METHODS OF INHIBITING CORROSION USING N-HALO-AZOLES

FIELD OF THE INVENTION

The present invention relates to the inhibition of corrosion of steel and copper alloys in aqueous systems characterized by adding N-halo-azoles prepared ex situ the aqueous system to the aqueous system.

BACKGROUND OF THE INVENTION

The use of triazoles for inhibiting the corrosion of copper and iron alloys in a wide variety of aqueous and non-aqueous systems is well known. In industrial cooling water systems, benzotriazole and tolyltriazole are used most often. Tolyltriazole is generally preferred because of its lower cost. Triazoles are film forming materials that provide efficient coverage of metal or metal oxide surfaces in a system thereby providing protection against corrosive elements present in an aqueous system. In addition to the film forming tendency of various azoles, they also precipitate soluble, divalent copper ions. The precipitation prevents transport of copper ions to ferrous surfaces, where galvanic reactions between copper ions and iron atoms leads to pitting corrosion of the ferrous metal.

While the use of azoles for corrosion inhibition is widespread, there are drawbacks to their use, specifically with tolyltriazole. The most important drawbacks are experienced when azoles are used in combination with oxidizing halogens. Oxidizing halogens such as elemental chlorine, bromine, their hypohalous acids, or their alkaline solutions (i.e., solutions of hypochlorite or hypobromite ion) are the most common materials used to control microbiological growth in cooling water systems. When copper or iron alloys that have previously been protected with azoles are exposed to an oxidizing halogen, corrosion protection breaks down. After breakdown, it is difficult to form new protective films in tolyltriazole treated cooling systems that are being chlorinated, particularly continuously chlorinated. Very high dosages of tolyltriazole are frequently applied in an attempt to improve performance, often with limited success.

The degradation of protection of azole films in the presence of oxidizing halogens is well-documented in the literature. For example, R. Holm, et al., concluded that hypochlorite penetrates an intact triazole film, leading to higher corrosion rates, and that secondly, hypochlorite attacks the prefilmed triazole surface, disrupting or degrading the film (53rd Annual Meeting of the International Water Conference, Paper No. IWC-92-40, 1992). Lu, et al., also studied interactions of triazole films with hypochlorite on copper and copper alloy surfaces ("Effects of Halogenation on Yellow Metal Corrosion: Inhibition by Triazoles", Corrosion, 50, 422 (1994)). Lu, et al., concluded:

(a) prefilmed tolyltriazole on copper and brass surfaces undergoes decomposition during chlorination;

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(b) the stability of prefilmed tolyltriazole on copper and brass to NaOCl was improved when tolyltriazole was added to the hypochlorite solution;

(c) clean (i.e., non-prefilmed) copper surfaces did not develop good protective films when placed in solutions containing mixtures of tolyltriazole and NaOCl.

Thus, the combination of tolyltriazole with NaOCl did not produce a composition capable of efficient film formation and corrosion inhibition.

The nature of the reaction products when azoles are exposed to oxidizing halogens in a cooling water system is not clear. The literature teaches that a compound is formed when chlorine and tolyltriazole are combined in cooling waters, and that it responds to analytical tests for chlorine. For example, Vanderpool, et al., state that chlorine reacts reversibly with tolyltriazole to produce 1-chlorotolyltriazole. They specifically state, "presumably this compound is not itself an inhibitor." Rather, they teach that it is readily hydrolyzed to the original tolyltriazole and hypochlorous acid so that free tolyltriazole becomes available for corrosion inhibition ("Improving the Corrosion Inhibitor Efficiency of Tolyltriazole in the Presence of Chlorine and Bromine", NACE Corrosion/87, Paper No. 157 (1987)). Hollander and May were able to isolate 1-chlorotolyltriazole from stored, more highly concentrated solutions, but they also teach that "at low concentrations (less than 10 mg/L) rapid hydrolysis made it impossible to isolate the chloro adducts." "The Chemistry of Azole Copper Corrosion Inhibitors in Cooling Water", NACE-Corrosion Vol. 41, No. 1, pp. 39-45, January 1995.Thus, the art teaches that solutions of tolyltriazole with hypochlorite used to treat cooling waters are not readily distinguishable as different from a simple mixture of these components.

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In contrast, the present authors have shown that 1-chlorotolyltriazole does not respond to analytical tests for chlorine, despite extended boiling. In solutions of 1-chlorotolyltriazole there is also the surprising absence of a very characteristic odor that is present whenever tolyltriazole and hypochlorite are combined in cooling waters.

There are also references in the literature to 5-chlorobenzotriazole (i.e., CAS number [94-97-3]). In "The Water Drop", Volume I No. 2, 1985, Puckorius & Associates state that chlorinated tolyltriazole is effective as a corrosion inhibitor and cite R.P. Carr as a reference. However, they imply a chlorination of the benzene ring as opposed to the azole ring. (Chlorination of the azole ring is the subject of the present invention to be described subsequently.) Further, a literature review of published work by Carr indicates that he actually teaches that reactions between tolyltriazole and chlorine do not occur under cooling water conditions ("The Performance of Tolyltriazole in the Presence of Sodium Hypochlorite Under Simulated Field Conditions", NACE Corrosion/83 Paper No. 283, 1983). In this Corrosion/83 paper, Carr does discuss the inhibiting action of a chloroazole but it is a reference to earlier literature and specifically to the action of 5-chlorobenzotriazole and related aryl substituted chlorinated azoles in sulfuric acid solutions ("Effects of Substituted Benzotriazole on the Electrochemical Behavior of Copper in H_2SO_4", Wu et al., Corrosion, Volume 37, No. 4, 223 (1981)). Again, 5-chlorobenzotriazole is formed as a result of chlorination of the benzene ring and not the azole ring. Since the 1985 Puckorius reference, there has been widespread use of tolyltriazole in chlorinated cooling systems with well established performance difficulties, indicating a continuing, unsolved problem in the art.

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Other problems are well-known when tolyltriazole and oxidizing halogens are combined in cooling waters. These include a loss in the extent of precipitation of transition metal ions such as copper, thus leading to improved transport and galvanic corrosion, a change in the response of the standard spectrophotometric test for tolyltriazole, leading to unintentional overfeed, and the objectionable odor mentioned above. This odor can be sensed even when the cooling water originally contained 1 ppm tolyltriazole, or less. Since cooling water often passes over cooling towers, evaporation and drift release the objectionable odor to the local environment.

The present authors believe that although the molecularity of the odorous material has not been identified, it may be the key in understanding the differences between true solutions of 1-chlorotolyltriazole in contrast to mixtures of tolyltriazole and hypochlorite: the odorous material is probably an intermediate in stepwise reactions leading to 1-chlorotolyltriazole, that it forms reversibly with tolyltriazole, and that it is absent when the reaction is driven to completion, i.e., tolyltriazole + $OCl^- \leftrightarrow$(intermediate)$\rightarrow$1-chlorotolyltriazole. The present inventors have found no evidence of reversion of 1-chlorotolyltriazole to either the odorous intermediate or to tolyltriazole. Nor is there any evidence of reactions between hypochlorite and 1-chlorotolyltriazole in dilute aqueous solutions.

SUMMARY OF THE INVENTION

The present inventors have discovered that N-halo-azoles such as 1-chlorotolyltriazole and 1-bromotolyltriazole prepared ex situ are more effective than tolyltriazole in inhibiting corrosion in aqueous systems. The N-halo-azoles are substantially more effective than tolyltriazole in the

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presence of chlorine. Furthermore, when 1-chlorotolyltriazole is exposed to chlorine, an objectionable odor does not form and the quantity of chlorine that is required to produce a residual in the aqueous system is reduced.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present inventors have discovered that N-halo-azoles such as 1-chlorotolyltriazole and 1-bromotolyltriazole prepared ex situ are more effective than tolyltriazole in inhibiting corrosion in aqueous systems. The N-halo-azoles are substantially more effective corrosion inhibitors than tolyltriazole in the presence of chlorine. The efficacy of the present invention is surprising given the prior knowledge that chlorination of an azole treated system leads to degradation of corrosion inhibition performance. Furthermore, the N-halo-azoles of the present invention are not subject to the formation of objectionable odors when exposed to chlorine as is tolyltriazole, the quantity of chlorine that is required to produce a residual in the aqueous system is notably reduced in comparison to systems treated with tolyltriazole, and the treatment is effective in the presence of sulfide ions.

The N-halo-azoles of the present invention can include chloro-, fluoro-, bromo- and iodo- as well as haloalkyl (trifluoromethyl) azoles. Preferred are 1-chlorotolyltriazole and 1-bromotolyltriazole. The azole may include tolyltriazole, benzotriazole, butylbenzotriazole, mercaptobenzothiazole and the like. The preferred azole is tolyltriazole.

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The preferred azole, tolyltriazole, is such that the preferred N-haloazole is 1-chlorotolyltriazole or 1-bromotolyltriazole. The ex situ preparation of the preferred 1-chlorotolyltriazole can be by any suitable means. Examples of preparation methods include but are not limited to reactions with hypochlorite, N-chlorosuccinimide, and other chlorinating agents. A method of forming 1-chlorotolyltriazole is through the reaction of tolyltriazole with hypochlorite, in which case the final reaction mixture is an alkaline solution that can be used with or without further modification. Alternatively, 1-chlorotolyltriazole can be formed through the reaction of tolyltriazole with hypochlorite in acetic acid solutions, (i.e., hypochlorous acid) and then isolated as a solid. For convenience of application, the solid can be redissolved in alcohols such as methanol or 2-propanol, aqueous solutions of alcohols or strong alkaline solutions such as sodium hydroxide or potassium hydroxide.

The preparation of 1-bromotolyltriazole can be by any suitable means. Examples of preparation methods include but are not limited to reactions with hypobromite, bromine, and other brominating agents. A method of forming 1-bromotolyltriazole is through the reaction of tolyltriazole with bromine, in an aqueous solution and then isolated as a solid. For convenience of application, the solid can be dissolved in a strong alkaline solution such as sodium hydroxide or potassium hydroxide.

The reaction products are isomeric mixtures since the tolyltriazole starting material is an isomeric mixture of 4- and 5-methylbenzotriazole. The distribution of isomers of 1-chlorotolyltriazole obtained is principally 1-chloro-4-methylbenzotriazole, 1-chloro-5-methylbenzotriazole, and

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1-chloro-6-methylbenzotriazole. The latter two materials appear to be somewhat preferred over the 4-methyl isomer, although mixtures of the isomers appear to be as effective as the individual isomers.

In treating an aqueous system in accordance with the present invention, the 1-chlorotolyltriazole (hereinafter 1-CITTA) is preferably fed continuously to the water. A preferred treatment concentration ranges from about 0.5 to 10 parts per million, most preferably at about 3 parts per million. Continuous feed is not, however, a requirement. The 1-chlorotolyltriazole can be fed at a concentration sufficient to form a protective film and thereafter feed can be discontinued for extended periods of time.

The N-halo-azole treatment of the present invention can be used in combination with other corrosion and/or deposit inhibiting treatments known in the art including but not limited to phosphates, phosphonates, acrylic homo- and copolymers, chelants, and oximes.

The present invention will now be further described with reference to a number of specific examples which are to be regarded solely as illustrative and not as restricting the scope of the present invention.

Examples

Example 1

The preparation of the solid samples was as follows:

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Tolyltriazole (hereinafter TTA) (30 g, 0.225 mol) was dissolved in aqueous acetic acid (60 mL, 1:1 ratio) by heating to 32°C. Sodium hypochlorite (366 g, 5.25% sodium hypochlorite as a bleach solution) was added while maintaining the reaction temperature at ~ 20°C. Following the addition, the reaction mixture was stirred at room temperature for 24 hours. A sticky precipitate formed during this time. The solid was filtered and taken into methylene chloride. The solid that did not dissolve was filtered and identified as a mixture of 1-ClTTA (principally the 4-methyl isomer), with minor amounts of TTA and dichlorotolyltriazole (diClTTA). The methylene chloride was removed to obtain a yellow solid which was identified as a mixture of 1-ClTTA (principally the 5- and 6-methyl isomers) with minor amounts of diClTTA. Unless noted, this latter solid was used in the following Examples.

Example 2

A slurry of TTA (50 g, 0.376 mol) in 25 g of water was warmed to 35°C. Sodium hypochlorite (27.9 g, 0.376 mol, added as 226.8 g of a 12.3% sodium hypochlorite solution) was added over a period of 2 hours. After the addition, the reaction was kept at 45°C for one hour. During the addition the pH of the reaction mixture increased to 12 and the solids dissolve. The final product was analyzed by ^{1}H and ^{13}C NMR and LC-UV and found to be composed of 81.9% Cl-TTA (approximately 2:1:1 molar ratio of the 4-, 5-, and 6-methyl isomers), 8.8% residual TTA, and 9.3% di-Cl-TTA based on the relative areas in the UV spectra.

On dilution to 1 to 100 ppm azole, with or without pH adjustment to about 7.2, there was no odor from the N-halo-azole solution of the present invention.

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Example 3

In the schemes below, TTA was present at 100 ppm, in contrast to Example 2 where the initial slurry contained about 200,000 ppm. "x" denotes a stoichiometric ratio.

Scheme 1

pH=7 solution containing slow
TTA+1.1xNaOCl<——>odorous by-product——>1-ClTTA(ppt)+odorous by-product

Scheme 2

pH=11.8 pH=8.2
TTA+1.1xNaOCl<——>solution, no odor——>1-ClTTA(ppt)+odorous by-product

Example 4

1-ClTTA, prepared as a solid according to Example 1, was dissolved in methanol and charged to a simulated cooling water solution. The solution contained 319 ppm Ca (calculated as $CaCO_3$), 7 ppm Mg (calculated as $CaCO_3$), 190 ppm $NaHCO_3$, 882 ppm Na_2SO_4, 1184 ppm NaCl, 5 ppm azole, and 2.4 ppm of hydroxyethylidene diphosphonic acid (HEDP). Hypochlorite was absent. The solution was maintained at 120°F by an admiralty brass heater tube and at pH=7.2 to 7.5 by a pH controller equipped to feed sulfuric acid on demand. The solution was recirculated past the heater and past both admiralty and copper/nickel alloy corrosion rate meters (CRM). After 1 hour the solution was drained and replaced by an identical solution with no azole, which was also fed to overflow and replenish the system with fresh solution at about 4% by volume per hour. This system was maintained under these conditions continuously until the

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bright admiralty tube was tarnished, at which point the experiment was terminated. Comparisons were made to identical experiments with TTA and benzotriazole.

TABLE I

Admiralty Tube Appearance

Pretreatment	40 hours	94 hours	336 hours
1-CITTA	Bright	Bright	Tarnished
TTA	Bright	Tarnished	*
Benzotriazole	Tarnished	*	*

TABLE II

	Admiralty Corrosion Rate (mpy)			Cu/Ni Corrosion Rate (mpy)		
Pretreatment	40 hrs.	94 hrs.	336 hrs.	40 hrs.	94 hrs.	336 hrs.
1-CITTA	0.2	0.3	0.5	0.7	0.4	0.8
TTA	<0.1	2.2	*	N/A	5.2	*
Benzotriazole	1.3	*	*	2.0	*	*

*Experiment previously terminated.

Example 5

Corrosion tests were carried out in the apparatus described in Example 4 with water containing 500 ppm Ca, 250 ppm Mg, 25 ppm Malk, 15 ppm o-PO_4, 3 ppm tetrapotassium pyrophosphate, 10 ppm of a 3:1, low molecular weight, acrylic acid/allyl 2-hydroxypropyl sulfonate ether copolymer, 2.4 ppm HEDP, and the pH maintained at 7.2 with a blended mixture of air and carbon dioxide at 49°C for 18 hours. Electrochemical corrosion rates were measured using admiralty brass (ADM) and low carbon steel (LCS) working electrodes. All tests also had both admiralty and LCS coupons in contact with the solution. The method differed from Example 4 in

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that the azole was fed continuously at 3 ppm during these experiments. The azole was supplied by dissolving the solid in potassium hydroxide solution and then diluting it into the feedwater for the system. Each experiment was duplicated: once with an admiralty brass heated tube, and once with a low carbon steel heated tube. Corrosion rates were measured as in Example 4 from admiralty and LCS working electrodes, and by weight changes of admiralty and LCS coupons. Rates for the coupons were measured for the initial day of each run, and a "differential" rate was calculated for the remaining days of the run by offsetting the initial rate from the overall rate.

TABLE III

CRM Corrosion Rates: Values at end of six days (mpy)

	LCS Heated Surface		ADM Heated Surface	
	1-CITTA	TTA	1-CITTA	TTA
LCS	0.2	0.4	0.45	0.75
ADM	0.00	0.00	0.05	0.07

TABLE IV

Gravimetric Coupon Corrosion Rates (mpy)
(First day and differential rates)

	LCS Heated Surface		ADM Heated Surface	
	1-CITTA	TTA	1-CITTA	TTA
Day 1 LCS	4.6	3.0	3.4	2.9
Day 6 LCS (diff.)	0.25	0.33	0.25	0.25
Day 1 ADM	1.9	2.1	1.6	1.8
Day 6 ADM (diff.)	0.00	0.20	0.00	0.10

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Example 6

The method of Example 5 was followed, except a solution of sodium hypochlorite was added after 20 hours and continued for an additional 72 hours. The feed rate of the sodium hypochlorite was controlled to produce a "chlorine residual" of about 0.1 to 0.3 ppm as Cl_2 using a standard DPD spectrophotometric test on the recirculating water. For the experiment with 1-CITTA, the feed rate of the sodium hypochlorite was about 30% of that required for TTA. For TTA, the characteristic odor was detected immediately after the first hypochlorite was added. With 1-CITTA, there was no odor upon initiating hypochlorite addition, and only a trace was sensed just prior to concluding the four day run.

TABLE V

CRM Corrosion Rates: Values at 90 hour mark (mpy)

	LCS Heated Surface	
	1-CITTA	TTA
LCS	0.5	2.3
ADM	0.06	0.02

TABLE VI

Gravimetric Corrosion Rates (mpy)

	LCS Heated Surface	
	1-CITTA	TTA
Day 2 to 4 LCS	1.1	2.6
Day 4 LCS (diff.)	0.4	1.4
Day 2 to 4 ADM	1.1	1.2
Day 4 ADM (diff.)	0.15	0.85

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Example 7

Solutions of azole at 6 ppm were made in deionized water, and the pH was adjusted to 7.0. Cu^{+2} ion was added (0.1 ppm from cupric sulfate) and the pH was again adjusted to 7.0. A sample was digested with nitric acid, analyzed for copper, and a second sample was filtered (0.2 micron pore size), digested, and analyzed for copper. The ratio was expressed as "% soluble Cu":

TABLE VII

Sample	% Soluble Cu
TTA	15
TTA+NaOCl	90
1-ClTTA	13

Example 8

Admiralty brass corrosion coupons and working electrodes were coated with a sulfide layer by exposing the metal to a sodium sulfide solution for 18 hours. These samples were rinsed and dried. Corrosion tests were carried out in aqueous solutions in stirred beakers containing 500 ppm Ca, 250 ppm Mg, 25 ppm Malk, 15 ppm o-PO_4, 3 ppm tetrapotassium pyrophosphate, 10 ppm of a 3:1, low molecular weight, acrylic acid/allyl 2-hydroxypropyl sulfonate ether copolymer, 2.4 ppm HEDP, and the pH was maintained at 7.2 with a blended mixture of air and carbon dioxide at 49°C for 18 hours. Electrochemical corrosion rates were measured using admiralty brass or low carbon steel working electrodes. All tests also had both admiralty and LCS coupons in contact with the solution.

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Each solution was tested with and without addition of sodium hypochlorite (added after 1 hour exposure). In a separate, but otherwise identical experiment, clean low carbon steel working electrodes were used in place of the sulfide-exposed admiralty brass, but the sulfide-exposed brass coupons were present as a source of copper. At the conclusion of the experiment, a sample of the supernatant solution was taken and analyzed for copper. Analyses were taken with and without filtration through a 0.2 micron membrane filter.

TABLE VII

Azole	NaOCl (ppm)	Admiralty Brass Corrosion Rate (mpy)	Low Carbon Steel Corrosion Rate (mpy)	Copper (ppm) Unfiltered	Copper (ppm) Filtered
none	0	1.01	5.4	0.354	0.103
3 ppm TTA	0	0.07	1.2	0.014	0.014
3 ppm 1-CITTA	0	0.06,0.05	1.0	0.005	0.004
none	2.0	2.09	5.2	0.417	0.059
3 ppm TTA	2.0	0.45	2.6	0.133	0.066
3 ppm 1-CITTA	2.0	0.13	1.7	0.086	0.039

Example 9

A sample was prepared from the methylene chloride-insoluble fraction of Example 1. This was compared to the sample from the methylene chloride-soluble fraction of Example 1 and the solution from Example 2. These samples, plus a mixture of the first two solids allows a comparison of isomeric fractions based on the position of the methyl group on the

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benzene ring of 1-CITTA (see Example 1), as follows (note that tolyltriazole is approximately equimolar in the 4- and 5-methyl isomers, and the 6-methyl isomer is equivalent to the 5-methyl isomer):

TABLE IX

1-Chlorotolyltriazole Isomers, Methyl Position(s)	Source
(4)	Example 1. methylene chloride insoluble fraction
(5) + (6)	Example 1, methylene chloride soluble fraction
(4) + (5) + (6) (approx. 2:1:1)	Mixture of the above two samples
(4) + (5) + (6) (approx. 2:1:1)	Example 2

The method of Example 8 was followed, using clean admiralty brass coupons and electrodes. The following were the 18 hour averaged electrochemical corrosion rates:

TABLE X

Azole (3 ppm total)	Isomers	Source	NaOCl	Average Corrosion Rate (mpy)
1-CITTA	(4)	Ex. 1	none	0.17
1-CITTA	(5)+(6)	Ex. 1	none	0.11
1-CITTA	(4)+(5)+(6)	Ex. 1	none	0.10
1-CITTA	(4)+(5)+(6)	Ex. 2	none	0.07
TTA	(4)+(5=6)		none	0.23
1-CITTA	(4)	Ex. 1	2 ppm	0.30
1-CITTA	(5)+(6)	Ex. 1	2 ppm	0.21
1-CITTA	(4)+(5)+(6)	Ex. 1	2 ppm	0.15
1-CITTA	(4)+(5)+(6)	Ex. 2	2 ppm	0.13
TTA	(4)+(5=6)		2 ppm	0.39

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Example 10

A synthetic sea water was formulated from deionized water plus 1010 ppm Ca as $CaCO_3$, 5226 ppm Mg (as $CaCO_3$), 18971 ppm Cl, 2660 ppm SO_4, 117 ppm M-alkalinity (as $CaCO_3$), 5 ppm azole (see below), and the pH was maintained at 7.8 with a blended mixture of air and carbon dioxide at 38°C.

Admiralty brass electrodes were exposed to this medium for 1 hour and then they were transferred to identical water with no azole present. Electrochemical corrosion rates were measured for 18 hours.

TABLE XI

Azole	Mean Electrochemical Corrosion Rate (mpy)
Benzotriazole	40
5-Butylbenzotriazole	15
Tolyltriazole	6
1-Chlorotolyltriazole	3.2

Example 11

Sodium hypochlorite (12.2%, 204.9 g, 0.336 mol) was added over 90 minutes to a stirring slurry of benzotriazole (40 g, 0.336 mol) in 30 g of water at room temperature. Following the addition, the reaction mixture was held at 45-50°C for one hour. Upon cooling, a precipitate formed. A clear yellow solution was obtained after adjusting the pH to 11. The final product was analyzed by LC/MS and ^{13}C and ^{1}H NMR and found to be composed of 54.6% 1-chlorobenzotriazole, 23.9% residual benzotriazole, and 21.5% di-chlorobenzotriazole.

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Example 12

Bromine (12.5 g, 0.078 mol) was added to a stirring slurry of TTA (10 g, 0.075 mol) in 66 g of water in a reactor protected from light, while maintaining the temperature at <25°C. After the addition, the reaction mixture was held at 35-40°C for one hour. Upon cooling, adjusting the pH to 11-12 did not produce a clear solution. The precipitate that formed upon standing was removed by filtration, the pH of the filtrate was adjusted to neutral, and the resulting precipitate filtered. This solid was characterized by LC/MS and ^{13}C and ^{1}H NMR and found to be composed of 90.5% Br-TTA, 4.9% residual TTA, and 4.2% di-bromo-TTA.

Example 13

The method of Example 8 was followed, using samples from Examples 2, 11 and 12 at 1 to 4 ppm total actives. The following were the 18 hour averaged electrochemical corrosion rates:

TABLE XII

Azole	Conc. (ppm)	Source	NaOCl	Average Corrosion Rate (mpy)
1-ClBZT	1	Ex. 11	none	0.21
	2			0.09
	4			0.03
1-ClTTA	1	Ex. 2	none	0.14
	2			0.09
	4			0.08
1-BrTTA	1	Ex. 12	none	0.17
	2			0.11
	4			0.07

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TABLE XII (cont'd)

Azole	Conc. (ppm)	Source	NaOCl	Average Corrosion Rate (mpy)
TTA	1		none	0.13
	2			0.14
	4			(n/a)
1-ClBZT	1	Ex. 11	2 ppm	0.55
	2			0.25
	4			0.09
1-ClTTA	1	Ex. 2	2 ppm	0.58
	2			0.24
	4			0.09
1-BrTTA	1	Ex. 12	2 ppm	0.45
	2			0.16
	4			0.09
TTA	1		2 ppm	(n/a)
	2			0.45
	4			0.27

The above examples show that the ex situ prepared N-halo-azoles of the present invention are effective corrosion inhibitors even in the presence of chlorine.

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CLAIMS

What is claimed is:

1. A method of inhibiting corrosion of metal surfaces contacted by an aqueous system characterized by adding to said aqueous system an N-halo-azole prepared ex situ said aqueous system.

2. The method of claim 1 wherein said aqueous system is being treated with a halogen.

3. The method of claim 1 wherein sulfide ions are present in said aqueous system.

4. The method of claim 1 wherein said N-halo-azole is selected from the group consisting of 1-chlorotolyltriazole and 1-bromotolyltriazole.

5. The method of claim 1 wherein said N-halo-azole is added to said aqueous system at a concentration of greater than 0.5 parts per million.

6. The method of claim 1 wherein said N-halo-azole is added to said aqueous system at a concentration of from 0.5 parts per million to 10 parts per million.

7. A method as claimed in any of claims 1 to 6, wherein a corrosion inhibiting layer is formed on said metal surfaces by said N-halo-azole.

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8. A method as claimed in any of claims 1 to 7, wherein chlorine demand, in said aqueous system, to inhibit microbiological growth is reduced by said N-halo-azole.

9. A method as claimed in any of claims 1 to 8, wherein copper ion transport in said aqueous system is inhibited by said N-halo-azole.

10. A corrosion inhibiting composition for metal surfaces contacted by an aqueous system comprising an aqueous solution of greater than 0.5 parts per million 1-bromotolyltriazole.

11. A composition comprising 1-bromotolyltriazole.

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(b) the stability of prefilmed tolyltriazole on copper and brass to NaOCl was improved when tolyltriazole was added to the hypochlorite solution;

(c) clean (i.e., non-prefilmed) copper surfaces did not develop good protective films when placed in solutions containing mixtures of tolyltriazole and NaOCl.

Thus, the combination of tolyltriazole with NaOCl did not produce a composition capable of efficient film formation and corrosion inhibition.

European Patent Application 0 592 118 discloses a method of controlling corrosion and biological matter in copper and copper alloy cooling water systems. The method requires that a triazole film be formed on copper and copper alloys by treating the system with a triazole. Thereafter, when needed, low levels of triazole and an oxidizing biocide are added to the system at the same time. Re-formation of the triazole film is accomplished by adding additional triazole when required. This method does not involve the ex situ reaction of a halogenating agent and a benzotriazole to form a halo-benzotriazole treatment.

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The nature of the reaction products when azoles are exposed to oxidizing halogens in a cooling water system is not clear. The literature teaches that a compound is formed when chlorine and tolyltriazole are combined in cooling waters, and that it responds to analytical tests for chlorine. For example, Vanderpool, et al., state that chlorine reacts reversibly with tolyltriazole to produce 1-chlorotolyltriazole. They specifically state, "presumably this compound is not itself an inhibitor." Rather, they teach that it is readily hydrolyzed to the original tolyltriazole and hypochlorous acid so that free tolyltriazole becomes available for corrosion inhibition ("Improving the Corrosion Inhibitor Efficiency of Tolyltriazole in the Presence of Chlorine and Bromine", NACE Corrosion/87, Paper No. 157 (1987)). Hollander and May were able to isolate 1-chlorotolyltriazole from stored, more highly concentrated solutions, but they also teach that "at low concentrations (less than 10 mg/L) rapid hydrolysis made it impossible to isolate the chloro adducts." "The Chemistry of Azole Copper Corrosion Inhibitors in Cooling Water", NACE-Corrosion Vol. 41, No. 1, pp. 39-45, January 1995.Thus, the art teaches that solutions of tolyltriazole with hypochlorite used to treat cooling waters are not readily distinguishable as different from a simple mixture of these components.

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In contrast, the present authors have shown that a treatment material obtainable by

i) dissolution of a benzotriazole in an aqueous acetic acid, thereafter adding a halogenating agent, recovering a resulting solid and dissolving recovered solid in an alcohol or strong alkaline solution to form ex situ said treatment material, or by

ii) the addition of a halogenating agent to an aqueous slurry of a benzotriazole at alkaline pH to form, ex situ, said treatment material does not respond to analytical tests for chlorine, despite extended boiling. In solutions of said treatment material there is also the surprising absence of a very characteristic odor that is present whenever tolyltriazole and hypochlorite are combined in cooling waters.

There are also references in the literature to 5-chlorobenzotriazole (i.e., CAS number [94-97-3]). In "The Water Drop", Volume I No. 2, 1985, Puckorius & Associates state that chlorinated tolyltriazole is effective as a corrosion inhibitor and cite R.P. Carr as a reference. However, they imply a chlorination of the benzene ring as opposed to the azole ring.

Further, a literature review of published work by Carr indicates that he actually teaches that reactions between tolyltriazole and chlorine do not occur under cooling water conditions ("The Performance of Tolyltriazole in the Presence of Sodium Hypochlorite Under Simulated Field Conditions", NACE Corrosion/83 Paper No. 283, 1983). In this Corrosion/83 paper, Carr does discuss the inhibiting action of a chloroazole but it is a reference to earlier literature and specifically to the action of 5-chlorobenzotriazole and related aryl substituted chlorinated azoles in sulfuric acid solutions ("Effects of Substituted Benzotriazole on the Electrochemical Behavior of Copper in H_2SO_4", Wu et al., Corrosion, Volume 37, No. 4, 223 (1981)). Since the 1985 Puckorius reference, there has been widespread use of tolyltriazole in chlorinated cooling systems with well established performance difficulties, indicating a continuing, unsolved problem in the art.

Other problems are well-known when tolyltriazole and oxidizing halogens are combined in cooling waters. These include a loss in the extent of precipitation of transition metal ions such as copper, thus leading to improved transport and galvanic corrosion, a change in the response of the standard spectrophotometric test for tolyltriazole, leading to unintentional overfeed, and the objectionable odor mentioned above. This odor can be sensed even when the cooling water originally contained 1 ppm tolyltriazole, or less. Since cooling water often passes over cooling towers, evaporation and drift release the objectionable odor to the local environment.

The present authors believe that although the molecularity of the odorous material has not been identified, it may be the key in understanding the differences between true solutions of 1-chlorotolyltriazole in contrast to mixtures of tolyltriazole and hypochlorite: the odorous material is probably an intermediate in stepwise reactions leading to 1-chlorotolyltriazole, that it forms reversibly with tolyltriazole, and that it is absent when the reaction is driven to completion, i.e., tolyltriazole + $OCl^- \leftrightarrow$(intermediate)$\rightarrow$1-chlorotolyltriazole. The present inventors have found no evidence of reversion of 1-chlorotolyltriazole to either the odorous intermediate or to tolyltriazole. Nor is there any evidence of reactions between hypochlorite and 1-chlorotolyltriazole in dilute aqueous solutions.

SUMMARY OF THE INVENTION

The present inventors have discovered that treatment materials obtainable by

i) dissolution of a benzotriazole in aqueous acetic acid, thereafter adding a halogenating agent, recovering a resulting solid and dissolving recovered solid in an alcohol or strong alkaline solution to form ex situ said treatment material, or by

ii) the addition of a halogenating agent to an aqueous slurry of benzotriazole at alkaline pH to form, ex situ, said treatment material, (and those prepared ex situ) are more effective than tolyltriazole in inhibiting corrosion in aqueous systems. The treatment materials of the invention are substantially more effective than tolyltriazole in the presence of chlorine. Furthermore, when the treatment materials of the invention are exposed to chlorine, an objectionable odor does not form and the quantity of chlorine that is required to produce a residual in the aqueous system is reduced.

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According to the present invention there is provided a method of inhibiting corrosion of metal surfaces contacted by an aqueous system characterized by adding to said aqueous system a treatment material obtainable by

i) dissolution of a benzotriazole in aqueous acetic acid, thereafter adding a halogenating agent, recovering a resulting solid and dissolving recovered solid in an alcohol or strong alkaline solution to form ex situ said treatment material, or by

ii) the addition of a halogenating agent to an aqueous slurry of a benzotriazole at alkaline pH to form, ex situ, said treatment material.

Also according to the present invention there is provided a composition for metal surfaces contacted by an aqueous system comprising an aqueous solution of greater than 0.5 parts per million of a treatment material obtainable by

i) dissolution of a benzotriazole in aqueous acetic acid, thereafter adding a halogenating agent, recovering a resulting solid and dissolving recovered solid in an alcohol or strong alkaline solution to form ex situ said treatment material, or by

ii) the addition of a halogenating agent to an aqueous slurry of a benzotriazole at alkaline pH to form, ex situ, said treatment material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present inventors have discovered that the treatment materials (prepared ex situ) are more effective than tolyltriazole in inhibiting corrosion in aqueous systems. The treatment materials are substantially more effective corrosion inhibitors than tolyltriazole in the presence of chlorine. The efficacy of the present invention is surprising given the prior knowledge that chlorination of an azole treated system leads to degradation of corrosion

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inhibition performance. Furthermore, the treatment materials of the present invention are not subject to the formation of objectionable odors when exposed to chlorine as is tolyltriazole, the quantity of chlorine that is required to produce a residual in the aqueous system is notably reduced in comparison to systems treated with tolyltriazole, and the treatment is effective in the presence of sulfide ions.

The treatment materials of the present invention can include chloro-, fluoro-, bromo- and iodo compounds. The azole may include tolyltriazole, benzotriazole, butylbenzotriazole, mercapto-benzothiazole and the like. The preferred azole is tolyltriazole. Preferred compounds are obtainable by chlorinating or brominating tolyltriazole.

The ex situ preparation of the preferred chlorinated tolyltriazole can be by any suitable means. Examples of preparation methods include but are not limited to reactions with hypochlorite, N-chlorosuccinimide, and other chlorinating agents. One method is through the reaction of tolyltriazole with hypochlorite, in which case the final reaction mixture is an alkaline solution that can be used with or without further modification. An alternative method involves the reaction of tolyltriazole with hypochlorite in acetic acid solutions, (i.e., hypochlorous acid) and then isolated as a solid. For convenience of application, the solid can be redissolved in alcohols such as methanol or 2-propanol, aqueous solutions of alcohols or strong alkaline solutions such as sodium hydroxide or potassium hydroxide.

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Bromination of tolyltriazole can be by any suitable means. Examples of preparation methods include but are not limited to reactions with hypobromite, bromine, and other brominating agents. A method of forming 1-bromotolyltriazole is through the reaction of tolyltriazole with bromine, in an aqueous solution and then isolated as a solid. For convenience of application, the solid can be dissolved in a strong alkaline solution such as sodium hydroxide or potassium hydroxide.

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In treating an aqueous system in accordance with the present invention, the chlorinated tolyltriazole treatment material (CTTTM) is preferably fed continuously to the water. A preferred treatment concentration ranges from about 0.5 to 10 parts per million, most preferably at about 3 parts per million. Continuous feed is not, however, a requirement. The CTTTM can be fed at a concentration sufficient to form a protective film and thereafter feed can be discontinued for extended periods of time.

The treatment of the present invention can be used in combination with other corrosion and/or deposit inhibiting treatments known in the art including but not limited to phosphates, phosphonates, acrylic homo- and copolymers, chelants, and oximes.

The present invention will now be further described with reference to a number of specific examples which are to be regarded solely as illustrative and not as restricting the scope of the present invention.

Examples

Example 1

The preparation of the solid samples was as follows:

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Tolyltriazole (hereinafter TTA) (30 g, 0.225 mol) was dissolved in aqueous acetic acid (60 mL, 1:1 ratio) by heating to 32°C. Sodium hypochlorite (366 g, 5.25% sodium hypochlorite as a bleach solution) was added while maintaining the reaction temperature at ~ 20°C. Following the addition, the reaction mixture was stirred at room temperature for 24 hours. A sticky precipitate formed during this time. The solid was filtered and taken into methylene chloride. The solid that did not dissolve was filtered and the methylene chloride was removed to obtain a yellow solid which was the CTTTM with minor amounts of di-Cl-TTA. Unless noted, this latter solid was used in the following Examples.

Example 2

A slurry of TTA (50 g, 0.376 mol) in 25 g of water was warmed to 35°C. Sodium hypochlorite (27.9 g, 0.376 mol, added as 226.8 g of a 12.3% sodium hypochlorite solution) was added over a period of 2 hours. After the addition, the reaction was kept at 45°C for one hour. During the addition the pH of the reaction mixture increased to 12 and the solids dissolve. The final product was analyzed by ^{1}H and ^{13}C NMR and LC-UV and found to be composed of 81.9% Cl-TTA, 8.8% residual TTA, and 9.3% di-Cl-TTA based on the relative areas in the UV spectra.

On dilution to 1 to 100 ppm azole, with or without pH adjustment to about 7.2, there was no odor from the solution of the treatment material of the present invention.

Example 3

In the schemes below, TTA was present at 100 ppm, in contrast to Example 2 where the initial slurry contained about 200,000 ppm. "x" denotes a stoichiometric ratio.

Scheme 1

pH=7 solution containing slow
TTA+1.1xNaOCl<——>odorous by-product——> CTTTM + odorous by-product

Scheme 2

pH=11.8 pH=8.2
TTA+1.1xNaOCl<——>solution, no odor——> CTTTM + odorous by-product

Example 4

A CTTTM prepared as a solid according to Example 1, was dissolved in methanol and charged to a simulated cooling water solution. The solution contained 319 ppm Ca (calculated as $CaCO_3$), 7 ppm Mg (calculated as $CaCO_3$), 190 ppm $NaHCO_3$, 882 ppm Na_2SO_4, 1184 ppm NaCl, 5 ppm azole, and 2.4 ppm of hydroxyethylidene diphosphonic acid (HEDP). Hypochlorite was absent. The solution was maintained at 120°F by an admiralty brass heater tube and at pH=7.2 to 7.5 by a pH controller equipped to feed sulfuric acid on demand. The solution was recirculated past the heater and past both admiralty and copper/nickel alloy corrosion rate meters (CRM). After 1 hour the solution was drained and replaced by an identical solution with no azole, which was also fed to overflow and replenish the system with fresh solution at about 4% by volume per hour. This system was maintained under these conditions continuously until the

bright admiralty tube was tarnished, at which point the experiment was terminated. Comparisons were made to identical experiments with TTA and benzotriazole.

TABLE I

Admiralty Tube Appearance

Pretreatment	40 hours	94 hours	336 hours
CTTTM	Bright	Bright	Tarnished
TTA	Bright	Tarnished	*
Benzotriazole	Tarnished	*	*

TABLE II

	Admiralty Corrosion Rate (mpy)			Cu/Ni Corrosion Rate (mpy)		
Pretreatment	40 hrs.	94 hrs.	336 hrs.	40 hrs.	94 hrs.	336 hrs.
CTTTM	0.2	0.3	0.5	0.7	0.4	0.8
TTA	<0.1	2.2	*	N/A	5.2	*
Benzotriazole	1.3	*	*	2.0	*	*

*Experiment previously terminated.

Example 5

Corrosion tests were carried out in the apparatus described in Example 4 with water containing 500 ppm Ca, 250 ppm Mg, 25 ppm M-alkalinity, 15 ppm o-PO_4, 3 ppm tetrapotassium pyrophosphate, 10 ppm of a 3:1, low molecular weight, acrylic acid/allyl 2-hydroxypropyl sulfonate ether copolymer, 2.4 ppm HEDP, and the pH maintained at 7.2 with a blended mixture of air and carbon dioxide at 49°C for 18 hours. Electrochemical corrosion rates were measured using admiralty brass (ADM) and low carbon steel (LCS) working electrodes. All tests also had both admiralty and LCS coupons in contact with the solution. The method differed from Example 4 in

that the CTTTM was fed continuously at 3 ppm during these experiments. The CTTTM was supplied by dissolving the solid in potassium hydroxide solution and then diluting it into the feedwater for the system. Each experiment was duplicated: once with an admiralty brass heated tube, and once with a low carbon steel heated tube. Corrosion rates were measured as in Example 4 from admiralty and LCS working electrodes, and by weight changes of admiralty and LCS coupons. Rates for the coupons were measured for the initial day of each run, and a "differential" rate was calculated for the remaining days of the run by offsetting the initial rate from the overall rate.

TABLE III

CRM Corrosion Rates: Values at end of six days (mpy)

	LCS Heated Surface		ADM Heated Surface	
	CTTTM	TTA	CTTTM	TTA
LCS	0.2	0.4	0.45	0.75
ADM	0.00	0.00	0.05	0.07

TABLE IV

Gravimetric Coupon Corrosion Rates (mpy)
(First day and differential rates)

	LCS Heated Surface		ADM Heated Surface	
	CTTTM	TTA	CTTTM	TTA
Day 1 LCS	4.6	3.0	3.4	2.9
Day 6 LCS (diff.)	0.25	0.33	0.25	0.25
Day 1 ADM	1.9	2.1	1.6	1.8
Day 6 ADM (diff.)	0.00	0.20	0.00	0.10

Example 6

The method of Example 5 was followed, except a solution of sodium hypochlorite was added after 20 hours and continued for an additional 72 hours. The feed rate of the sodium hypochlorite was controlled to produce a "chlorine residual" of about 0.1 to 0.3 ppm as Cl_2 using a standard DPD spectrophotometric test on the recirculating water. For the experiment with CTTTM the feed rate of the sodium hypochlorite was about 30% of that required for TTA. For TTA, the characteristic odor was detected immediately after the first hypochlorite was added. With CTTTM; there was no odor upon initiating hypochlorite addition, and only a trace was sensed just prior to concluding the four day run.

TABLE V

CRM Corrosion Rates: Values at 90 hour mark (mpy)

	LCS Heated Surface	
	CTTTM	TTA
LCS	0.5	2.3
ADM	0.06	0.02

TABLE VI

Gravimetric Corrosion Rates (mpy)

	LCS Heated Surface	
	CTTTM	TTA
Day 2 to 4 LCS	1.1	2.6
Day 4 LCS (diff.)	0.4	1.4
Day 2 to 4 ADM	1.1	1.2
Day 4 ADM (diff.)	0.15	0.85

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Example 7

Solutions of azole at 6 ppm were made in deionized water, and the pH was adjusted to 7.0. Cu^{+2} ion was added (0.1 ppm from cupric sulfate) and the pH was again adjusted to 7.0. A sample was digested with nitric acid, analyzed for copper, and a second sample was filtered (0.2 micron pore size), digested, and analyzed for copper. The ratio was expressed as "% soluble Cu":

TABLE VII

Sample	% Soluble Cu
TTA	15
TTA+NaOCl	90
CTTTM	13

Example 8

Admiralty brass corrosion coupons and working electrodes were coated with a sulfide layer by exposing the metal to a sodium sulfide solution for 18 hours. These samples were rinsed and dried. Corrosion tests were carried out in aqueous solutions in stirred beakers containing 500 ppm Ca, 250 ppm Mg, 25 ppm M-alkalinity, 15 ppm o-PO_4, 3 ppm tetrapotassium pyrophosphate, 10 ppm of a 3:1, low molecular weight, acrylic acid/allyl 2-hydroxypropyl sulfonate ether copolymer, 2.4 ppm HEDP, and the pH was maintained at 7.2 with a blended mixture of air and carbon dioxide at 49°C for 18 hours. Electrochemical corrosion rates were measured using admiralty brass or low carbon steel working electrodes. All tests also had both admiralty and LCS coupons in contact with the solution.

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Each solution was tested with and without addition of sodium hypochlorite (added after 1 hour exposure). In a separate, but otherwise identical experiment, clean low carbon steel working electrodes were used in place of the sulfide-exposed admiralty brass, but the sulfide-exposed brass coupons were present as a source of copper. At the conclusion of the experiment, a sample of the supernatant solution was taken and analyzed for copper. Analyses were taken with and without filtration through a 0.2 micron membrane filter.

TABLE VII

Azole	NaOCl (ppm)	Admiralty Brass Corrosion Rate (mpy)	Low Carbon Steel Corrosion Rate (mpy)	Copper (ppm) Unfiltered	Copper (ppm) Filtered
none	0	1.01	5.4	0.354	0.103
3 ppm TTA	0	0.07	1.2	0.014	0.014
3 ppm CTTTM	0	0.06,0.05	1.0	0.005	0.004
none	2.0	2.09	5.2	0.417	0.059
3 ppm TTA	2.0	0.45	2.6	0.133	0.066
3 ppm CTTTM	2.0	0.13	1.7	0.086	0.039

Example 9

A sample was prepared from the methylene chloride-insoluble fraction of Example 1. This was compared to the sample from the methylene chloride-soluble fraction of Example 1 and the solution from Example 2. These samples, plus a mixture of the first two solids allows a comparison of isomeric fractions based on the position of the methyl group on the

benzene ring of 1-CITTA (see Example 1), as follows (note that tolyltriazole is approximately equimolar in the 4- and 5-methyl isomers, and the 6-methyl isomer is equivalent to the 5-methyl isomer):

TABLE IX

CTTTM Isomers, Methyl Position(s)	Source
(4)	Example 1. methylene chloride insoluble fraction
(5) + (6)	Example 1, methylene chloride soluble fraction
(4) + (5) + (6) (approx. 2:1:1)	Mixture of the above two samples
(4) + (5) + (6) (approx. 2:1:1)	Example 2

The method of Example 8 was followed, using clean admiralty brass coupons and electrodes. The following were the 18 hour averaged electrochemical corrosion rates:

TABLE X

Azole (3 ppm total)	Isomers	Source	NaOCl	Average Corrosion Rate (mpy)
CTTTM	(4)	Ex. 1	none	0.17
CTTTM	(5)+(6)	Ex. 1	none	0.11
CTTTM	(4)+(5)+(6)	Ex. 1	none	0.10
CTTTM	(4)+(5)+(6)	Ex. 2	none	0.07
TTA	(4)+(5=6)		none	0.23
CTTTM	(4)	Ex. 1	2 ppm	0.30
CTTTM	(5)+(6)	Ex. 1	2 ppm	0.21
CTTTM	(4)+(5)+(6)	Ex. 1	2 ppm	0.15
CTTTM	(4)+(5)+(6)	Ex. 2	2 ppm	0.13
TTA	(4)+(5=6)		2 ppm	0.39

Example 10

A synthetic sea water was formulated from deionized water plus 1010 ppm Ca as $CaCO_3$, 5226 ppm Mg (as $CaCO_3$), 18971 ppm Cl, 2660 ppm SO_4, 117 ppm M-alkalinity (as $CaCO_3$), 5 ppm azole (see below), and the pH was maintained at 7.8 with a blended mixture of air and carbon dioxide at 38°C.

Admiralty brass electrodes were exposed to this medium for 1 hour and then they were transferred to identical water with no azole present. Electrochemical corrosion rates were measured for 18 hours.

TABLE XI

Azole	Mean Electrochemical Corrosion Rate (mpy)
Benzotriazole	40
5-Butylbenzotriazole	15
Tolyltriazole	6
CTTTM	3.2

Example 11

Sodium hypochlorite (12.2%, 204.9g, 0.336 mol) was added over 90 minutes to a stirring slurry of benzotriazole (40g, 0.336 mol) in 30g of water at room temperature. Following the addition, the reaction mixture was held at 45-50°C for one hour. Upon cooling, a precipitate formed. A clear yellow solution of a chlorinated benzotriazole treatment material of the invention (CBTTM) was obtained after adjusting the pH to 11.

Example 12

Bromine (12.5 g, 0.078 mol) was added to a stirring slurry of TTA (10 g, 0.075 mol) in 66 g of water in a reactor protected from light, while maintaining the temperature at <25°C. After the addition, the reaction mixture was held at 35-40°C for one hour. Upon cooling, adjusting the pH to 11-12 did not produce a clear solution. The precipitate that formed upon standing was removed by filtration, the pH of the filtrate was adjusted to neutral, and the resulting precipitate filtered. This solid was characterized by LC/MS and ^{13}C and ^{1}H NMR and found to be composed of 90.5% bromo-tolyltriazole Br-TTA, 4.9% residual TTA, and 4.2% di-bromo-TTA.

Example 13

The method of Example 8 was followed, using samples from Examples 2, 11 and 12 at 1 to 4 ppm total actives. The following were the 18 hour averaged electrochemical corrosion rates:

TABLE XII

Azole	Conc. (ppm)	Source	NaOCl	Average Corrosion Rate (mpy)
CBTTM	1	Ex. 11	none	0.21
	2			0.09
	4			0.03
CTTTM	1	Ex. 2	none	0.14
	2			0.09
	4			0.08
BrTTA	1	Ex. 12	none	0.17
	2			0.11
	4			0.07

TABLE XII (cont'd)

Azole	Conc. (ppm)	Source	NaOCl	Average Corrosion Rate (mpy)
TTA	1		none	0.13
	2			0.14
	4			(n/a)
CBTTM	1	Ex. 11	2 ppm	0.55
	2			0.25
	4			0.09
CTTTM	1	Ex. 2	2 ppm	0.58
	2			0.24
	4			0.09
Br-TTA	1	Ex. 12	2 ppm	0.45
	2			0.16
	4			0.09
TTA	1		2 ppm	(n/a)
	2			0.45
	4			0.27

The above examples show that the ex situ prepared treatment materials of the present invention are effective corrosion inhibitors even in the presence of chlorine.

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CLAIMS

1. A method of inhibiting corrosion of metal surfaces contacted by an aqueous system characterized by adding to said aqueous system a treatment material obtainable by

i) dissolution of a benzotriazole in aqueous acetic acid, thereafter adding a halogenating agent, recovering a resulting solid and dissolving recovered solid in an alcohol or strong alkaline solution to form ex situ said treatment material, or by

ii) the addition of a halogenating agent to an aqueous slurry of a benzotriazole at alkaline pH to form, ex situ, said treatment material.

2. A method as claimed in claim 1, wherein said aqueous system is being treated with a halogen.

3. A method as claimed in claim 1 or 2, wherein sulfide ions are present in said aqueous system.

4. A method as claimed in any one of the preceding claims, wherein said benzotriazole is tolyltriazole.

5. A method as claimed in any one of the preceding claims, wherein said treatment material is added to said aqueous system at a concentration of greater than 0.5 parts per million.

6. A method as claimed in any one of the preceding claims, wherein said treatment material is added to said aqueous system at a concentration of from 0.5 parts per million to 10 parts per million.

7. A method as claimed in any one of the preceding claims, wherein a corrosion inhibiting layer is formed on said metal surfaces by said treatment material.

8. A method as claimed in any one of the preceding claims, wherein chlorine demand, in said

* C L M S *

aqueous system, to inhibit microbiological growth is reduced by said treatment material.

9. A method as claimed in any one of the preceding claims, wherein copper ion transport in said aqueous system is inhibited by said treatment material.

10. A corrosion inhibiting composition for metal surfaces contacted by an aqueous system comprising an aqueous solution of greater than 0.5 parts per million of a treatment material obtainable by

i) dissolution of a benzotriazole in aqueous acetic acid, thereafter adding a halogenating agent, recovering a resulting solid and dissolving recovered solid in an alcohol or strong alkaline solution to form ex situ said treatment material, or by

ii) the addition of a halogenating agent to an aqueous slurry of a benzotriazole at alkaline pH to form, ex situ, said treatment material.

11. A composition as claimed in claim 10, wherein said benzotriazole is tolyltriazole.

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(57) Abstract

The use of N-halo-azoles as corrosion inhibitors in aqueous systems is disclosed. N-halo-azoles such as 1-chlorotolyltriazole and 1-bromotolyetriazole prepared *ex situ* the aqueous system being treated were found to be more effective corrosion inhibitors than tolyltriazole.