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CORROSION INHIBITION COMPOSITIONS

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This invention relates to new and improved corrosion inhibiting compositions and to new and improved methods for inhibiting corrosion. More particularly, this invention relates to compositions and methods for inhibiting the corrosion of both iron and copper-bearing metals in contact with the same aqueous solution.

Where copper or its alloys and iron or its alloys are in contact with the same aqueous solution serious pitting of the ferrous metals and generalized corrosion of the cupro-metals frequently occurs. The pitting and corrosion have been attributed to the fact that a small amount of copper dissolves in the aqueous solution and deposits onto the ferrous metals resulting in the formation of a larger number of galvanic cels. The electrolytic action of the cells in turn causes localized pitting resulting in damage to the ferrous metals.

Protection against such corrosion has been obtained to some extent by the addition of small amounts of soluble phosphates to the aqueous solution. Improved corrosion resistance has been obtained to a limited extent by the addition of sodium mercaptobenzothiazole to such phosphate solutions. However, at temperatures above 140° F., the known formulations fail to provide good corrosion protection.

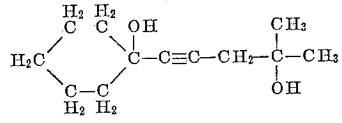
It is an object of this invention to provide new and improved corrosion inhibiting compositions and methods for use in aqueous systems in contact with both ferrous and cupro-metals.

Another object of this invention is to provide new and improved ferrous and cupro-metal corrosion inhibiting compositions and methods which are effective at elevated temperatures.

Further objects will be apparent to those skilled in the art from reading the following description.

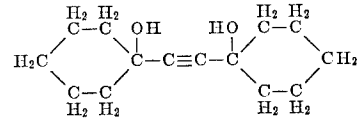
It has been found that when a member of a particular class of glycols and a quaternary amine are added to an aqueous solution containing a water soluble polyphosphate and a water-soluble alkali salt of mercaptobenzothiazole (hereinafter sometimes referred to as "MBT") consistently superior corrosion protection is provided in a bimetallic system at temperatures above about 140° F. The operative class of glycols includes (1) ditertiary acetylenic glycols and (2) copolymers of propylene oxide and ethylene oxide containing from about 10 to 80% by weight of polyoxyethylene and about 20 to 90% by weight of polyoxypropylene and having a molecular weight of between about 4,000 to 18,000 and a polyoxyethylene to polyoxypropylene ratio between about 1:9 and 4:1. Members of the class may be prepared according to the process described in U.S. Patent 2,674,619.

One suitable ditertiary acetylenic glycol is 1-hydroxy cyclohexyl, hydroxy methylisobutylacetylene. The glycol is manufactured and sold under the trade name of Surfynol #104 and has formula:



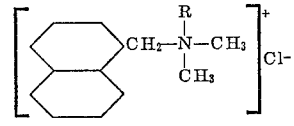
Another specific example of a suitable ditertiary acetylenic

glycol is ethynylene dicyclohexanol [bis (1-hydroxy cyclohexyl) acetylene] having the formula:



An example of the class of copolymers of propylene oxide and ethylene oxide is a copolymer of 20% polyoxypropylene and 80% polyoxyethylene having a molecular weight of about 8760 which is manufactured under the name of Pluronic F–68.

It has also been found that quaternary amines useful in the practice of this invention must have at least one alkylated phenyl group bound to the nitrogen, where the alkyl group contains at least 12 carbon atoms. A quaternary amine which is typical of the class useful in this invention is n-alkyl dimethyl 1-naphthyl methyl ammonium chloride monohydrate which is sold under the trade name BTC 1100 and has the formula:



where R is an alkyl group containing 10 to 14 carbon atoms and which preferably is composed of alkyl groups, 98% of which contain 12 carbon atoms and 2% of which contain 14 carbon atoms. Another example of a quaternary amine which has been found useful is marketed under the name Hyamine 2389, the active ingredient of which is methyl dodecylbenzyl trimethyl ammonium chloride.

The invention is not limited to the use of any particular water soluble polyphosphate. At the lower water temperatures, and with water that has a low calcium content, orthophosphates can be used, such as disodium phosphate, trisodium phosphate, sodium potassium phosphate, monosodium dihydrogen phosphate, disodium monohydrogen phosphate, ammonium phosphates and other soluble orthophosphates. For other purposes, and at higher temperatures, other polyphosphates may be used, for instance, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium tetraphosphate, calcium pyrophosphate, sodium trithiotetraphosphate, hexametaphosphate and any of the water soluble glassy polyphosphates, including glassy heptaphosphate, as well as those containing calcium-sodium, magnesium-sodium and aluminum-sodium groups.

The water-soluble alkali salt of mercaptobenzothiazole may take many forms, such as an alkaline earth metal salt, including the salts of strontium or calcuim, or an alkali-metal salt, including the salts of cesium, lithium, potassium and sodium. The sodium salt is preferred.

The concentration of the additive corrosion inhibitor of this invention may be maintained in amounts up to several thousand parts per million (p.p.m) limited by economics and the solubilities of the components. The glycols and quaternary amines exemplified above, for example, are soluble in water only in the amount of about 1000 p.p.m.; the MBT may be used up to 500 p.p.m. The level of concentration is preferably maintained in the range of 40 to 70 p.p.m. of the total of the components. The preferred soluble phosphate or polyphosphate concentration is 45 to 55 p.p.m., that of MBT from 2 to 10 p.p.m., while the glycol and quaternary amine are preferably used in a concentration of 1 to 10 p.p.m. each.

In order more clearly to disclose the nature of the present invention, the following examples are presented. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the invention, nor limit the ambit of the

appended claims. The expression "p.p.m." is used to designate parts per million by weight. The expression "m.p.y." is used to designate mils of metal loss per year. Throughout the specification percentages are given in percentages by weight.

EXAMPLE I

The corrosion inhibiting capabilities of the novel compositions of this invention were evaluated by suspending accurately weighed pairs of 1" x 2" coupons of copper and mild steel (S.A.E. 120) in close proximity to each other in glass jars having a capacity of 3000 ml. and containing 2600 ml. of an aqueous solution of a composition to be tested. To simulate actual operating conditions, small quantities of electrolytes which are normally found in unsoftened water were added to the aqueous solution. The latter electrolytes were present in amounts representative of a typical concentration before blow-down as follows:

	p.p.m.
Ca (as $CaCO_3$) from $CaCl_2$	250
Mg (as $CaCO_3$) from $MgSO_4.7H_2O$	150
HCO_3 (as $CaCO_3$) from $NaHCO_3$	5
Na_2SO_4 (as Na_2SO_4)	1400
NaCl (as Na_2SO_4)	400

The jars were immersed in a large electrically heated water bath suitable for maintaining a predetermined temperature. Each jar was provided with aeration means consisting of perforated tubing inserted through the top of the jar and extending to near the bottom of the jar by means of which filtered, compressed air was constantly introduced into each of the jars. Electrically driven agitators kept the solution in motion around the coupons. Make-up solution identical to the contents of each of the jars was added from a reservoir through feed tubes which extended into the jars. Through the feed tubes, 20 ml. of make-up liquor were added to each jar at 20 minute intervals controlled by timed solenoid valves.

Coupons were withdrawn after from one to twenty days. The steel coupons were immersed in inhibited hydrochloric acid (Clark's reagent), rinsed, dried and reweighed. The copper coupons were descaled with 5% sulfuric acid. The weight loss of each coupon was expressed in terms of mils of metal loss per year (m.p.y.).

Using the above procedure, 50 p.p.m. of sodium polyphosphate ($Na_6P_4O_{13}$) were dissolved in water, and placed in the jars at 140° F. The corrosion rate was determined to be 14 to 16 m.p.y. for the iron coupons and 2 to 2.8 m.p.y. for the copper coupons. This example is indicative of the corrosion inhibiting effect of sodium polyphosphate alone.

EXAMPLE II

Using the procedure of Example I, 50 p.p.m. of sodium polyphosphate and 2 p.p.m. of sodium mercaptobenzothiazole (MBT) were dissolved in water and placed in the jars at 140° F. The corrosion rate for the iron coupons was found to be 10 to 11 m.p.y., and the corrosion rate for the copper coupons was found to be 3.8 to 4 m.p.y. This example is indicative of the effect of MBT in conjunction with the sodium polyphosphate. A slight improvement in the steel corrosion rate was noticed, but the corrosion rate of the copper increased markedly.

EXAMPLE III

Using the procedure of Example I, 50 p.p.m. of sodium polyphosphate, 5 p.p.m. of MBT, 5 p.p.m. of BTC 1100, and 2 p.p.m. of Surfynol #104 were dissolved in water and placed in the jars at 140° F. The corrosion rate for iron was found to be 0.8 to 1.0 m.p.y. while the corrosion rate for copper was found to be 0.6 to 1.0 m.p.y. This example illustrates the effect of a particular concentration of the novel combination of this invention.

EXAMPLE IV

Following the procedure outlined in Example I, 50 p.p.m. of sodium polyphosphate, 2 p.p.m. MBT, 1 p.p.m. of BTC 1100 and 2 p.p.m. of Surfynol #104 were dissolved in water, placed in the jars and heated to 140° F. The corrosion rate of the coupons was found to be 1.2 to 1.7 m.p.y. for iron and 1.0 m.p.y. for copper. This example illustrates the effect of another particular concentration of the novel combination of this invention.

EXAMPLE V

Using the procedure outlined in Example I, 50 p.p.m. of sodium polyphosphate, 2 p.p.m. of MBT, 2 p.p.m. of BTC 1100 and 1 p.p.m. of Surfynol #104 were dissolved in water, placed in the jars and heated to 140° F. The corrosion rate of the iron coupons was found to be 7.7 to 8.5 m.p.y. The corrosion rate of the copper coupons was found to be 1.8 to 2.0 m.p.y. This example illustrates the effect of another particular concentration of the novel combination of this invention.

EXAMPLE VI

Using the procedure outlined in Example I, 50 p.p.m. of sodium polyphosphate, 0.2 p.p.m. MBT, 2 p.p.m. of BTC 1100 and 1 p.p.m. of Surfynol #104 were dissolved in water, placed in the jars and heated to 140° F. The corrosion rate of steel was found to be 21 m.p.y.; the corrosion rate of copper was found to be 3.0 m.p.y. This example illustrates another particular concentration of the novel combination of this invention.

The results of Examples I–VI are summarized in Table I.

Table I

Example	Solution Components (p.p.m.)				Corrosion rate Ferrous Metal	m.p.y. at 140° F. Copro-metal
	A	B	C	D		
I	50				14–16	2–2.8
II	50	2			10–11	3.8–4.0
III	50	5	5	2	0.8–1.0	0.6–1.0
IV	50	2	1	2	1.2–1.7	1.0
V	50	2	2	1	7.7–8.5	1.8–2.0
VI	50	0.2	2	1	21	3.0

A—sodium polyphosphate ($Na_6P_4O_{13}$).
B—sodium mercaptobenzothiazole.
C—BTC 1100.
D—Surfynol #104.

Examples III, IV and V showed improved corrosion inhibition over Example I which utilized the sodium polyphosphate alone, and over Example II which utilized the combination of sodium polyphosphate and MBT. Examples III–VI contain the novel combination of compounds which form the basis of this invention.

We have found that the compounds are present in critical amounts. For instance, Example VI which contains the same number of compounds and the same type of compounds as Examples III, IV and V shows a poorer corrosion inhibition than does Example I with the sodium polyphosphate alone. Example VI has one-tenth the concentration of the MBT which characterizes Examples II, IV and V, and only one-twenty-fifth the MBT concentration which appears in Example III. These examples demonstrate the limit below which the utility of the MBT is lost. Thus, is demonstrated the feature of the invention that the MBT must be present in at least a minimum amount to cooperate and to produce a synergistic effect with the sodium polyphosphate, quaternary amine and glycol. Below a concentration of about 2 p.p.m. of MBT, the formulation loses its capability to synergistically inhibit the corrosion.

Example III employs a higher concentration of the MBT and quaternary amine and results in the lowest corrosion rate among the examples and is typical of the corrosion rates which may be achieved with our invention. The

components of Example III, however, are relatively expensive and a reasonably comparable corrosion inhibition can be obtained more economically with the concentration employed in Example IV. The composition of Example IV is a preferred embodiment of the invention and is as follows:

	P.p.m.
Water soluble polyphosphate	50
Sodium mercaptobenzothiazole	2
Glycol	2
Quaternary amine	1

Example V yielded results which are markedly inferior to those of Example IV by reason of reducing by one-half the concentration of the glycol. The results of Examples IV and V are illustrative of the dependence on minimum concentrations of the additives in order to achieve the maximum synergistic effect of the four component system.

The concentrations of the components are of great importance as demonstrated above. The examples indicate the minimum effective concentrations of the components. Greater amounts of the components may be used with beneficial results. However, the cost of the composition becomes greater than is necessary to achieve satisfactory results.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions, of excluding any equivalents of the featurs shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A composition for inhibiting corrosion of both

cupro-metals and ferrous metals in contact with the same aqueous solution at temperatures above about 140° F. consisting essentially of from about 45 to 55 p.p.m. of sodium polyphosphate having the formula $Na_6P_4O_{13}$; from about 2 to 10 p.p.m. of sodium mercaptobenzothiazole; from about 1 to 10 p.p.m. of at least one water soluble quaternary amine selected from the class consisting of n-alkyl dimethyl 1-naphthyl methyl ammonium chloride monohydrate where the alkyl group contains 10 to 14 carbon atoms and methyl dodecylbenzyl trimethyl ammonium chloride; and from about 1 to 10 p.p.m. of a water soluble glycol selected from the class consisting of 1-hydroxy cyclohexyl hydroxy methylisobutylacetylene, bis(1-hydroxy cyclohexyl) acetylene and a copolymer of 20% polyoxypropylene and 80% polyoxyethylene having a molecular weight of about 8760.

2. A composition as defined in claim **1** wherein said alkyl group contains 12 carbon atoms.

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