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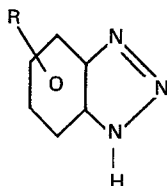
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Corrosion inhibition.

(57)

The present invention provides a method of inhibiting the corrosion of non-ferrous metals in contact with an aqueous system, which comprises adding to the aqueous system a sufficient amount for the purpose of a water soluble compound having the formula:



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wherein R is a hydrocarbon group containing from 3 to about 8 carbon atoms. There may also be present a corrosion inhibitor composition for any ferrous metal present in contact with the aqueous composition.

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DESCRIPTION
CORROSION INHIBITION

The present invention relates to the inhibition of corrosion of metal parts in contact with an aqueous system and compositions therefor.

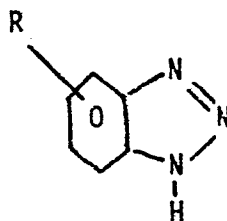
5 The use of benzotriazole as corrosion or tarnish or staining inhibitors for copper and copper alloys is well known. In addition to the use of this compound for aesthetic purposes, it together with tolyltriazole have found widespread use in the water treatment industry and in particular in the cooling water industry.

10 As indicated in the BETZ HANDBOOK OF INDUSTRIAL WATER CONDITIONING, 1980, Betz Laboratories, Inc., Trevose, PA, pp 202-231, corrosion and deposit control treatments are always necessary to ensure the economical and continued operations of cooling water systems, whether the systems be open, recirculating or closed. On pages 207 to 209, many individual corrosion
15 inhibitors, as well as combination systems, are discussed including the well known chromate; phosphate, zinc inhibitors, Dianodic[®] and Dianodic II[®] treatments. However, as the last paragraph on page 208 of the Handbook indicates, if copper or copper alloys are present in the structural parts of the cooling water system, and
20 these parts are contacted by the cooling water, copper corrosion inhibitors must necessarily be included. U.S. Patents 4,303,568; 3,837,803; and 3,950,576 provide illustrations as to the type of corrosion inhibitors commonly used in conjunction with basic ferrous metal inhibitors and/or compositions.

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As established by the above references, mercaptobenzothiazole as well as certain other thiazoles, and benzotriazole and derivatives thereof, primarily tolyltriazole, have found widespread use. As is apparent, the water treatment industry is continually evaluating additional compounds in an attempt to discover more effective, more economical, more easily applied treatments, and a significant part of this effort is the development of copper inhibitors. While these inhibitors are in fact significant in the water treatment industry, they are also important in general use for inhibiting the staining and/or tarnishing of items such as decorative pieces, pots, structural parts of lamps, etc. which are fabricated from copper or copper containing alloys. As is well known, items such as the decorative pieces, when exposed to even a slightly humid atmosphere, tarnish or stain. Accordingly, that industry is also looking for ways to avoid the problem.

It has now been found that the application of a compound comprising the formula



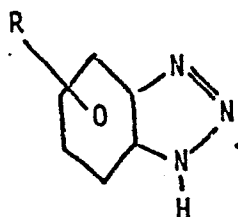
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wherein R is a linear or branched, substituted or unsubstituted, hydrocarbon group containing 3 to about 8, and preferably about 4 to about 6, carbon atoms to a non-ferrous metal surface, and in particular copper or copper containing surfaces, will promote corrosion

protection, as well as tarnish and stain resistance. Of particular interest in this regard is butylbenzotriazole.

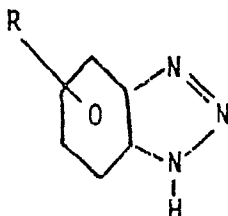
The present invention provides a method of inhibiting the corrosion of non-ferrous metals in contact with an aqueous system, which comprises adding to the aqueous system a sufficient amount for the purpose of a water soluble compound having the formula:



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wherein R is a hydrocarbon group containing from 3 to about 8 carbon atoms.

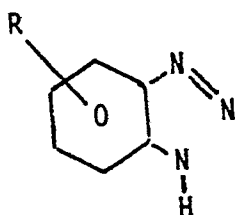
The present invention further provides a method of inhibiting the corrosion of metal parts in contact with an aqueous system, the metal parts being composed of both ferrous and non-ferrous metals, which comprises adding to the aqueous system a sufficient amount for the purpose of a corrosion inhibitor composition for the ferrous metal, and also adding to the aqueous system an effective amount for the purpose of a corrosion inhibitor for the non-ferrous metal, the corrosion inhibitor for the non-ferrous metal comprising a compound represented by the formula:



I

wherein R is a hydrocarbon group containing from 3 to about 8 carbon atoms.

The present invention still further provides a composition effective for inhibiting the corrosion of metallic parts or systems composed of both ferrous and non-ferrous metals in contact with water, which composition comprises a corrosion inhibiting composition for the ferrous metals, and a corrosion inhibitor for the non-ferrous metals, comprising a compound of the formula:



I

wherein R is a hydrocarbon group containing about 3 to about 8 carbon atoms.

As indicated earlier, extensive use of the subject compounds is projected in the water treatment, and in particular the cooling water, industry for the protection of the structural parts of cooling water systems, where such parts are fabricated from copper and/or copper alloys and the water contained in such is aggressive thereto.

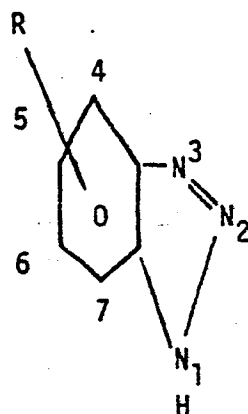
The compounds used in the present invention may be added to the system or applied to the copper surfaces either alone or in conjunction with other treatment agents.

If the benzotriazole compounds are used for the treatment of cooling water systems, they may be added individually as an aqueous solution, or may be combined with the well known corrosion inhibiting compositions designed to protect the ferrous

structures of the cooling water system. For example, these compounds may be formulated in the proper amount (sufficient that when the total product is added to the cooling water, there is a sufficient amount of the present compound(s) to perform the function and provide the protection) with such well known treatments. Such treatments include: the Dianodic II treatments which are directed to the use of an acrylic acid hydroxyalkylacrylate/orthophosphate to provide corrosion protection. (See U.S. Patent 4,303,568); the zinc chromate and/or phosphate-based treatments; the phosphonate containing treatments; the poly and orthophosphate-polymer treatments, e.g., those containing polyacrylic acids polymers, sulfonated styrene-maleic anhydride polymers, acrylic acid/-acrylamide copolymers, the acrylamidomethylpropane sulfonate-based polymers (See Betz U.S. Patent 3,898,037) and the like. For more definitive explanations, note the BETZ Handbook at the sections cited earlier.

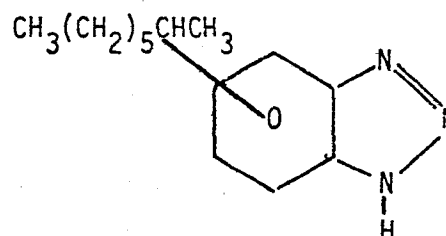
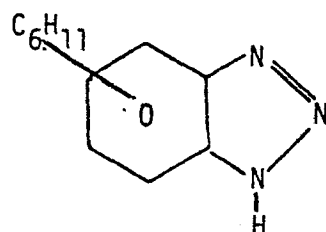
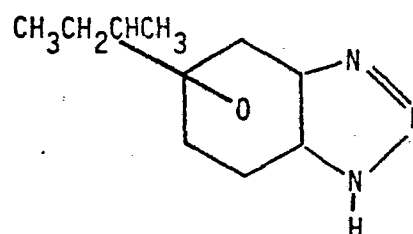
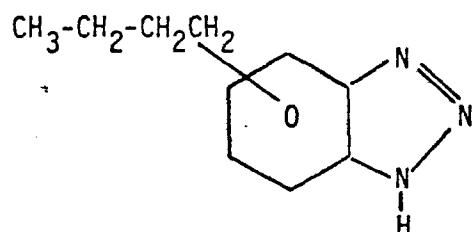
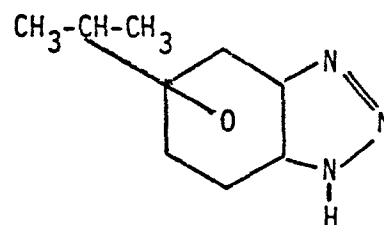
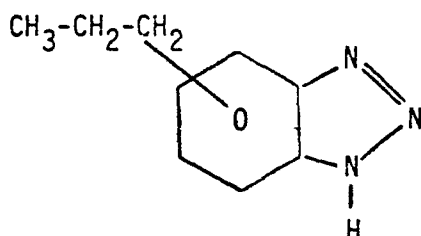
The compounds used in the present invention would appear to be utilizable with any ferrous metal protective system whether it be by the passivation technique or the barrier protection technique.

5 As earlier indicated, the compounds have the formula



The atoms comprising the structure are numbered in order to lend greater specificity to the particular compounds which have been found to be unexpectedly superior, i.e., the 4 or 5 butyl-
10 benzotriazoles.

While the R group has earlier been described as having C_3 to C_8 groups, the compounds are more specifically represented as follows:



and the like, where the 4 or 5 position is preferred. It is also possible to substitute additional function groups both on the hydrocarbon group and in the ring at the 6 and/or 7 positions. Such groups as alkyl, haloalkyl, halo, amino, alkoxy, and carboxamido groups might be useful.

The compounds used in the present invention should be used, obviously, in an amount sufficient for the purpose, but more specifically can be added to the aqueous system in an amount of from about 0.1 to 200 (preferably 0.1 to 100) parts per million of water in the aqueous system.

5 Figures 1 to 4 are described in the Results.

Specific Examples

In order to establish the efficacy of the present compounds over the known compounds, the following experiments and studies were conducted.

10 Description of Experiments

I. Electrochemical Methods

Since corrosion is a primarily electrochemical phenomenon it is possible to use electrochemical techniques to study its mechanisms and activity. The experiments are performed by
15 placing an electrode (the working electrode) of the metal alloy of interest in a suitable medium (a conductive liquid) along with a suitable reference electrode (results reported herein are referenced to the Saturated Calomel Electrode [SCE]), and by means of various types of electronic devices
20 (generally referred to as potentiostats) controlling either the electrostatic potential (voltage) or current, and simultaneously measuring the resultant current or potential. The first major technique is potentiostatic polarization or "Tafel" polarization.

A. Tafel Polarization

5 Since during the corrosion process electrons are transferred from the corroding metal to the environment, the rate of electron flow, or current, is directly related to the rate of corrosion using Faraday's law:

$$N = i/nF$$

where N = number of moles undergoing reaction per unit time (i.e., the corrosion rate)

10 n = number of electrons per atom required (or equivalents per mole)

i = electric current (charge per unit time)

F = Faraday (coulombs per equivalent)

The rate of corrosion, expressed as an average penetration rate, is given by:

15
$$C. R. = (N \times At.Wt)/(d \times A)$$

where C. R. = corrosion rate in suitable units

N = previously defined

At. Wt. = mass per mole of the alloy

d = density of alloy

A = surface area of test specimen

5 The polarization technique involves perturbing the system electrically well away from the corrosion potential so as to effectively suppress one of the current components, thereby allowing a determination of the other component. Thus, by applying a positive potential the cathodic reaction is suppressed, allowing measurement of anodic currents. Applying negative potentials accomplishes the opposite process. By 10 suitable mathematical treatment of the data the corrosion current can be determined. Furthermore, detailed analysis of the current-potential relationships reveals mechanistic details. For example, comparison of the shapes of the anodic and cathodic curves with and without inhibitors can reveal the 15 principal mode of inhibition. In the attached data, showing such tests, it can be seen that the cathodic reduction of oxygen is most significantly affected by the inhibitor molecules, and that butylbenzotriazole exhibits the greatest degree of cathodic reaction retardation.

20 B. Linear Polarization

One drawback of Tafel Polarization is that the passage of significant currents through the sample and solution causes permanent changes in the system. Repeated measurements are precluded as the results cannot be 25 related to a known state of the system. Typical changes are solution pH, solution composition, and surface structure of the test specimen. Linear polarization

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solves this problem by using very small perturbation currents so that any changes in the state of the system remain negligible. The non-linearity of system response, however, creates complications with respect to the treatment of the data. Various algorithms are available for such treatment and are employed in computer programs used for this purpose.

A measurement of the instantaneous slope of the current-potential curve at the corrosion potential has units of ohms, or electrical resistance units. For samples of the same composition and surface area this polarization resistance value is inversely proportional to the corrosion rate. Thus, the greater the resistance the lower the corrosion rate.

This technique has the advantage of allowing repeated measurements on the same system, but sacrifices the mechanistic details obtainable by Tafel polarization.

The attached linear polarization data shows a significant and completely unexpected improvement for butylbenzotriazole over tolyltriazole and benzotriazole.

II. Performance Studies

Apart from the purely electrochemical aspects of corrosion and its inhibition there arises the question of the effect of external conditions. Of primary interest to open recirculating cooling system treatment technology are the effects of water chemistry, flowrate, and temperature.

Accordingly, test equipment is designed to simulate a wide range of potential operating conditions, and additionally, provision is made for the insertion of test specimens. These specimens may then be studied visually, electrochemically or gravimetrically as is desired. The two principal tests employed for the current studies are spinners and recirculators (RTU's).

A. Spinner Tests

A 17 liter tank is provided in which the test water is placed. Provision is made for maintaining constant temperature in the range of room temperature to 100°C (212°F); additionally, air saturation of the test solution is maintained. Cleaned, weighed metal samples in the form of coupons (metal strips of varying dimension based on the alloy) are affixed to the periphery of a mandrel. The coupons are then immersed in the test solution and rotated around a vertical axis at constant speed. The rim velocity is maintained at 48.77cm/sec. (1.6 feet/second).

Following exposure for a predetermined period (typically 3-7 days) the test coupons are removed and inspected, cleaned, dried and weighed. From these data corrosion rates are calculated.

B. Recirculating Test Unit (RTU)

This test procedure is conceptually similar to the spinner test, but rather than rotate the test specimens in a stationary liquid the test specimens are stationary and

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the liquid is circulated at a fixed but adjustable velocity. Additionally, means are provided to replenish the test solution at a fixed, adjustable rate and to regulate pH to within ± 0.2 pH units. Provision is made for conducting electrochemical corrosion measurements in the flowing stream. Furthermore, a test specimen can be inserted into the flowing stream to which a constant heat flux may be applied via an internal resistance heating device in order to regulate the surface temperature of the specimen.

III. Results of Tests

A. Tafel Polarizations

Copper electrodes were placed in the test vessel containing 0.1N sodium sulfate adjusted to pH 7.0 and are air saturated. A control had no treatment, and subsequent tests incorporated one part-per-million (ppm) of either benzotriazole (BZT), tolyltriazole (TTA), or butylbenzotriazole (b-BZT).

A potential sweep of 10 millivolts per minute (mV/min) from -550 mV to + 250 mV (versus a saturated calomel reference electrode) was applied. A plot of log current vs. potential is shown in Figure 1. The salient feature is the decrease in cathodic current at a given potential as one examines the series: no treatment (1); tolyltriazole (2); b-BZT (3 and 4). Abatement of the anodic current is the same for TTA and b-BZT, and is several orders of magnitude below that of the untreated control.

These results show that both TTA and b-BZT act as anodic and cathodic inhibitors, that the degree of anodic inhibition is essentially the same for both, and that b-BZT is a superior cathodic inhibitor to TTA by a factor of 10-100 fold.

Figure 2 is a cathodic-only sweep which further illustrates the increase in cathodic inhibition of b-BZT over that of TTA. The decrease in cathodic current at equal potential is tenfold for b-BZT versus TTA.

B. Linear Polarization/Recirculator

1. Prefilmed Tests

Cleaned electrodes were exposed to 10 ppm (pH = 7) solutions of TTA, b-BZT, and BZT for 24 hours. The electrodes were placed in holders in the test rack of an RTU. The test conditions were Ca (as CaCO_3) 600 ppm, Mg (as CaCO_3) 300 ppm, Cl^- 1000 ppm, pH = 7, 120°F.

Linear Polarization vs. time is as follows:

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	<u>Elapsed Time</u> (hrs)	<u>Polarization Resistance</u> (ohms)			
		<u>Control</u>	<u>TTA</u>	<u>BZT</u>	<u>b-BZT</u>
5	3	186	223	360	3030
	4	308	348	468	9804
	22	533	620	195	6667
	26.5	526	556	342	743
	28	563	602	377	1099
	46	442	526	402	381

10 The data show that the new material (rightmost column) is 10 to 30 times as inhibitive as TTA or BZT. Fluctuations in the data are due to slight oscillations of the pH over time.

15 In another test using the same water conditions but prefilming at 100 ppm the results are as follows:

	<u>Elapsed Time</u> (hrs)	<u>Polarization Resistance</u> (ohms)		
		<u>Control</u>	<u>TTA</u>	<u>b-BZT</u>
20	2	580	13,000	601,500
	22.5	2,900	60,100	455,000
	28.5	8,250	91,950	305,350
	50.0	14,200	178,600	434,800
	122.5	16,000	69,600	298,500
	189.5	21,300	55,600	232,600
25	215.5	16,400	42,100	219,200
	315.5	10,000	27,400	110,400

5

The results indicate an inhibitive effect for the new material on the average of five times that of TTA. Of greater significance is the failure of the TTA film after 190 hours whereas the film formed by b-BZT was still more inhibitive than the average TTA film for an additional 150 hours at least as seen in Figure 3.

10

In another run the water conditions were as follows: 600 ppm Ca (as CaCO_3), 300 ppm Mg (as CaCO_3), 440 ppm Cl^- . The test electrodes were prefilmed at 100 ppm. Results were as follows:

	<u>Elapsed Time</u> (hrs)	<u>Polarization Resistance</u> (ohms)			
		<u>Control</u>	<u>TTA</u>	<u>BZT</u>	<u>b-BZT</u>
15	2	816	9,592	12,346	131,148
	21	20,513	20,725	72,727	210,526
	48	21,740	19,048	48,780	248,440
	117	15,504	15,873	16,529	110,497
	171	16,000	11,696	23,256	231,231
	214	14,286	8,811	8,811	57,971
20	264	7,512	7,326	6,400	16,260

Figure 4 is a plot of resistance vs. time. Again the results indicate a significant increase in the inhibitory power and film longevity for b-BZT.

2. On-line Filming Test

Another test, designed to mimic real field conditions, was run using the following water conditions: Ca 780 ppm (as CaCO_3), Mg 280 ppm (as CaCO_3), Cl^- 12 ppm, SO_4^{2-} 1000 ppm, pH = 7.3, 120°F. This time prefilming was at 10 ppm, but the filming was done under dynamic conditions in the flowing system for four hours rather than in a static jar for 24 hours as was done in the previous tests. This is a realistic test of an actual field use since the on-line pretreatment is the only mode possible in a real system.

	<u>Elapsed Time</u> (hrs)	<u>Polarization Resistance</u> (ohms)		
		<u>Control</u>	<u>b-BZT</u>	<u>b-BZT^a</u>
15	2	1,231	366,972	48,193
	24	19,753	185,803	183,908
	45	56,338	119,403	164,948
	117	75,472	120,301	--- ^b
20	283	61,766	105,960	95,808

^a prefilmed statically at 100 ppm

^b blown fuse precluded measurement

3. Spinner Tests

The b-BZT was tested against TTA at three

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concentration levels. The water was as follows: Ca (as CaCO_3) 170 ppm, Mg (as CaCO_3) 110 ppm, 15 ppm SiO_2 , pH = 7.0, 120°F. The corrosion rates of Admiralty brass were as follows:

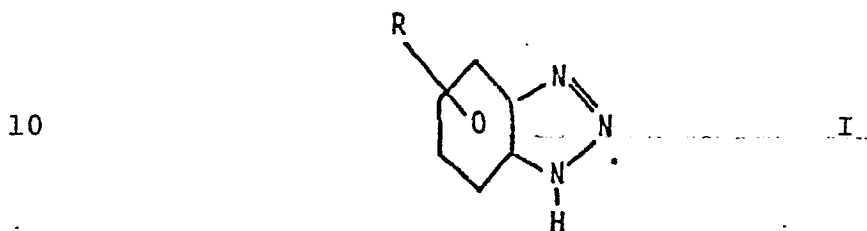
5	<u>Treatment</u>	<u>Corrosion Rates (mpy)</u>			
		<u>0</u>	<u>0.5 ppm</u>	<u>1.0 ppm</u>	<u>2.0 ppm</u>
	Control	1.6	-	-	-
	TTA	-	0.65	0.59	0.42
	b-BZT	-	0.42	0.44	0.48

10 These tests, which are not particularly stressful or precise, show that b-BZT is equal to or superior to TTA.

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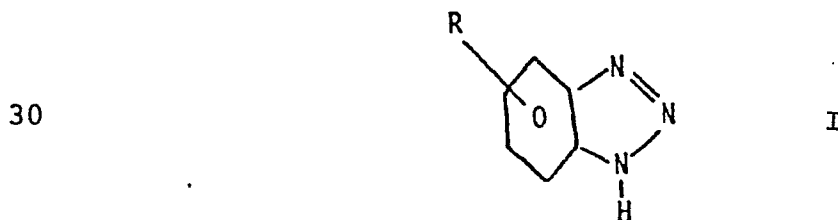
CLAIMS

1. A method of inhibiting the corrosion of non-ferrous metals in contact with an aqueous system, which comprises adding to the aqueous system a sufficient amount for the purpose of a water soluble compound having the formula:



wherein R is a hydrocarbon group containing from 3 to about 8 carbon atoms.

2. A method of inhibiting the corrosion of metal parts in contact with an aqueous system, the metal parts being composed of both ferrous and non-ferrous metals, which comprises adding to the aqueous system a sufficient amount for the purpose of a corrosion inhibitor composition for the ferrous metal, and also adding to the aqueous system an effective amount for the purpose of a corrosion inhibitor for the non-ferrous metal, the corrosion inhibitor for the non-ferrous metal comprising a compound represented by the formula:



3. A method according to claim 1 or 2 wherein R contains from about 4 to about 6 carbon atoms.

4. A method according to claim 3 wherein R is an alkyl group.

5 5. A method according to claim 4 wherein the compound having formula I is a butylbenzotriazole.

6. A method according to claim 5 wherein the benzotriazole is 4 or 5 butylbenzotriazole.

7. A method according to any of claims 1 to 6,
10 wherein the compound having formula I is added to the aqueous system in an amount of 0.1 to 200 parts per million parts of water in said system.

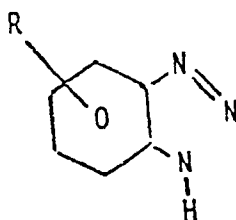
8. A method according to claim 7 wherein the compound having formula I is added to the aqueous
15 system in an amount of about 0.1 to 100 parts per million parts of water in said system.

9. A method according to any of claims 1 to 8 wherein the non-ferrous metal is or contains copper.

10. A method according to any of claims 1 to 9
20 wherein the aqueous system is a cooling water system.

11. A method according to claim 10 wherein the water contained within the cooling water system and/or the conditions of operation of the aqueous system is or are such as to provide a highly corrosive medium
25 for the copper or copper containing metal.

12. A composition effective for inhibiting the corrosion of metallic parts or systems composed of both ferrous and non-ferrous metals in contact with water, which composition comprises a corrosion
30 inhibiting composition for the ferrous metals, and a corrosion inhibitor for the non-ferrous metals, comprising a compound of the formula:



I

5 wherein R is a hydrocarbon group containing about 3 to about 8 carbon atoms.

13. A composition according to claim 12 wherein said group contains from about 4 to about 6 carbon atoms.

10 14. A composition according to claim 13 wherein the group is an alkyl group.

15. A composition according to claim 14 wherein the corrosion inhibitor for the non-ferrous metal is 4 or 5 butylbenzotriazole.

15 16. A composition according to any of claims 12 to 15 wherein the non-ferrous metal is or contains copper.

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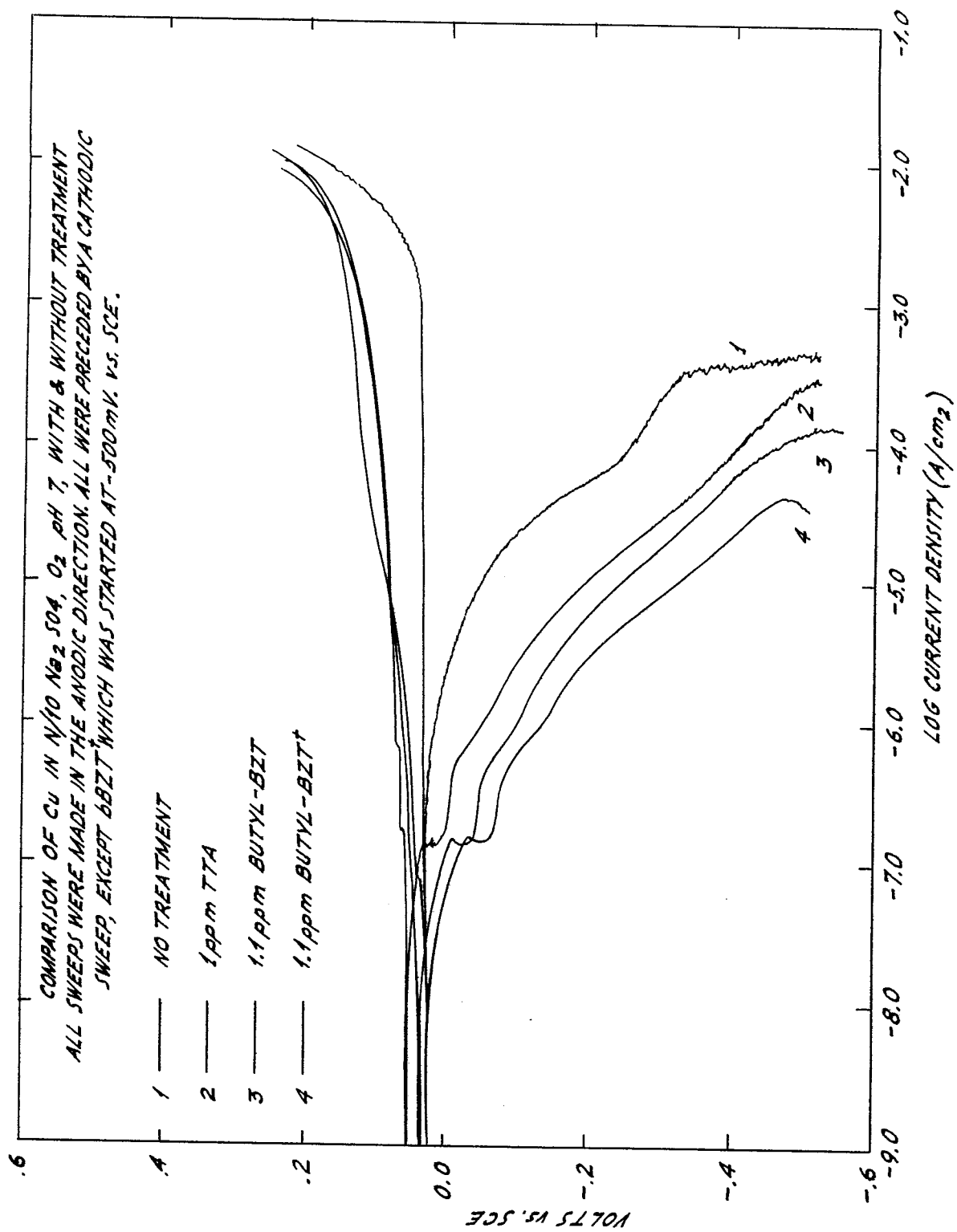


FIG. 1.

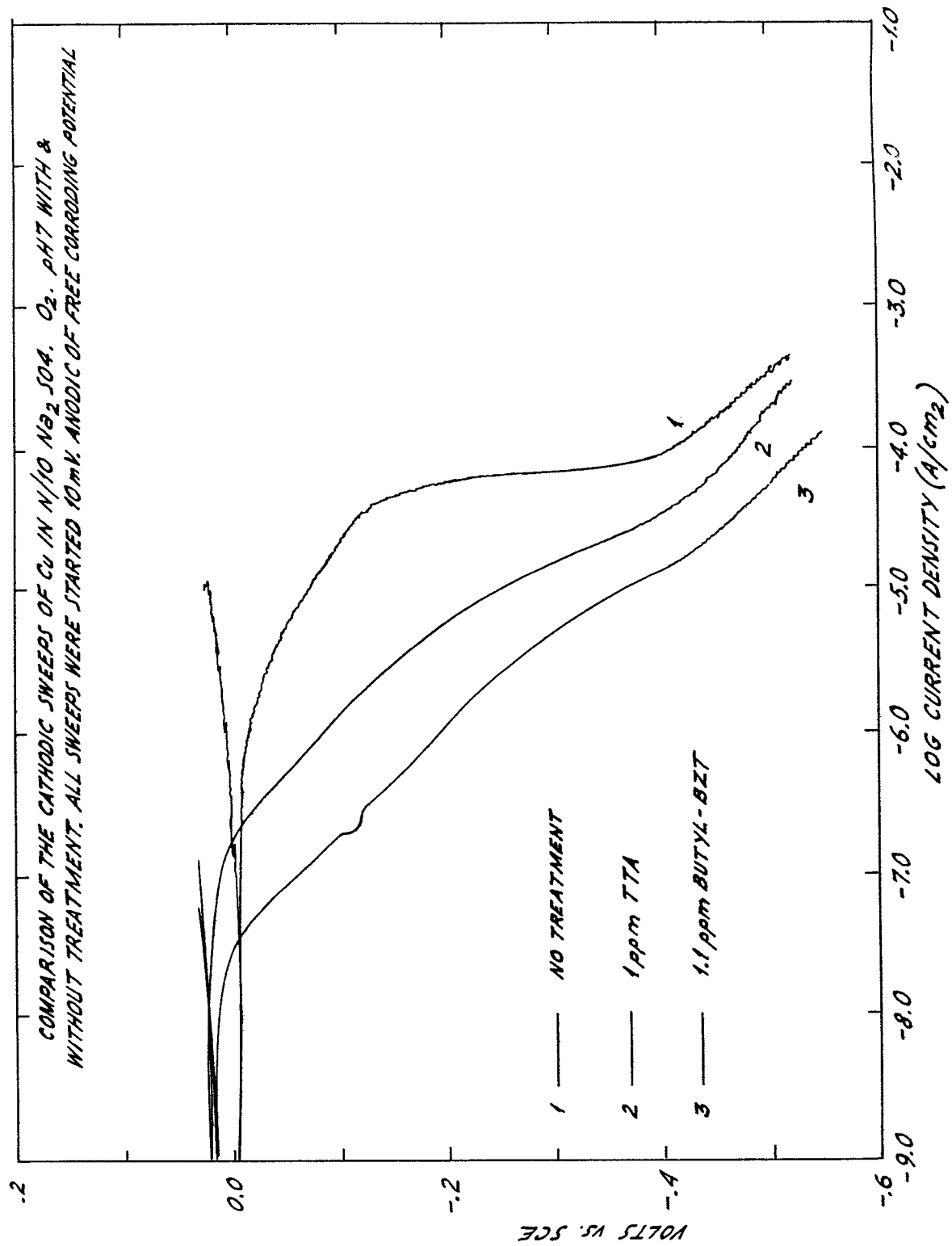


FIG. 2.

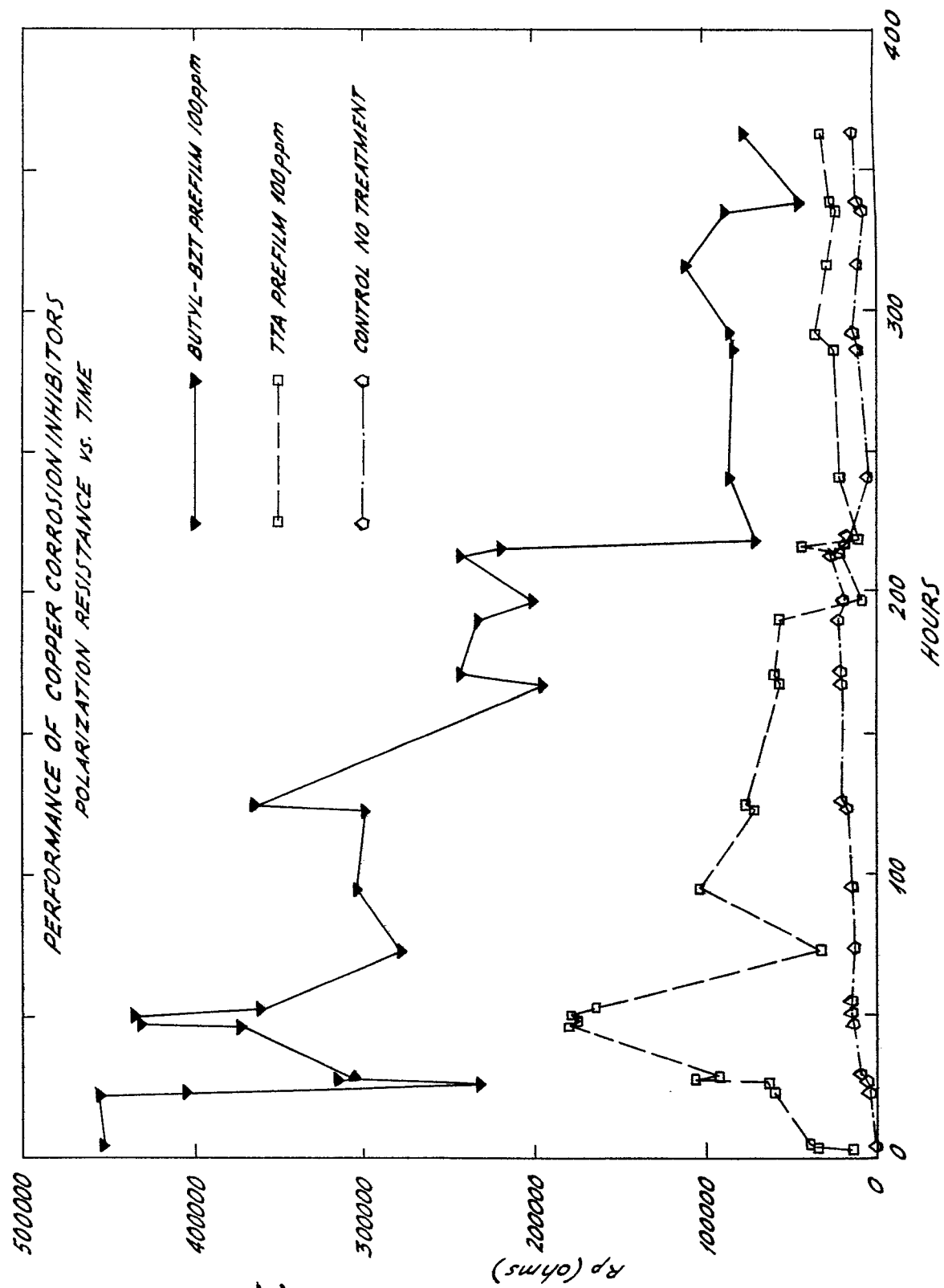


FIG. 3.

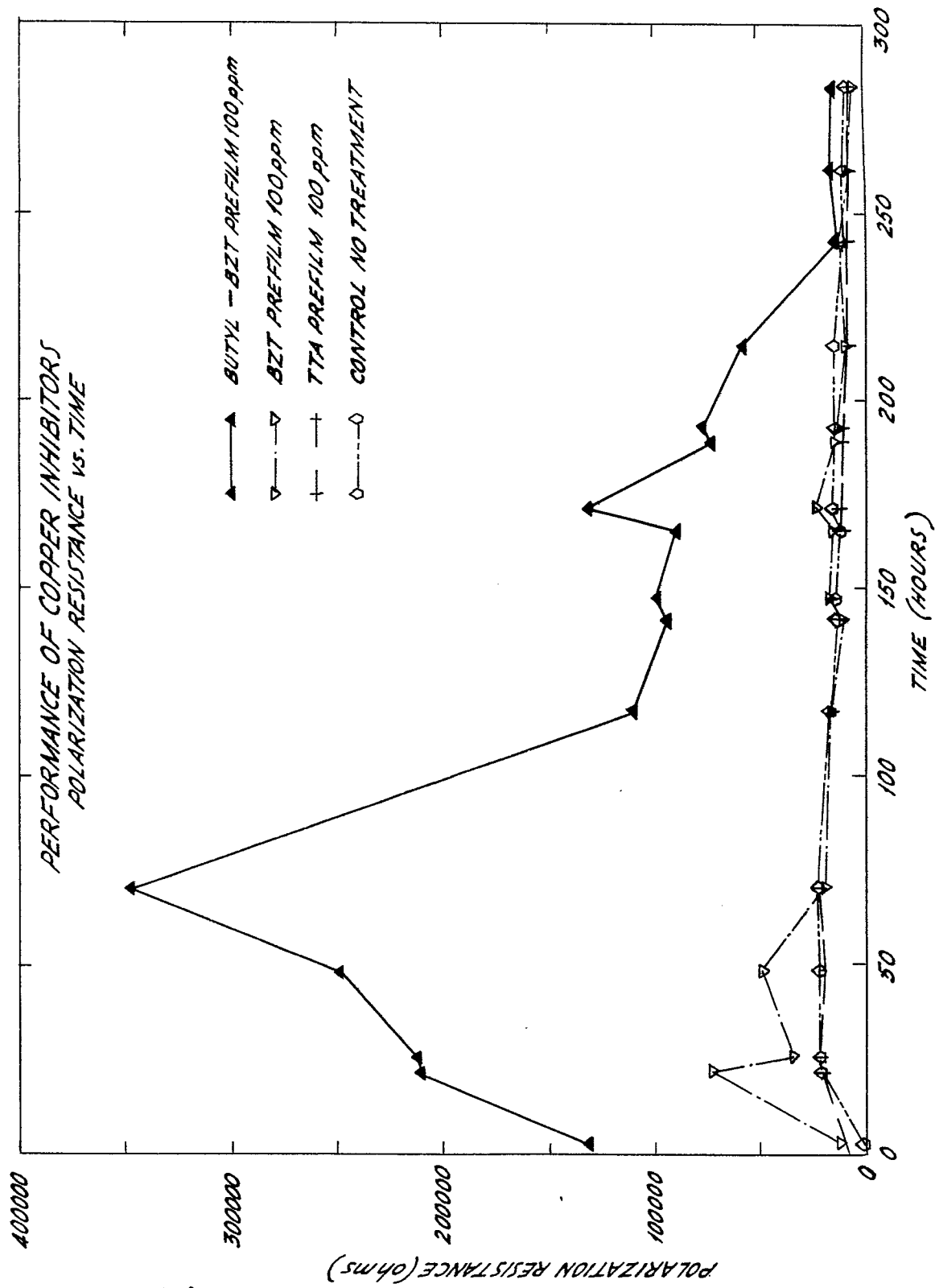


FIG. 4.