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(71) Applicant (for all designated States except US): TAMINCO [BE/BE]; Pantserschipstraat, 207, B-9000 Gent (BE).

(72) Inventors and


(54) Title: INHIBITION OF CORROSION IN COOLING WATER SYSTEM

(57) Abstract: A method of controlling corrosion in cooling water systems is disclosed which includes introducing into the cooling water system certain alkylalkanolamine compounds having the general formula: R1-NH-(CH2CH2OH)n, wherein R1 is a C3 to C4 alkyl group either linear or branched, x and y are 1 or 2, z is 0 or 1, x+y is not greater than 3, z = 3-x-y and the R groups are either the same or different C3 to C4 alkyl groups.
Inhibition of corrosion in cooling water system.

FIELD OF THE INVENTION

This present invention relates to novel methods of controlling corrosion in cooling water systems, and more particularly to certain alkylalkanolamines which have been found to be effective for controlling corrosion of ferrous-based and copper-based metals which are in contact with cooling water systems.

BACKGROUND OF THE INVENTION

Iron and iron-based metal alloys containing alloys such as mild steel are well-known materials used in constructing the apparatus of cooling water systems. Copper and copper-base metals also find significant use in cooling water systems. In these systems cooling water circulates, contacts the iron and/or copper based metal surfaces, and may be concentrated, such as by evaporation of a portion of the water from the system. Even though iron and copper based metals are readily subject to corrosion in aqueous environments, they are used over other metals due to their strength and availability.

It is known that various materials which are naturally or synthetically occurring in the cooling water systems, especially systems using water derived from natural resources such as seawater, rivers, lakes and the like, attack such metals. The term "ferrous-based metals", as used herein, shall mean any iron metal and/or metal alloys containing iron therein. The term "copper based metal", as used herein, shall mean any copper metal and/or metal alloys containing copper therein. Typical systems in which the iron and/or copper metal parts are subject to corrosion include evaporators, single and multi-pass heat exchangers, cooling towers, and associated equipment and the like. As the cooling water passes through or over the system, a portion of the system water evaporates thereby increasing the concentration of the dissolved materials contained in the system. These materials approach and reach a concentration at which they may cause severe pitting and corrosion which eventually requires replacement of the metal parts. Various corrosion inhibitors have been previously used to treat these
systems.

For example, chromates, inorganic phosphates and/or polyphosphates have been used to inhibit the corrosion of metals which are in contact with water. The chromates, though effective, are highly toxic and consequently present handling and disposal problems. While phosphates are non-toxic, due to the limited solubility of calcium phosphate, it is difficult to maintain adequate concentrations of phosphates in many cooling water systems. Polyphosphates are also relatively non-toxic, but tend to hydrolyze to form orthophosphate which in turn, like phosphate itself, can create scale and sludge problems in cooling water systems (e.g. by combining with calcium in the system to form calcium phosphate). Moreover, where there is concern over eutrophication of receiving waters, excess phosphate compounds can serve as nutrient sources. Borates, nitrates, and nitrites have also been used for corrosion inhibition. These too can serve as nutrients in low concentrations, and/or represent potential health concerns at high concentrations.

Environmental considerations have also recently increased concerns over the discharge of other corrosion inhibiting metals such as zinc, which previously were considered acceptable for water treatment.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a method of inhibiting the corrosion of ferrous and/or copper based metals in contact with a cooling water system.

It is another object of this invention to provide a method of inhibiting corrosion of ferrous and/or copper based metals in contact with a cooling water system with surprisingly enhanced results.

In accordance, with the present invention, there has been provided a method for inhibiting corrosion of ferrous and/or copper based metals which are in contact with a cooling water system comprising adding to the system a corrosion inhibiting amount of an alkylalkanolamine.
DESCRIPTION OF THE INVENTION

This invention is directed to certain alkylalkanolamine compounds and to their use as corrosion control agents for treating cooling water systems. The method of this invention comprises adding to a cooling water system, in an amount effective to inhibit corrosion of ferrous-based and/or copper-based metals which are in contact with the cooling water system alkylalkanolamine compounds having the following general formula:

$$R_x\text{-NH}_2\text{-(CH}_2\text{CH}_2\text{OH)}_y$$

wherein R is a C$_3$ to C$_8$ alkyl group either linear or branched, x and y are 1 or 2, z is 0 or 1, x+y is not greater than 3, z = 3-x-y and the R groups are either the same or different C$_3$ to C$_8$ alkyl groups.
The precise dosage of the corrosion inhibiting agents of this invention depends, to some extent, on the nature of the cooling water system in which it is to be incorporated and the degree of protection desired. In general, however, the concentration of alkylalkanolamine compounds maintained in the system preferably range from about 1,000 ppm to about 6,000 ppm. Within this range, generally lower dosages of about 2,000 ppm or less are more preferred, with a dosage of about 1,500 ppm or less being most preferred for many cooling water systems, such as for example, many closed recirculating cooling water systems. The exact amount required with respect to a particular aqueous system can be readily determined by one of ordinary skill in the art in conventional manner. The corrosion inhibiting agents of the present invention are best suited for recirculating cooling water systems, open or closed, because of the preferred treatment dosages. However, use in once through systems would recognize the corrosion protection provided by the present invention. As is typical of most cooling water systems, the pH is preferably maintained at 7 or above, and is most preferably maintained at 8 or above. In addition to providing for corrosion control, the alkylalkanolamine compounds of the present invention also provide for pH control/adjustment of the cooling water system.

The corrosion inhibiting compositions of this invention may be added to the system water by any convenient mode, such as by first forming a concentrated solution of the treating agent with water, preferably containing between 1 and 50 total weight percent of the alkylalkanolamine compounds. This concentrate is then feed to the cooling water system at some convenient point in the system. In many instances, the treatment compositions may be added to the make-up water or feed water lines through which water enters the system. For example, an injection calibrated to deliver a predetermined amount periodically or continuously to the make-up water may be employed.

The present invention is particularly useful in the treatment of cooling water systems which operate at temperatures between 60 °F and 200 °F, particularly recirculating cooling water systems which operate at temperatures of from about 80 °F to 150 °F.
It will be appreciated that while the chemical corrosion inhibiting compositions of the present invention may be used as the sole corrosion inhibitor for the cooling water system, other conventional water treatment compositions customarily employed in cooling water systems may advantageously be used in combination with the claimed treatment agents. Thus, other water treatment additives which may be used include, but are not limited to, biocides, scale inhibitors, chelants, sequestering agents, dispersing agents, other corrosion inhibitors, polymeric agents, oxygen scavengers and the like.

EXAMPLES

Glossary:

BAE: 2-butyraminoethanol

BDEA: butyldiethanolamine

AMP-95: 2-amino-2-methyl-1-propanol

DGA: diglycolamine, 2-(2-hydroxyethoxy)ethylamine

MEA: monoethanolamine

TEA: triethanolamine

DIPAE: diisopropylaminoethanol

IPAE: isopropylaminoethanol

Example 1:

Brass (2” x 2” x 0.032”) panels were immersed into aqueous solutions of alkanolamine (0.3 M) and octanoic acid (0.2 M) adjusted with H₃PO₄ and/or KOH to pH = 8.5 at room temperature. A 450 gram portion of each solution was weighed carefully and transferred to a wide-mouth screw-cap glass bottle. The brass panels were washed with 10% liquid-Nox (Alcanox product) and buffed dry with a paper towel. The panels were immersed in the solutions (all panels
oriented at the same angle within the solution) and the cap placed tightly on the jar. A 5 gram sample of each solution was collected at regular intervals and analyzed by ICP/emission for metals content. In the case of brass, both a leaded (CA-360, 3% Pb) and an unleaded (CA-260) alloy were employed. The results for leaching of copper, zinc and lead after 30 days of immersion are shown below.

Table I
Cu, Pb, and Zn Results – Day 30, Octanoic Acid, Unleaded Brass:

<table>
<thead>
<tr>
<th>Amine</th>
<th>Cu (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAE</td>
<td>10</td>
<td>&lt; 0.02</td>
<td>7</td>
</tr>
<tr>
<td>BDEA</td>
<td>44</td>
<td>&lt; 0.02</td>
<td>9</td>
</tr>
<tr>
<td>AMP-95</td>
<td>123</td>
<td>&lt; 0.02</td>
<td>66</td>
</tr>
<tr>
<td>DGA</td>
<td>234</td>
<td>&lt; 0.02</td>
<td>19</td>
</tr>
<tr>
<td>MEA</td>
<td>211</td>
<td>&lt; 0.02</td>
<td>14</td>
</tr>
<tr>
<td>TEA</td>
<td>171</td>
<td>&lt; 0.02</td>
<td>3</td>
</tr>
<tr>
<td>DIPAE</td>
<td>2</td>
<td>&lt; 0.02</td>
<td>0.8</td>
</tr>
<tr>
<td>IPAЕ</td>
<td>44</td>
<td>&lt; 0.02</td>
<td>16</td>
</tr>
</tbody>
</table>

The data in Table I clearly show that the alkylalkanolamine compounds of the present invention (BAE, BDEA, DIPAE and IPAЕ) provided inhibition of corrosion of the copper alloys.
Table II

Cu, Pb, and Zn Results – Day 30, Octanoic Acid, Leaded Brass:

<table>
<thead>
<tr>
<th>Amine</th>
<th>Cu (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAE</td>
<td>9</td>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>BDEA</td>
<td>66</td>
<td>0.7</td>
<td>12</td>
</tr>
<tr>
<td>AMP-95</td>
<td>74</td>
<td>1</td>
<td>37</td>
</tr>
<tr>
<td>DGA</td>
<td>168</td>
<td>2</td>
<td>31</td>
</tr>
<tr>
<td>MEA</td>
<td>134</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>TEA</td>
<td>165</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>DIPAE</td>
<td>1</td>
<td>0.06</td>
<td>0.6</td>
</tr>
<tr>
<td>IPAЕ</td>
<td>19</td>
<td>0.3</td>
<td>7</td>
</tr>
</tbody>
</table>

The data in Table II clearly shows that the alkylalkanolamine compounds of the present invention (BAE, BDEA, DIPAE and IPAЕ) provide improved inhibition of corrosion of copper alloys.

Example 2:

The corrosion of carbon steel in 0.3M solutions of octanoic acid neutralized with 0.2M alkanolamine followed by pH adjustment with KOH/H₃PO₄ to pH = 8.5 was assessed with polarization resistance experiments. The data, converted to a corrosion rate in mils per year, is set forth in Table III. The data in Table III shows the low corrosion rate provided by the alkylalkanolamine, BAE, in accordance with the present invention.
Table III

<table>
<thead>
<tr>
<th>Alkanolamine</th>
<th>Corrosion Rate (mils/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAE</td>
<td>0.4</td>
</tr>
<tr>
<td>AMP</td>
<td>0.25</td>
</tr>
<tr>
<td>DGA</td>
<td>2.90</td>
</tr>
<tr>
<td>MEA</td>
<td>7.03</td>
</tr>
</tbody>
</table>

Example 3:

The HLB of an alkanolamine can be calculated with the following formula:

\[
HLB = 20 \left[ \{ 60 \text{ (for monoethoxylate) or } 104 \text{ (for diethoxylate)} \} \div GMW \right]
\]

A Table of HLB values calculated by this formula is given below:

Table IV

<table>
<thead>
<tr>
<th>Alkanolamine</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAE</td>
<td>10</td>
</tr>
<tr>
<td>AMP</td>
<td>13</td>
</tr>
<tr>
<td>DGA</td>
<td>20 (entire molecule hydrophilic)</td>
</tr>
<tr>
<td>MEA</td>
<td>20</td>
</tr>
</tbody>
</table>

The data in Table IV, in combination with data in Tables I, II and III shows that alkanolamines having lower HLB values provide enhanced corrosion control of ferrous-based and/or copper-based metals in cooling water systems. Alkanolamines having HLB values of 7 - 12 are preferred.

Having described the invention, we now claim the following and their equivalents.
CLAIMS

1. A method for inhibiting corrosion of ferrous and/or copper metals in contact with a cooling water system comprising adding to the system an alkylalkanolamine of the general formula

\[ R_x\cdot \text{NH}_2\cdot (\text{CH}_2\text{CH}_2\text{OH})_y \]

wherein R is a C3-C8 linear or branched alkyl group, x and y are 1 or 2, z is 0 or 1, x+y if less than or equal to 3, and z=3-x-y.

2. The method of claim 1 wherein said alkylalkanolamine is selected from the group consisting of 2-butylaminoethanol, butylidethanolamine, diisopropylaminoethanol and isopropylaminoethanol.

3. The method for claim 1 wherein said cooling water system is a recirculating cooling water system.

4. The method of claim 1 wherein said cooling water system operated in a temperature range of from about 60°F to about 200°F.

5. The method of claim 1 further comprising added biocides, scale inhibitors, chelants, sequestering agent, dispersing agents and mixtures thereof to said cooling water system.

6. The method of claim 1 wherein from about 1,000 ppm to about 6,000 ppm of said alkylalkanolamine is added to said cooling water system.