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(54) Method of controlling corrosion and biological matter in copper and copper alloy cooling water systems.

(57) A method of controlling corrosion of copper and copper alloys in cooling water systems being treated with oxidizing biocides wherein a low level of triazole is maintained in the presence of the oxidizing biocide into a cooling water system.

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This invention relates generally to corrosion control and, more particularly, to a method of controlling corrosion of copper and copper alloys in cooling water systems, in the presence of oxidizing biocides.

Corrosion occurs when metals are oxidized to their respective soluble ions or insoluble salts. Metal loss due to solubilization can cause the structural integrity of the system to deteriorate over time. This can cause leakage between the water system and process streams. Also, the formation of insoluble salts in the corrosion process can produce a build-up of deposits which impede heat transfer and fluid flow.

Triazoles, such as tolyltriazole and benzotriazole are commonly used in cooling water systems as corrosion inhibitors for yellow metals, namely copper and copper alloys. Typically, triazoles are continuously fed into a recirculating cooling water system for inhibiting corrosion of copper and copper alloys. The purpose of this continuous feed is to maintain a low level of triazole first to form and then to maintain a protective triazole layer.

The continuous feed method, however, is too expensive to apply to once-through and high blowdown rate cooling water systems since large amounts of water are discharged from these systems in a short period of time. It would be both economically and environmentally unsound to continuously discharge such high volumes of triazole-loaded cooling water.

U.S. Patent No. 4,744,950 discloses the use of an alkyl benzotriazole to form a protective film on copper and copper alloys in cooling water systems by intermittently feeding the alkyl benzotriazole into once-through and high blowdown rate cooling water systems. While it is claimed in this patent that a corrosion inhibitive film is formed which will stand up to overfeeds of oxidizing biocides, it is also acknowledged that corrosion inhibitive films formed using benzotriazole and tolytriazole will be destroyed in the presence of the oxidizing biocides.

Oxidizing biocides are commonly added to cooling water systems. They are an inexpensive, yet effective means by which to control the formation of biological matter such as algae and bacteria. Chlorinating and brominating agents, which are the most widely used biocides in the cooling water treatment industry, are commonly fed intermittently. Unfortunately, as already noted, oxidizing biocides disrupt tolyltriazole and benzotriazole corrosion inhibitive films. More particularly, chlorine ($OClO^-$ HClO) and bromine ($OBrO^-$, HOBr) penetrate and attack prefilmed triazole surfaces, thereby destroying the effectiveness of such cuprous metal corrosion inhibitors. Tolyltriazole and benzotriazole protective films are especially susceptible to attack by oxidizing biocides.

Therefore, it would be highly desirable to develop a new method of controlling corrosion of copper and copper alloys in cooling water systems which is economically and environmentally acceptable and effective in the presence of oxidizing biocides.

SUMMARY OF THE INVENTION

This invention entails a method of controlling corrosion and biological matter, especially in once-through and high blowdown rate cooling water systems,by establishing a protective triazole film on copper and copper alloy surfaces and then intermittently introducing a combination of a low level of triazole and an oxidizing biocide. Additionally, the corrosion rates and copper concentrations in the system discharge should be continuously monitored to determine if the formation of subsequent protective triazole films on the copper or copper alloy is required, and sufficient triazole should then be added, as required.

The addition of the triazole concomitantly with the oxidizing biocide surprisingly and effectively overcomes the loss of triazole protection formerly encountered when oxidizing biocides were used alone. The present invention is thus economically appealing, environmentally acceptable, and effective in controlling not only corrosion, but biological matter, such as algae and bacteria, as well.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of the corrosion rate of copper versus the treatment cycle, as discussed in Example 1;
Figure 2 is a plot of the corrosion rate of cooper versus the treatment cycle, as discussed in Example 2;
Figure 3 is a plot of the corrosion rate of admiralty versus the treatment cycle, as discussed in Example 3; and
Figure 4 is a plot of the corrosion rate of admiralty versus the treatment cycle, as discussed in Example 4.

DETAILED DESCRIPTION OF THE INVENTION

In the practice of the present invention, a protective triazole film is established on a copper or copper alloy surface. Tolyltriazole, benzotriazole, or C_1 to C_{12} alkyl substituted benzotriazoles may be used as the cuprous metal corrosion inhibitor. Tolyltriazole is preferred. The triazole should be present in the system water at a level ranging from about 0.5 to 50 ppm by weight for a time period of at least about 2 hours, and preferably in the range of about 3 to 5 ppm for about 4 to 48 hours.

After the protective triazole film has formed on the copper or copper alloy surface, further triazole application is not necessary until the need for intermittent triazole/oxidizing biocide arises. This will be determined on a case-by-case basis by, e.g., monitoring the bacterial count in the cooling system water to determine when to begin the feed and how often to repeat it. Oxidizing biocides from the group comprising chlorine ($OCl0^-$, HCl0), bromine ($OBrO^-$, HOBr) NaOCl and NaOBr may be used at this stage in the treatment. In a preferred embodiment, NaOCl or NaOBr is used.

In accordance with the intermittent oxidizing biocide treatment step, a low level of triazole is introduced into the cooling water system along with the oxidizing biocide. Tolyltriazole, benzotriazole, C_1 to C_{12} alkyl substituted benzotriazoles, or other commercially available triazoles may be used as the cuprous metal corrosion inhibitor. Tolyltriazole is preferred. A low level of triazole, as prescribed below in Table 1, is added at the same time as the oxidizing biocide:

Table 1

Tolyltriazole Dosage During Oxidizing Biocide Treatments (ppm)			
Metallurgy	Broad Range	Preferred Range	Most Preferred Range
Copper	0.1-50	0.2-5	0.2 - 2.0
Admiralty (FRC* = 1 ppm)	0.1-50	0.2-5	0.5 - 2.0
Admiralty (FRC* = 10 ppm)	0.1-50	0.2-5	1.0 - 2.0
Al - bronze	0.1-50	0.2-5	1.0 - 2.0
Cu-Ni 90/10	0.1-50	0.2-5	1.0 - 2.0

*FRC - Free Residual Chlorine

The corrosion rates and copper concentrations in the discharge are then continuously monitored with a suitable device such as a corrater, until it is determined that the formation of another subsequent protective triazole film on the copper or copper alloy is required. When this occurs, sufficient triazole is added to raise the level to at least about 0.5 to 50 ppm for at least about 2 hours, and preferably to the range of about 3 to 5 ppm for about 4 to 48 hours.

EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

The examples explained below are bench-top experimental tests which simulate intermittent feed programs, with and without the simultaneous addition of tolyltriazole.

EXAMPLE 1

Copper electrodes were prefilmed by immersing them in a 5 ppm tolyltriazole solution for about 20 hours. The prefilmed electrodes were then subjected to 12 cycles of intermittent NaOBr treatment. Each cycle included a 2 hour immersion in a 1 ppm free residual chlorine (FRC) NaOBr solution followed by a 22 hour immersion in tap water, which was aerated at room temperature.

Corrosion rates were then obtained by taking linear polarization resistance measurements in the tap water. The polarization resistance data were converted to mpy (mils per year of metal loss) using equation (1), where Rp represents polarization resistance.

$$\text{mpy} = \frac{10.58}{\text{Rp (Kohm x cm}^2\text{)}} \qquad (1)$$

The corrosion rate at each of the 12 cycles of intermittent NaOBr treatment is plotted in FIGURE 1. The corrosion rates were unacceptable, as will be evident to those skilled in the art.

EXAMPLE 2

The same procedure as described in Example 1 was followed, except that each cycle also included the simultaneous addition of 0.5 ppm tolyltriazole with the 1 ppm (FRC) NaOBr solution.

FIGURE 2 illustrates that the corrosion rates decreased significantly when the tolyltriazole was added simultaneously with the NaOBr. A comparison of FIGURES 1 and 2 indicates that superior corrosion control is achieved when a low level of tolyltriazole is simultaneously added during intermittent NaOBr treatment.

EXAMPLE 3

Admiralty electrodes were prefilmed by immersing them in a 5 ppm tolytriazole or 5 ppm butylbenzotriazole solution for about 20 hours. The blank was a freshly polished admiralty electrode with 600 grit SiC which was etched with 10% H_2SO_4.

The prefilmed and blank electrodes were then subjected to 6 cycles of intermittent NaOBr treatment. Each cycle included a 2 hour immersion in a 10 ppm (FRC) NaOBr solution followed by a 22 hour immersion in tap water, which was aerated at room temperature.

The corrosion rates were determined as explained above in Example 1.

The corrosion rate at each of the 6 cycles of intermittent NaOBr treatment is plotted in FIGURE 3. The unacceptable corrosion rates will be evident to those skilled in the art.

EXAMPLE 4

The same procedure as described in Example 3 was followed, except that each cycle also included the simultaneous addition of either 0.2 ppm tolyltriazole, 0.5 ppm tolytriazole, 1.0 ppm tolytriazole, or 2.0 ppm tolytriazole with the 10 ppm (FRC) NaOBr solution.

FIGURE 4 shows that the corrosion rates decreased significantly when the tolyltriazole was added simultaneously with the NaOBr. A comparison of FIGURES 3 and 4 indicates that superior corrosion control is achieved when a low level of tolyltriazole is introduced along with the intermittent NaOBr treatment.

While the present invention is described above in connection with preferred or illustrative embodiments, these embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover all alternatives, modifications and equivalents included within its spirit and scope, as defined by the appended claims.

Claims

1. A method of controlling corrosion of copper and copper alloys in cooling water systems subjected to oxidizing biocide treatment comprising the steps of:
a. establishing a protective triazole film on the copper and copper alloy surfaces in the system; and then
b. intermittently introducing into the cooling water system a low level of triazole during oxidizing biocide treatment.

2. The method of claim 1 including the steps of:
c. continuously monitoring corrosion rates and copper concentrations to determine the state of the protective triazole film on the copper or copper alloy; and
d. reestablishing the protective triazole film, when determined necessary, before continuing step b..

3. The method of claim 1 in which the triazole may be chosen from the group consisting of tolyltriazole, benzotriazole, and C_1 to C_{12} alkyl substituted benzotriazoles.

4. The method of claim 3 in which the triazole is tolyltriazole.

5. The method of claim 1 in which the protective triazole film is formed by applying triazole at a level of about 0.5 to 50 ppm by weight for a time period of about at least about 2 hours.

6. The method of claim 5 in which the protective triazole film is formed by applying triazole at a level of about 3 to 5 ppm by weight for a time period of about 4-48 hours.

7. The method of claim 1 in which the level of triazole maintained during the oxidizing biocide treatment ranges from about 0.2 to about 5.0 ppm by weight.

8. The method of claim 7 in which the level of triazole maintained during the oxidizing biocide treatment ranges from about 0.2 to about 2 ppm by weight.

9. The method of claim 1 in which the oxidizing biocide is chosen from the group consisting of chlorine ($OClO^-$, $HClO$), bromine ($OBrO^-$, $HOBr$), $NaOCl$, and $NaOBr$.

10. A cooling water system in which a protective triazole film is maintained in order to control corrosion of copper and copper alloys and an oxidizing biocide is applied to control the formation of biological matter, the improvement comprising: maintaining a low level of triazole in the cooling water during the oxidizing biocide treatment.

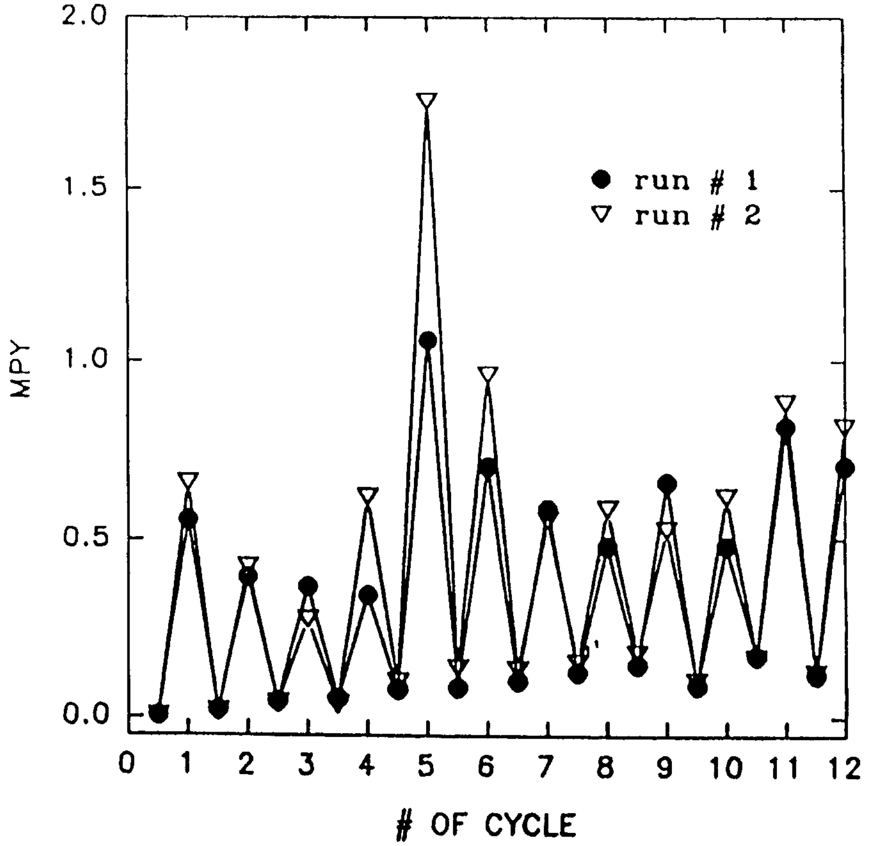
11. The system of claim 10 in which to the triazole may be chosen from the group consisting of tolyltriazole, benzotriazole, C_1 to C_{12} alkyl substituted benzotriazoles.

12. The system of claim 11 in which the triazole is tolyltriazole.

13. The system of claim 10 in which the low level of triazole ranges from about 0.2 to about 2.0 ppm by weight.

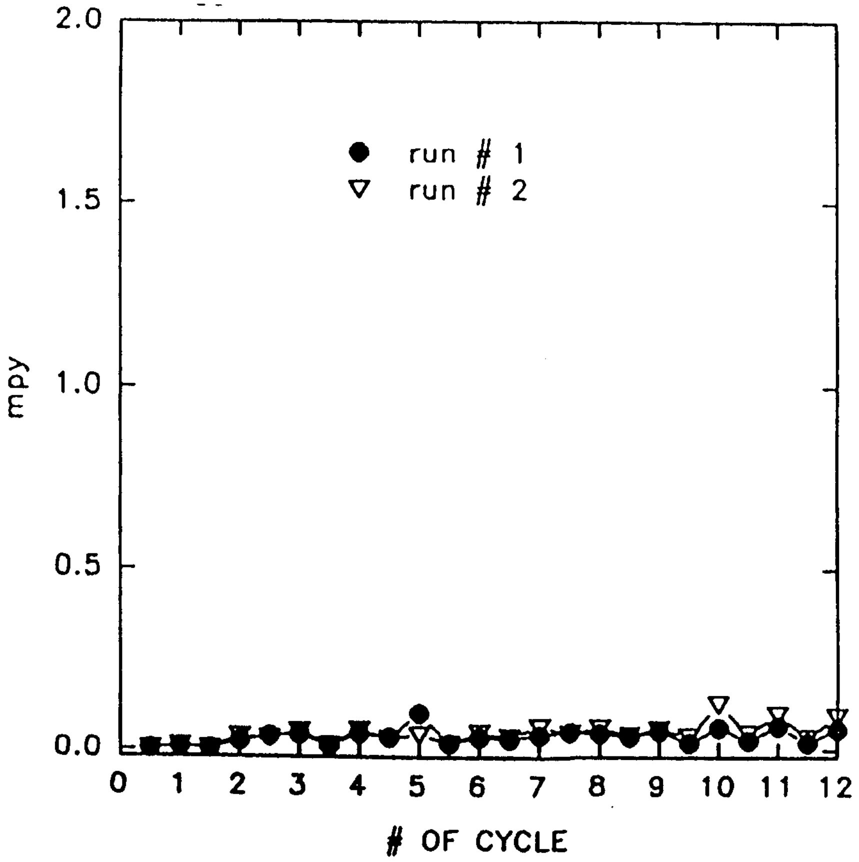
14. The method of claim 10 in which the oxidizing biocide is chosen from the group consisting of chlorine ($OClO^-$, $HClO^-$), Bromine ($OBrO^-$, $HOBr$), $NaOCl$ and $NaOBr$.

Figure 1. Corrosion Rates (mpy) of Tolyltriazole (TT) Prefilmed Copper Electrodes During 12 Cycles of Intermittent Treatment with 1ppm (Free Residual Chlorine) NaOBr.



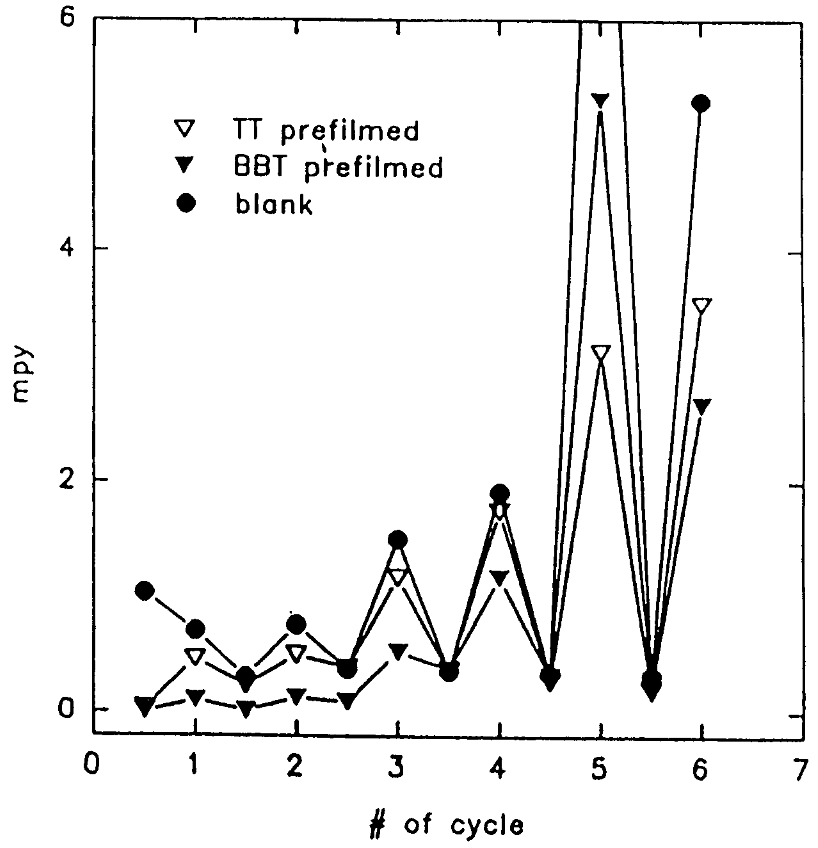
Each cycle of intermittent NaOBr treatment included a 2 hours immersion in a 1ppm (free residual chlorine) NaOBr solution followed by a 22 hours immersion in tap water

Figure 2. Corrosion Rates (mpy) of Tolyltriazole (TT) Prefilmed Copper Electrodes During 12 Cycles of Intermittent Treatment with 1ppm NaOBr + 0.5ppm Tolyltriazole (TT).



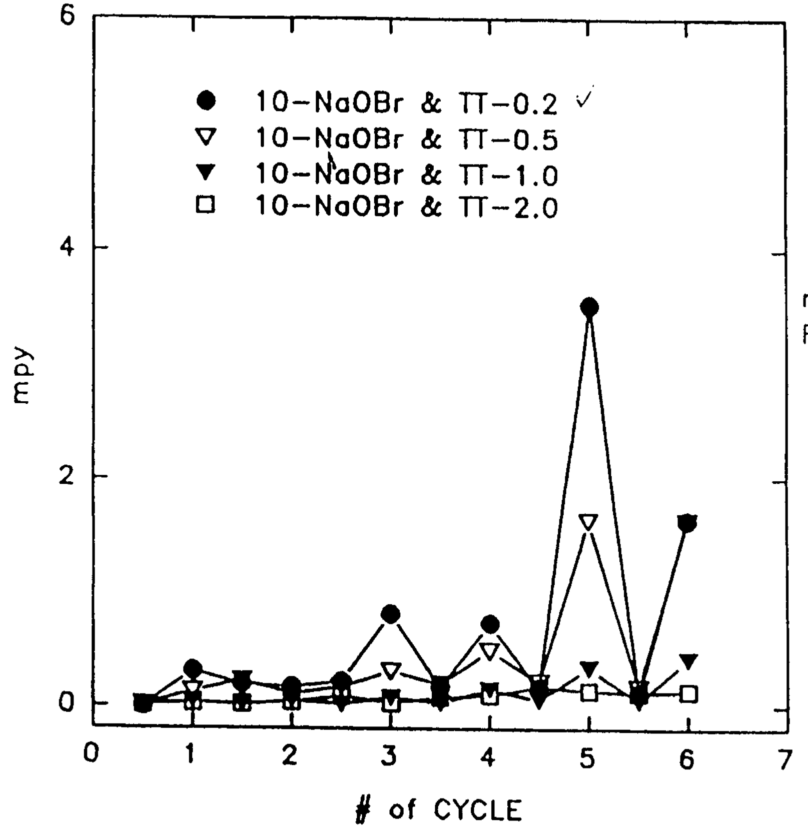
Each cycle of intermittent NaOBr treatment included a 2 hours immersion in a 1ppm (free residual chlorine) NaOBr + 0.5ppm TT solution followed by a 22 hours immersion in tap water

Figure 3. Corrosion Rates (mpy) of Blank (●), Tolyltriazole (TT) Prefilmed (▽), and Butylbenzotriazole (BBT) Prefilmed (▼) Admiralty Electrodes During 6 Cycles of Intermittent Treatment with 10ppm (Free Residual Chlorine) NaOBr.



Each cycle of intermittent NaOBr treatment included a 2 hours immersion in a 10ppm (free residual chlorine) NaOBr solution followed by a 22 hours immersion in tap water.

Figure 4. Corrosion Rates (mpy) of Tolyltriazole (TT) Prefilmed Admiralty Electrodes During 6 Cycles of Intermittent Treatment with 10ppm (Free Residual Chlorine) NaOBr and 0.2ppm TT (●), 0.5ppm TT (▽), 1.0ppm TT (▼), 2.0ppm TT (□).



mpy = mil per year
FRC = free residual chlorine

Each cycle of intermittent NaOBr treatment included a 2 hours immersion in 10ppm (free residual chlorine) NaOBr solutions dosed with 0.2ppm TT (●), 0.5ppm TT (▽), 1.0ppm TT (▼), 2.0ppm TT (□) followed by a 22 hours immersion in tap water.

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EUROPEAN SEARCH REPORT

Application Number
EP 93307345.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP - A - 0 478 247 (CALGON CORPORATION) * Page 2, lines 24-31; claims * --	1-14	C 23 F 11/14
X	EP - A - 0 462 809 (CALGON CORPORATION) * Page 2, lines 23-29; claims * --	1-14	
A	EP - A - 0 479 572 (BETZ EUROPE) * Totality * --	1-14	
A	GB - A - 933 979 (ICI) * Totality * ----	1-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 23 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	30-12-1993	SEIRAFI

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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