United States Patent Office

2,941,953

Patented June 21, 1960

2,941,953

METHOD OF INHIBITING CORROSION OF COPPER AND CUPROUS ALLOYS IN CONTACT WITH WATER

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No Drawing. Filed July 27, 1956, Ser. No. 600,369

10 Claims. (Cl. 252—389)

This invention relates in general to the over-all inhibition of corrosion in systems where copper or its alloys are present together with more anodic metals such as iron, zinc, and aluminum or their alloys.

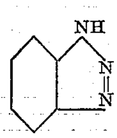
It relates in particular to (*a*) a method of rapidly reducing the galvanic attack of steel coupled to cuprous metals, (*b*) the reduction or elimination of the dissolving of copper by water in passing through portions of a water system which are made from cuprous materials, (*c*) the reduction or elimination of the deleterious action of dissolved copper on the corrosion of more anodic metals such as steel, zinc and aluminum in a water system and (*d*) the reduction or elimination of the deleterious action of mercury salts in the corrosion of copper.

In U.S. Patent 2,337,856 of which I am co-patentee, the method of preventing corrosion of ferrous metals by the addition of small amounts of molecularly dehydrated phosphates to water in contact with these metals is fully outlined. These methods have been extensively practiced for many years with satisfactory results.

In U.S. Patent 2,742,369 a method of inhibiting corrosion in water systems discovered by me is described in detail. In these water-containing systems both cuprous and ferrous metals are present and I found that certain well-known copper corrosion inhibitors and the molecularly dehydrated phosphates were not compatible unless a zinc compound is added to the mixture. The copper corrosion inhibitors used in this particular patented process are the thiols of compounds selected from the group consisting of thiazoles, oxazoles, and imidazoles.

I have discovered that the heterocyclic compounds known as 1,2,3-triazoles having the general configuration

particularly the compound benzotriazole (sometimes known as 1,2,3-benzotriazole), having the structural formula



possess certain features which make them extremely useful in controlling corrosion of copper, both in the presence of the molecularly dehydrated phosphates or in their absence. These compounds are of particular advantage in treating recirculating water, where addition of certain chlorinated compounds is required to control algae and other objectionable growths.

Although the direct addition of chlorine per se will destroy any protective film of benzotriazole on copper, if a chloramine is employed as a source of chlorine, the benzotriazole is not affected, but on the contrary, chloramine will oxidize mercaptobenzothiazole or other thiazoles rendering them completely ineffective for protecting copper or copper alloys. Chloramine-T is a well known source of chlorine having the formula

$$CH_3C_6H_4SO_2NClNa$$

and it, as well as other chloramines, are used for algae and slime control.

I have also found that 1,2,3-benzotriazole is quite effective in preventing the deposition of mercury and mercury salts on both copper and aluminum and in certain cooling water installations where mercury salts tend to contaminate the water, this can be quite important, particularly where mercury is to be recovered from the cooling water effluent for subsequent conversion to mercury itself.

To determine the effect of benzotriazole as a copper corrosion inhibitor, I prepared a number of copper strips 1½ inch x 1½ inch which were immersed in beakers of Pittsburgh city tap water adjusted to pH 5.5 with hydrochloric acid. These were agitated for five days at 35 degrees centigrade. In Table 1 is shown the influence of benzotriazole concentrations on the weight loss of the copper and on the amounts of copper picked up by the water. In this series of tests 25 parts per million of Calgon brand sodium phosphate glass, a commonly used molecularly dehydrated phosphate, were present in solution.

Table 1

Benzotriazole (Parts per million)	Copper weight loss in milligrams per square decimeter per day	Copper pickup by water in parts per million
0	1.3	1.66
0.1	0.28	0.23
0.2	0.14	0.20
0.5	0.07	0.04
1	0	0.01
2	0	0.01

In Table 2 below I have reported data from tests using 2 parts per million of benzotriazole at solution pH values ranging from 2 through 7. Here again I added 25 parts per million of Calgon brand sodium phosphate glass which has a molar ratio of sodium oxide to phosphorus pentoxide of 1.1:1 as well as 2 parts per million of the benzotriazole.

Table 2

pH Values	Weight loss of copper milligrams per square decimeter per day	Pickup of copper in in water in parts per million
2	862	------
3	79	90
4	0.21	0.56
5	0.14	0.17
6	0.07	0.04
7	0.14	$<$0.01

The foregoing data illustrates the effect of pH on the performance of the benzotriazole, the compound being most effective in the range of 5–7.

To illustrate the effect of chlorine and chloramine-T on the protective effect of benzotriazole on copper, I ran a series of tests similar in all respects as to time and temperature, at a pH value of 5.5, adding chlorine in the form of sodium hypochlorite (in an amount equivalent to 2 parts per million of chlorine), one-half hour after starting the beaker tests, and chloramine-T (in an amount equivalent to 2 parts per million of chlorine) one-half hour after starting the tests. This data is summarized below in Table 3.

Table 3

Inhibitor Solution	Weight loss in mg./dm.^{2}/day	Copper pickup in parts per million
1. 2 p.p.m. benzotriazole	0.0	0.02
2. 1.+2 p.p.m. chlorine	0.77	0.57
3. 1.+ chloramine-T	0.06	<0.01

With regard to the inhibition of the deleterious action of dissolved mercury on copper, I prepared a series of copper strips 1½ inch. These were immersed in Pittsburgh city tap water at a pH of 5.5 and a concentration of 2 parts per million of benzotriazole and 25 parts per million of phosphate in the form of a sodium-zinc phosphate glass having the molar composition

$$1.12Na_2O.0.29ZnO.P_2O_5$$

was maintained. In this experiment (identified as Series A below) the concentration of mercury (added in the form of a water soluble mercury slat, in this instance, mercuric chloride) varied from 0 to 0.5 part per million and the weight loss of copper, indicating the deleterious action of mercury on the copper strips, as well as the copper pickup in parts per million of copper found in the water, are indicated, the comparison being in each instance between water to which the benzotriazole and phosphate were added on the one hand, and the same water containing phosphate alone.

A similar experiment (Series B below) was conducted using Calgon brand phosphate instead of the zinc-containing phosphate, and data from both tests is shown below.

Table 4

	Mercury in Solution Parts per million	Wt. loss of copper in mg./dm.^{2}/day	Copper pickup in parts per million
Series A	0	0.0	<0.01
	0.1	0.14	<0.01
	0.2	0.0	<0.05
	0.5	0.07	0.10
Series B	0	0.28	0.04
	0.1	0.07	0.04
	0.2	0.07	0.05
	0.5	0.21	0.06

Weight losses ranged from 2.5–5.0 mg./dm.^{2}/day in the case of water to which no benzotriazole was added and the copper pickup ranged from 0.74 to 2.47 parts per million. In making these comparisons the phosphates in a 25 parts per million concentration were added to the water.

Prevention of the deposition of copper on aluminum which has heretofore been indicated as one of the benefits conferred by using benzotriazole is shown in the table below where Pittsburgh city tap water containing 0.5 part per million of copper (added in the form of cupric sulfate), the water being maintained at a pH of 5.5, was prepared. Strips of 3004–H14 aluminum were immersed with agition at 35 degrees centigrade for five days in this water, the benzotriazole concentration in parts per million ranging from 0 to 10. The weight loss in milligrams per square decimeter per day of aluminum is shown in Table 5.

Table 5

Concentration of Benzotriazole in parts per million	Weight loss of aluminum in mg./dm.^{2}/day
0	12.2
0.5	0.99
1.0	0.85
2.0	0.57
5.0	0.92
10.0	1.30

The effectiveness of benzotriazole for inhibiting the

galvanic attack of steel coupled to copper when the benzotriazole is used in conjunction with molecularly dehydrated phosphates was established by certain procedures hereinafter to be disclosed.

To illustrate the effectiveness of benzotriazole in the inhibition of the galvanic attack of steel coupled to copper, a test procedure described in Industrial and Engineering Chemistry, vol. 44, page 1781 (1952), was followed. The salient features of this method are as follows:

The test strips were 1½ x 1½-inch metal plates. The steel test panels were cold-rolled low carbon strips. Pittsburgh tap water adjusted to the desired pH with HCl served as the test medium. The analysis of the water used in the tests is shown in Table 1. Agitation was provided by lateral movement of the plates back and forth over a distance of two inches through one liter portions of water at a rate of 32 cyles/minute. The tests were conducted at 35 C±0.2. The metal plates were cleaned to a zero waterbreak in an alkaline cleaner prior to use. Copper test panels were pickled by a 10 percent nitric acid dip after the alkaline cleaning. At the conclusion of the tests where weight loss data were collected, the steel panels were pickled in 36 percent hydrochloric acid inhibited with 5 percent stannous chloride and 2 percent antimony oxide; the copper panels were pickled in 5 percent sulfuric acid. Pickling blanks were determined and the observed weight losses corrected accordingly.

Pittsburgh tap water was used as the corrosive medium with the pH adjusted to 5.5 with hydrochloric acid. The following data appearing in Table 6 was obtained:

Table 6

A. CONTROL (UNTREATED TAP WATER pH 5.5)

Time in Hours	Current in Milliamperes
0	0
½	1.57
1	1.62
2	1.63
4	1.67
5	1.71

B. TAP WATER +5 P.P.M. BENZOTRIAZOLE (pH 5.5)

Time in Hours	Current in Milliamperes
0	0
½	0.32
1	0.29
2	0.33
4	0.33
5	0.33

C. TAP WATER +50 P.P.M. CALGON BRAND PHOSPHATE (pH 5.5)

Time in Hours	Current in Milliamperes
0	0
½	0.84
1	0.67
2	0.44
4	0.26
5	0.22

D. TAP WATER +50 P.P.M. CALGON +5 P.P.M. BENZOTRIAZOLE (pH 5.5)

Time in Hours	Current in Milliamperes
0	0
½	0.13
1	0.073
2	0.058
4	0.048
5	0.045

The foregoing data forcefully demonstrates that there is a synergistic coaction between the polyphosphate (molecularly dehydrated phosphate) and the benzotriazole to inhibit galvanic action with extreme rapidity. At the end of 5 hours, for example, the current in the water treated with phosphate-benzotriazole is only 0.045 milliampere as compared with 0.33 in the water treated with benzotriazole alone, 0.22 in the water treated with phosphate alone and 1.71 in the control. Observation of the data shown in B and C above would not indicate in any way the extremely low values which might be obtained when B and C are combined in D.

I have found that benzotriazole is soluble in water under the conditions of use which I comtemplate to the extent of about 1.4%. Although any amount of benzotriazole up to the limit of its solubility can be used for my purposes, surprisingly small amounts are quite effective, as little as 0.05 part per million showing an inhibitory effect. Practically, I prefer to use from 0.5 part per million to about 5 parts per million for the various corrosion inhibiting uses which I have herein outlined.

Although I have used specific concentrations of certain polyphosphates in some of the examples set forth herein, the range of concentrations and the particular phosphates which may be used will generally follow the applicable part of the teachings outlined in U.S. Patent 2,742,369 hereinbefore mentioned, a detailed discussion appearing in columns 5 and 6 thereof U.S. Patent 2,742,369 contains, as a part of its disclosure, the entire disclosure of U.S. Patent 2,337,856, hereinbefore mentioned. These two patents abundantly establish that very small amounts of molecularly dehydrated phosphates, indeed as little as 0.1 p.p.m., are sufficient to form a protective film on metals. The present invention deals with the efficacy of benzotriazole as a copper corrosion inhibitor, used in some applications with polyphosphates and in others demonstrating its effectiveness without the addition of the phosphates. As a practical matter where iron or steel are present in a water system, I must inhibit their corrosion, preferably by using one of the above mentioned phosphates in the manner of U.S. Patent 2,337,856 and U.S. Patent 2,742,369, if the benzotriazole is to function effectively as a copper inhibitor.

Although I have demonstrated the unusual effects of the 1,2,3-triazoles with 1,2,3-benzotriazole, I may use any water-soluble 1,2,3-triazoles such as 1,2,3-triazole itself or a substituted 1,2,3-triazole where the substitution takes place in either the 4 or 5 position (or both) of the triazole ring as shown here by the structural formula

I claim:

1. The method of retarding the corrosion of copper and cuprous alloys in contact with water under conditions where said water is also in contact with ferrous metals which comprises adding to the water from about 0.05 to about 5.0 parts of a water-soluble 1,2,3-triazole per million parts of water and a water-soluble alkali-metal polyphosphate in an amount sufficient to form a protective film, but not exceeding 50 parts per million parts of water.

2. The method as described in claim 1 where the 1,2,3-triazole is 1,2,3-benzotriazole, and the alkali-metal polyphosphate has a molar ratio of alkali-metal oxide to phosphorous pentoxide of from about 0.9 to 1 to about 2 to 1.

3. A method of protecting copper and copper alloys in contact with aqueous media against corrosion in the presence of chloramine which comprises maintaining in the aqueous media a concentration of from about 0.05 part to about 5.0 parts of a water-soluble 1,2,3-triazole.

4. The method as described in claim 3 where the 1,2,3-triazole is 1,2,3-benzotriazole.

5. A method of protecting copper and cuprous metals in a system for transporting aqueous media against corrosion in the presence of ferrous metals where chloramine is also present in the system, which comprises maintaining in the system from about 0.05 part to about 5.0 parts per million of a 1,2,3-triazole and a water-soluble alkali-metal polyphosphate the latter being present in a concentration not exceeding 50 parts per million.

6. The method as described in claim 5 where the 1,2,3-triazole is 1,2,3-benzotriazole.

7. A method of reducing the corrosion of copper by dissolved mercury salts in a water system which comprises maintaining in said system from about 0.05 part to about 5.0 parts of a water soluble 1,2,3-triazole per million parts of water.

8. The method as described in claim 7 where the triazole is 1,2,3-benzotriazole in an amount which is from about 0.5 part to about 5.0 parts per million parts of water in said system.

9. A method of inhibiting the deleterious action of dissolved copper in aqueous media on ferrous metals and aluminum and its alloys by maintaining in solution in said aqueous media from about 0.05 part to about 5.0 parts of a 1,2,3-triazole per million parts of water.

10. The method as described in claim 9 where the 1,2,3-triazole is 1,2,3-benzotriazole.

References Cited in the file of this patent

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