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INHIBITION OF CORROSION IN COOLING WATER SYSTEMS WITH MIXTURES OF GLUCONATE SALTS AND SILICATE SALTS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Oxidative corrosion in cooling water systems is substantially reduced by the addition of small amounts of a silicate and a gluconate. A polyphosphate can also be added if desired.

BACKGROUND OF THE INVENTION

This invention relates to methods of preventing oxidative corrosion of metals by aqueous solutions. In particular, this invention relates to methods of inhibiting oxidative corrosion in recirculating cooling water systems.

Cooling water systems are widely used in oil refineries and in chemical plants, as well as in homes, factories and public buildings. Each day huge volumes of water are circulated through tremendous numbers of such systems. This obviously represents a large dollar volume in capital investment and operating expense.

Cooling water systems may be classified generally into two types. One type is the once-through cooling system, where cooling water is picked up from a convenient source, such as a river, sent once through the cooling equipment, and then discharged. Corrosion problems in such systems are generally minor. However, in most localities cooling water is not sufficiently abundant to permit the use of a once-through system and the number of such systems is on the decrease.

The other general type of cooling water system is the recirculating cooling water system. Recirculating systems include a cooling tower or equivalent type of equipment. Heat picked up by the water in such systems is passed on to the atmosphere by passing air through the heated water in the cooling tower or equivalent equipment. However, during the course of such contact with the air, a substantial amount of air dissolves in the cooling water and is circulated throughout the cooling system. The oxygen dissolved in the water diffuses to the water-metal interface and will produce corrosion in the heat exchangers and on the metal pipes and vessels in the cooling system. Admiralty metal, copper, and steel, particularly carbon steels, are the most commonly used materials in such systems, and unfortunately such materials are particularly prone to oxidative attack.

The prior art has recognized this problem and has attempted to inhibit this oxidative corrosion in water cooling systems by introducing various inorganic inhibitor systems which produce thin metal oxide films on the metal surfaces of the cooling systems so as to retard or hopefully prevent the diffusion of oxygen to the metal surfaces. Substances which have achieved wide acceptance in the art for this purpose include chromate and phosphate salts. Silicate salts have also been used for this purpose. Unfortunately, these substances have serious drawbacks when used as corrosion inhibitors.

Chromates under certain conditions can give rise to accelerated corrosion. For example, chromates can promote pitting when introduced in low concentrations. This pitting attack may be quite serious and may result in perforation, particularly in areas of breaks or discon-

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tinuities in the film produced by the chromate inhibitor. Since setting up virtually perfect thin film in large scale equipment with high flow rates is tricky to say the least, it is safe to say that effective inhibition will be most unpredictable from unit to unit, and even from day to day in the same unit.

A further and most serious drawback in the use of chromates as inhibitors arises from the fact that chromates are pollutants. Chromates have toxic properties and their presence in streams and rivers is coming under ever-stricter control in new anti-pollution laws. Thus, in order to be able to circulate used cooling water with an environmental sewage system, it would be necessary for the cooling system operator to install adequate purification equipment to remove the chromate prior to water disposal. This procedure adds substantially to plant investment and operating costs. As a practical matter, it is very difficult and prohibitively expensive to remove chromate to an adequately low level, with the result that chromate is rapidly falling into disuse as a corrosion inhibitor.

Polyphosphates have also been used as corrosion inhibitors. These substances have the further advantage of acting as sequestering agents for calcium and magnesium ions which are frequently present in cooling water. However, it is known that polyphosphates are quite corrosive in concentrated solutions and that under certain conditions when used in high concentrations they suffer from conversion to orthophosphates with the resulting formation of sludge or scale which can promote serious corrosion. In addition, polyphosphates are also stream pollutants when discharged into a sewage system, although the acceptable concentration of phosphates is considerably higher than the acceptable concentration of chromates.

Alkali metal silicates have also been suggested as corrosion inhibitors. A problem with alkali metal silicates is that they promote the formation of scale in pipes and cooling equipment, especially when calcium or magnesium is present in the cooling water, thereby promoting corrosion and fouling.

There exists a need for a new and effective corrosion inhibitor combination which will effectively inhibit corrosion of metal surfaces in cooling water systems while at the same time does not result in excessive concentrations of pollutants which cannot be discharged into environmental sewage systems. It has previously been proposed to inhibit the corrosion of metal surfaces in cooling water systems by adding to the water an alkali metal or ammonium gluconate. Sodium gluconate has been particularly suggested for this purpose. The gluconate salts are not toxic in the concentrations utilized and do not pose pollution problems if discharged into environmental waste water systems. Gluconates are suitable for preventing corrosion of soft waters having low concentrations of calcium or magnesium, although the minimum concentration required is generally somewhat higher than in the case of polyphosphates. The gluconates are not quite effective in inhibiting corrosion in hard waters having substantial concentrations of calcium and magnesium. Hence, the art is seeking new corrosion inhibitor combinations for cooling water systems which will effectively inhibit corrosion and at the same time will not cause stream pollution when waste water is discharged from the system.

SUMMARY OF THE INVENTION

It has now been found that small amounts of an inhibitor combination comprising a water-soluble inorganic silicate salt and a water-soluble inorganic gluconate salt is effective as an oxidative corrosion inhibitor in recirculating cooling water systems. A small amount of a

water-soluble polyphosphate salt can also be included in the inhibitor combination. Cooling water systems can be inhibited against corrosion simply by adding the silicate salt, the gluconate salt, and the polyphosphate salt also where desired, to the cooling water in effective corrosion inhibiting amounts.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The water-soluble silicate salts for use in the present invention are the water-soluble alkali metal silicates. These may be represented generically by the formula $\text{Na}_2\text{O} \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$, where x is in the range of about 1 to about 3.5. Commercial sodium silicate solutions in which the mole ratio of silica to soda is about 3.3 may be used to advantage. However, more alkaline solutions having an $\text{SiO}_2\text{:Na}_2\text{O}$ mole ratio as low as about 1:1, or less alkaline solutions having an $\text{SiO}_2\text{:Na}_2\text{O}$ mole ratio up to about 3.5:1 can also be used.

The preferred inorganic water-soluble gluconate salts are the alkali metal gluconates and ammonium gluconate. The term, "inorganic gluconate," as used herein denotes a gluconate salt having an inorganic cation, such as an alkali metal or ammonium. The suitable alkali metal gluconates include lithium gluconate, sodium gluconate and potassium gluconate. Sodium gluconate is especially preferred because it gives an effective inhibition and is an article of commerce which is readily available at relatively low cost.

Preferred polyphosphates for use in the present invention are the water-soluble inorganic hexametaphosphates, and particularly the alkali metal and ammonium hexametaphosphates. Sodium hexametaphosphate is a preferred salt of this type. Sodium hexametaphosphate is a readily available article of commerce which is used as the chelating agent in aqueous systems containing calcium and magnesium ions. Polyphosphates are primarily useful in cooling water systems using hard water, since they prevent or minimize calcium precipitation. In addition, they improve the corrosion inhibiting properties of the silicate-gluconate combination at concentrations low enough to be acceptable from the standpoint of stream pollution.

The concentration of alkali metal silicate in the cooling water according to this invention is in the range of about 2 to about 200 p.p.m., and preferably about 10 to about 80 p.p.m. The water-soluble gluconate salt is present in a concentration of about 2 to about 1000 p.p.m., and preferably about 20 to about 90 p.p.m. The water-soluble polyphosphate is present in a concentration of about 0 to about 100 p.p.m.

The silicate, gluconate, and polyphosphate where used, can be added as either solids or as aqueous solutions to the cooling water system in amounts which will give the above-specified concentrations. The alkali metal silicate, for example, may be a commercially available sodium silicate ("water glass") solution containing approximately 3.3 moles of silica per mole of soda; other silicate solutions or alkali metal silicates in solid form may be used instead. The gluconate and polyphosphate salts will most often be added as solids, although again aqueous solutions are acceptable.

It is believed that the contact of the cooling water containing dissolved silicate, gluconate, and (optionally) phosphate salts in the desired concentration range with metal surfaces of the cooling water system results in the formation of a thin protective film on these metal surfaces. This film serves to inhibit the diffusion of oxygen from the water phase to the metal surfaces, thereby substantially lowering the corrosion rate of the metal.

In some applications, a single treatment with the inhibitor combination will be sufficient to adequately protect a cooling water system up to two or three weeks. However, in cases where there is unusually turbulent

flow or a vessel configuration which makes it difficult to preserve film integrity on the metal surfaces, or in instances where inhibitor and water losses are excessive, it may be necessary to repeat the addition of inhibitors on occasion or alternatively to maintain a continuous inhibitor concentration in the desired range by constant addition of inhibitors in order to preserve the protective film. Generally, a higher concentration of inhibitor is required on startup of a cooling water system than is required thereafter. Thus, it is generally desirable to add enough inhibitor to establish a total inhibitor concentration of at least about 50 p.p.m. when a system is being started up. This will cause a protective film to form on the metal surfaces in the system. Once this film is formed, it can frequently be maintained at lower inhibitor concentrations, in many cases as low as about 25 total inhibitor concentration.

The present invention will be described more fully with reference to the following example.

Example

This example describes the efficacy of a mixture of sodium silicate and sodium gluconate as an inhibitor of oxidative corrosion in carbon steel exposed to water saturated with dissolved oxygen.

The test procedure involves placing a small specimen of known weight of 1020 carbon steel (1" x 4" x 1/8") in tap water through which air is constantly being bubbled. The concentration of dissolved oxygen will thus be kept at a very high level and will duplicate a long period of exposure of the metal in a cooling water system environment. A second specimen of 1020 carbon steel of known weight is placed in water which is also saturated with air by means of a bubbler. A desired quantity of the corrosion inhibitor is dissolved in this water. The temperature of both the blank and the test solutions is maintained at 120° F.

The specimens before their introduction into the solutions are abraded through 4-0 emery paper, degreased in benzene, pickled in dilute sulfuric acid and washed in distilled water.

After six days the samples are removed, cleaned with a soft brush, washed with water and then acetone, and are weighed after drying. The amount of corroded metal is determined by weight loss by weighing before and after the test. The corrosion rate is calculated in mils per year, a mil being .001 inch. The effectiveness of an inhibitor to reduce corrosion is expressed as percentage inhibitor efficiency

$$E = \frac{I_0 - I}{I_0} \times 100$$

where E equals inhibitor efficiency, I_0 is the corrosion rate without inhibitor, and I is the corrosion rate with inhibitor.

The inhibitor salts in this example were sodium silicate and sodium gluconate. The sodium silicate was commercial sodium silicate having an $\text{Na}_2\text{O}:\text{SiO}_2$ mole ratio of 1:1. The sodium gluconate was commercial anhydrous sodium gluconate. For comparison purposes a blank run (no inhibitor) and samples using sodium silicate alone and sodium gluconate alone were also tested by the same procedure.

Results of representative experiments using the above procedure and inhibitor combination are summarized in Table I below.

TABLE I

Inhibitor	Concentration (p.p.m.)	Corrosion rate, mils per year	Inhibitor efficiency, percent
Blank		18.8	0
Sodium silicate	100	12.7	48.5
Sodium gluconate	100	5.9	68.6
Sodium silicate plus sodium gluconate	80, 20	5.5	71
Do.	50, 50	5.3	72
Do.	20, 80	6.5	65

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Good corrosion inhibition is also obtained in solutions containing a silicate, a gluconate, and a polyphosphate. For example, a solution containing 50 p.p.m. of sodium silicate, 25 p.p.m. of sodium gluconate, and 25 p.p.m. of sodium hexametaphosphate, when tested under the conditions of the above example, gave a corrosion rate of 5.7 mils per year and an inhibitor efficiency of 70%. This inhibitor efficiency is nearly as great as the inhibitor efficiency obtained with 50 p.p.m. of sodium silicate and 50 p.p.m. of sodium gluconate, in spite of the lower combined concentrations of silicate and gluconate. Sodium hexametaphosphate appears to make some contribution to the corrosion inhibiting properties of the solution in addition to serving as a sequestering agent for calcium ions.

What is claimed is:

1. A method of inhibiting oxidative corrosion in a circulating cooling water system in which the cooling water contains substantial amounts of dissolved oxygen, said method comprising adding an alkali metal silicate and an alkali metal or ammonium gluconate salt to said water in amounts giving a corrosion inhibited aqueous solution containing about 2 to 200 parts per million of said alkali metal silicate and about 2 to about 1000 parts per million of said gluconate.

2. A method according to claim 1 in which an alkali metal or ammonium polyphosphate salt is also added to said water in an amount giving a concentration of 0 to about 100 parts per million of said polyphosphate in said corrosion inhibited aqueous solution.

3. A method according to claim 2 in which said polyphosphate salt is an alkali metal hexametaphosphate.

4. A method according to claim 1 in which said silicate and said gluconate are added in amounts giving a corrosion inhibited aqueous solution containing about 10 to about 80 parts per million of said alkali metal silicate and about 20 to about 90 parts per million of said gluconate.

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5. A method according to claim 4 in which an alkali metal or ammonium polyphosphate salt is also added to said water in an amount giving a concentration of 0 to about 100 parts per million of said polyphosphate in said corrosion inhibited aqueous solution.

6. The method according to claim 1 in which said silicate and said gluconate are added in amounts of about 10 to about 80 parts by weight of said silicate and about 20 to about 90 parts by weight of said gluconate, based on 100 parts of combined weight of said silicate and said gluconate.

7. A method of inhibiting oxidative corrosion in a circulating cooling water system which comprises forming a corrosion inhibited aqueous solution consisting essentially of water having oxygen dissolved therein, about 2 to 200 parts per million of an alkali metal silicate, about 2 to 1000 parts per million of a water-soluble alkali metal or ammonium gluconate salt, and about 0 to 100 parts per million of a water-soluble alkali metal or ammonium polyphosphate salt, and circulating said solution through said system.

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