantially the following parts by weight in relation to each other:

A member selected from the group consisting of water-soluble chromates and dichromates	1 to 10,000 (calculated as Na_2CrO_4).
A thiourea compound corresponding  where R, R_1, R_2 and R_3 are each selected from the group consisting of hydrogen, alkali metal, and alkyl radicals containing from 1 to 4 carbon atoms	0.01 to 200.

5. A composition in accordance with claim 4, including from 0.5 to 25 parts calculated as zinc.

6. A corrosion inhibiting composition useful upon addition to water to inhibit corrosion of ferrous metals in contact with said water, said composition consisting essentially of the following ingredients in substantially the following parts by weight in relation to each other:

A member selected from the group consisting of water-soluble chromates and dichromates	2 to 100 (calculated as Na_2CrO_4).
Thiourea	0.01 to 25.

7. A corrosion inhibiting composition useful upon addition to water to inhibit corrosion of ferrous metals in contact with said water, said composition consisting essentially of the following ingredients in substantially the following parts by weight in relation to each other:

A member selected from the group consisting of water-soluble chromates and dichromates	5 to 30 (calculated as Na_2CrO_4).
Chomic acid	5 to 30
Thiourea	0.02 to 10

8. A process of protecting ferrous metals against corrosion by water circulated in contact therewith, the step which consists essentially in adding to the water the following ingredients in the stated concentration in p.p.m. based on the water:

Hexavalent chromium calculated as Na_2CrO_4	1 to 10,000
Water-soluble thiocyanate compound	0.01 to 100

9. A process of protecting ferrous metals against corrosion by water circulated in contact therewith, the step which consists essentially in adding to the water the following ingredients in the stated concentrations in p.p.m. based on the water:

Hexavalent chromium calculated as Na_2CrO_4	1 to 10,000
Water-soluble zinc compound calculated as in zinc ion	0.5 to 20
Ammonium thiocyanate	0.01 to 200

10. The method of retarding the corrosion of a ferrous metal upon contact with water which comprises effecting such contact in the presence of a water-soluble corrosion inhibitor dissolved in said water, said inhibitor consisting essentially of a water-soluble hexavalent chromium compound, a water-soluble zinc compound, and a water-soluble thiocyanate, said ingredients being present in the water in the following amounts in terms of p.p.m.:

Hexavalent chromium compound (calculated as Na_2CrO_4)	5 to 30
Zinc compound (calculated as zinc ion)	1 to 8
Thiocyanate	0.02 to 10

11. The method of retarding the corrosion of a ferrous metal upon contact with water which comprises effecting such contact in the presence of a water-soluble corrosion inhibitor dissolved in said water, said inhibitor consisting essentially of a water-soluble hexavalent chromium compound, a water-soluble zinc compound, and thiourea, said ingredients being present in the water in the following amounts in terms of p.p.m.:

Hexavalent chromium compound (calculated as Na_2CrO_4)	5 to 30
Zinc compound (calculated as zinc ion)	1 to 8
Thiourea	0.02 to 10

References Cited in the file of this patent

UNITED STATES PATENTS

2,215,077	Beekhuis et al.	Sept. 17, 1940
2,398,202	Zublin et al.	Apr. 9, 1946
2,459,119	Rucker	Jan. 11, 1949
2,602,779	Moyer et al.	July 8, 1952
2,617,771	Rucker	Nov. 11, 1952
2,618,605	Schaeffer	Nov. 18, 1952
2,695,876	Farris	Nov. 30, 1954
2,797,199	Chittum	June 25, 1957
2,840,610	Pullig	June 24, 1958
2,900,222	Kahler et al.	Aug. 18, 1959