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1

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GLUCONATE SALT INHIBITORS

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ABSTRACT OF THE DISCLOSURE

The addition of small amounts of gluconate salts to cooling water systems effectively inhibits oxidative corrosion in such systems. Further, combinations of gluconate salts with other corrosion inhibitors such as benzoate salts and salicylate salts result in synergistic improvement of such inhibition.

BACKGROUND OF THE INVENTION

Water is utilized as the heat exchange medium of choice in the chemical and petroleum process industries. It is also used for the same purpose in air cooling systems in homes, factories, public buildings (such as theaters, halls, etc.). Thus, each day huge volumes of water are being circulated through tremendous numbers of such systems. This obviously represents a large dollar value in capital investment and operating expense.

Heat picked up by the water in most systems is passed on to the atmosphere by passing air through the heated water in cooling towers or equivalent types of 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. Steel, Admiralty metal, copper and in particular 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 substances 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 the chromate and phosphate salts and mixtures thereof.

Unfortunately, these substances do have two very serious drawbacks when used as corrosion inhibitors. In the first place under certain conditions chromate, as well as phosphate corrosion inhibitors, 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 discontinuities in the film produced by the chromate inhibitor. Since setting up virtually perfect thin film in large scale equipment with high flow conditions 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. In the case of polyphosphates it is well known that these substances are very corrosive when present in concentrated solutions, and that they suffer from reversion to orthophosphates with the resulting formation of sludge or scale which can promote serious corrosion.

A further and most serious drawback in the use of metal oxide inhibitors arises from the fact that such substances are pollutants. Chromates, for example, 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 employing such inorganic metal oxide salts to install adequate purification equipment to remove such substances prior to water disposal. This procedure adds substantially to plant investment and operating costs.

2

SUMMARY OF THE PRESENT INVENTION

It is the object of the present invention to provide a substance which will effectively inhibit oxidative corrosion in cooling water systems at low concentrations. It is a further object of this invention to provide a corrosion inhibitor which is non-toxic and will not pose a pollution problem if it were purged to environmental water systems with used cooling water.

It has now been found that very small amounts of an inorganic gluconate salt will be effective as an oxidative corrosion inhibitor in cooling water systems. These gluconate salts are non-toxic in the concentrations utilized and pose no pollution problems if vented to the environmental waste water systems.

It has further been found that such gluconate salts surprisingly exhibit a higher degree of inhibition efficiency at temperatures above ambient temperature. For example, increasing the temperature from about 77° F. to about 120° F. can result in an increase of about 5% in inhibitor efficiency which will more than compensate for any increase in the rate of corrosion due to the temperature rise. Thus, one will observe a lower absolute corrosion rate at the higher temperature than for the lower temperature when using a gluconate salt inhibitor, although the corrosion rate on an uninhibited sample blank will nearly double for the same rise in temperature. Obviously, this temperature effect will be most useful in water cooling systems where temperatures of about 120° F. are not uncommon.

As still another embodiment of the present invention, it has been discovered that gluconate salts will interact synergistically with other corrosion inhibitors such as for example the salts of organic acids, particularly the salts of an aromatic acid to yield a mixture which is more effective than either of its components alone. Specifically, a mixture of a gluconate salt and a benzoate salt or a mixture of a gluconate salt and a salicylate salt will yield an extremely effective composition for inhibiting oxidative corrosion in water cooling systems.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The gluconate salts of preference for use in inhibiting corrosion in the practice of the present invention include the alkali metal and the ammonium salts. In particular, lithium gluconate, sodium gluconate, potassium gluconate and ammonium gluconate are eminently suitable for use herein. The most preferred salt is sodium gluconate. This material is an article of commerce and is readily available at relatively low cost.

Generally, the gluconate salts will be used in a concentration in the range between about 1 to 4000 p.p.m., more preferably in the range between about 100 to 2000 p.p.m. The inhibitor may be added as a solid to the cooling water system in an amount sufficient to yield the desired concentration. It is also possible to add the gluconate salt as a concentrated aqueous solution also in the desired amount to yield the requisite concentration. The choice of mode of treatment is completely within the discretion of the user and the selection is made purely on the relative convenience of the respective modes.

It is believed that the contact of the cooling water containing dissolved gluconate salt inhibitor in the desired concentration range with the metal surfaces of the cooling water system results in the formation of a thin protective gluconate film on those metal surfaces. This film serves to inhibit the diffusion of dissolved 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 gluconate salt inhibitor by the method disclosed above will be sufficient to adequately protect a cooling water system for up to 2 to 3 weeks. However, in cases where there is unusually turbulent water flow or singular 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 treatment on occasion or alternatively to maintain a continuous low concentration of the gluconate inhibitor in the cooling water by constant addition in order to preserve the protective film.

When synergistic mixtures of gluconate salts are used in conjunction with other inhibiting materials such as benzoate or salicylate salts, the desired proportions of the inhibitors in the mixture are in the range of from 0.001 to 0.4 wt. percent gluconate, preferably from 0.010 to 0.10 wt. percent and from 0.001 to 0.40 wt. percent benzoate or salicylate, preferably from 0.010 to 0.10 wt. percent. A most preferable synergistic mixture contains equal quantities by weight of each component. The desired range of concentrations for the synergistic mixture in water is from 10 to 4000 p.p.m., preferably from 100 to 2000 p.p.m.

The present invention will be more fully understood by referring to the following examples.

Example 1

This example demonstrates the efficacy of sodium gluconate as an inhibitor of oxidative corrosion in carbon steel exposed to water containing a substantial quantity of dissolved oxygen. The test procedure involves placing a small specimen of known weight of 1020 carbon steel (1″ x 4 x ⅛″) in 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 piece 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 test solutions are maintained at a fixed desired level by means of a water bath or other form of temperature regulator known to the art.

The specimens before their introduction in the test solution are abraded through 4–0 emery paper, degreased in benzene, pickled in dilute sulfuric acid and washed in distilled water. Immediately after drying the specimens are weighed and placed in the test solution.

After the desired test period of about four days the samples are removed, cleaned with a soft brush, washed with water, then acetone and are weighed after drying. The amount of the corroded metal is determined by weight loss by weighing before and after the test. The effectiveness of an inhibitor to reduce corrosion is expressed as percent inhibitor efficiency

$$\left[=\frac{I_o-I_i}{I_o}\times 100\right]$$

where I_o is the corrosion rate without and I_i the corrosion rate with inhibitor.

The results of representative experiments utilizing the above procedure are summarized in Table I for tests conducted with sodium gluconate.

TABLE I

[Oxidative corrosion inhibition by 200 p.p.m. of sodium gluconate for 1020 carbon steel in aerated (but not air saturated) tap water]

Testing temperature, °F.	Inhibition concentration	Corrosion rate, mg./dm.²/day	Percent inhibitor efficiency
77	Blank	27.1	
77	200 p.p.m. sodium gluconate	1.52	94.4
120	Blank	49	
120	200 p.p.m. sodium gluconate	0.36	99.2

Examination of Table I clearly demonstrates that sodium gluconate is an extremely effective oxidation corrosion inhibitor even when employed at a concentration of about 200 p.p.m. This example also demonstrates the effect of temperature on the efficiency of sodium gluconate as an oxidation corrosion inhibitor.

Reference to Table I shows rather unexpectedly that while the corrosion rate for the blank sample at 120° F. nearly doubled as a result of increasing the temperature about 43° F., the corrosion rate for the sample exposed to oxygen in the presence of small amounts of sodium gluconate at 120° F. decreased when compared to the test results at 77° F. The results for the sodium gluconate sample at the higher temperature reveal a higher percent corrosion inhibition efficiency than for the lower temperature run.

Example 2

This example also demonstrates the effectiveness of sodium gluconate as corrosion inhibitor for cooling water corrosion systems. In addition, this example illustrates the variation of the corrosion inhibitor efficiency with the inhibitor concentration and defines the threshold inhibitor concentration of about 50 to 100 p.p.m. for effective corrosion control.

TABLE II

Oxidative corrosion inhibition by sodium gluconate for 1020 carbon steel in air saturated tap water at 120° F. (4 days runs)]

Inhibitor concentration	Corrosion rate, mg./dm.²/day	Percent inhibitor efficiency
Blank	93.7	
1 p.p.m.	68.5	26.9
5 p.p.m.	68.8	26.6
10 p.p.m.	77	17.8
25 p.p.m.	83.8	10.6
50 p.p.m.	78	16.8
100 p.p.m.	20	78.6
250 p.p.m.	10	89.3
500 p.p.m.	12	87.2
1,000 p.p.m.	13.8	85.3
1,500 p.p.m.	4	95.7
2,000 p.p.m.	3.5	96.3

Example 3

This example demonstrates the surprising synergism resulting from combining sodium gluconate with sodium benzoate as oxidative corrosion inhibitors. The test procedure utilized for this demonstration was that of Example 1, with the exception that the temperature used in this case was 120° F. The results of the synergism experiments are compiled below in Table III.

TABLE III

[Synergism of mixtures of sodium gluconate and sodium benzoate in corrosion inhibition of 1020 carbon steel in aerated tap water at 120° F.]

Inhibitor	Corrosion rate, mg./dm.²/day	Percent inhibitor efficiency
Blank	93.7	
Sodium gluconate (500 p.p.m.)	12	87.2
Sodium benzoate (500 p.p.m.)	74.1	20.9
Mixture: Sodium gluconate (250 p.p.m.), Sodium benzoate (250 p.p.m.)	5.9	93.7
Sodium gluconate (1,000 p.p.m.)	13.8	85.3
Sodium benzoate (1,000 p.p.m.)	44.0	53.0
Mixture: Sodium gluconate (500 p.p.m.), Sodium benzoate (500 p.p.m.)	2.7	97.1

Examination of Table III shows that although sodium benzoate is a far less effective corrosion inhibitor than sodium gluconate, equal concentrations of both compounds is the same solution will result in a substantially improved inhibitor efficiency than was obtainable from the use of either inhibitor alone at equivalent total inhibitor concentrations.

Example 4

This example demonstrates the corrosion inhibition properties of potassium gluconate to control cooling water corrosion. Examination of Table IV demonstrates that potassium gluconate is an effective corrosion inhibitor at concentrations higher than 100 p.p.m. As in the case of sodium gluconate, there is a concentration range between 10 p.p.m and about 100 p.p.m that the inhibitor effectiveness is very low. At concentrations higher than 100 p.p.m. and lower than 10 p.p.m., the effectiveness of the inhibitor increases.

TABLE IV

[Oxidative corrosion inhibition by potassium gluconate for 1020 carbon steel in air saturated tap water at 120° F. (4 days runs)]

Inhibitor concentration	Corrosion rate, mg./dm.²/day	Percent inhibitor efficiency
Blank	93.7	
1 p.p.m. potassium gluconate	65.0	30.6
10 p.p.m. potassium gluconate	85.3	9.0
100 p.p.m. potassium gluconate	87	7.2
1,000 p.p.m. potassium gluconate	5.2	94.4

Example 5

This example demonstrates the synergism resulting from combining sodium gluconate with sodium salicylate as corrosion inhibitor for cooling water systems. The same test procedure was utilized as in Example 1 cited earlier. The temperature of testing was 120° F. The results of these experiments are compiled in Table V.

TABLE V

[Synergism of mixtures of sodium gluconate and sodium salicylate in corrosion inhibition of 1020 carbon steel in air saturated tap water at 120° F.]

Inhibitor	Corrosion rate, mg./dm.²/day	Percent inhibitor efficiency
Blank	93.7	
Sodium gluconate (500 p.p.m.)	12	87.2
Sodium salicylate (500 p.p.m.)	69.2	26.1
Mixture: Sodium gluconate (250 p.p.m.), Sodium salicylate (250 p.p.m.)	5.0	94.7
Sodium gluconate (1,000 p.p.m.)	13.8	85.3
Mixture: Sodium gluconate (500 p.p.m.), Sodium salicylate (500 p.p.m.)	2.5	97.3

The data in Table V shows that although sodium salicylate is a far less effective inhibitor than sodium gluconate, a mixture of equal concentrations of both compounds in solution results in substantial improvement in inhibition efficiency than was obtainable from the use of either inhibitor alone at equivalent total concentrations.

Example 6

This example demonstrates the corrosion inhibition properties of another salt form of the gluconate series. In this example ammonium gluconate was tested by the procedure of Example 1 and the results are summarized in Table VI.

TABLE VI

[Protective properties of ammonium gluconate to control corrosion of 1020 carbon steel in air saturated tap water at 120° F. (4 days runs)]

Inhibitor	Corrosion rate, mg./dm.²/day	Percent inhibitor efficiency
Blank	93.7	
Ammonium gluconate (5 p.p.m.)	49.0	47.6
Ammonium gluconate (20 p.p.m.)	51.2	45.4
Ammonium gluconate (80 p.p.m.)	22.4	76.1
Ammonium gluconate (100 p.p.m.)	57.1	39.1
Ammonium gluconate (500 p.p.m.)	6.4	93.2
Ammonium gluconate (1,000 p.p.m.)	5.6	94

Examination of Table VI clearly demonstrates the effectiveness of ammonium gluconate especially in concentrations greater than 100 p.p.m. The reason for the discontinuity in the 80–100 p.p.m. region is not fully understood. It is possible that the data reflect the influence of concentration on the orientation of the inhibitor molecules on the metal surface and that at the 100 p.p.m. level the inhibitor molecules are not packing in the most efficient manner needed for high levels of inhibition. In any case, this tendency is completely reversed at levels above 100 p.p.m. and very excellent results are observed at the 500+ p.p.m. levels.

What is claimed is:

1. An improved method for inhibiting metal oxidative corrosion in circulating cooling water systems in which the cooling water contains substantial amounts of dissolved air, said method consisting essentially of adding corrosion inhibiting amounts of a water soluble gluconate salt and a water soluble benzoate or salicylate salt to said water.

2. The method of claim 1 wherein a gluconate salt concentration in the range between 1 to 4000 p.p.m. is added to said cooling water system, said gluconate salt being selected from the group consisting of the alkali metal and ammonium salts of gluconate.

3. The method of claim 2 wherein said gluconate salt comprises sodium gluconate.

4. The method of claim 2 wherein said gluconate salt comprises potassium gluconate.

5. The method of claim 2 wherein said gluconate salt comprises ammonium gluconate.

6. The method of claim 1 wherein said organic aromatic acid water soluble salt comprises sodium benzoate.

7. The method of claim 1 wherein said organic aromatic acid water soluble salt comprises sodium salicylate.

8. The method of claim 1 wherein said gluconate salt and said benzoate or salicylate salt are each added to said cooling water system in concentrations of about 100 to about 2000 p.p.m., said gluconate salt being selected from the group consisting of the alkali metal and ammonium gluconate.

9. The method of claim 1 wherein said gluconate salt and said benzoate or salicylate salt are added in approximately equal amounts.

References Cited

UNITED STATES PATENTS

3,110,684 11/1963 Miller ---------- 21—2.7X
3,240,708 3/1966 Dulat et al. -------- 252—389X

OTHER REFERENCES

Kurita Industrial Ltd., Chem. Abstracts, 54:15784 (1960).
King et al., Chem. Abstracts, 49:2981 (1955).
Imperial Chem. Ind. Ltd., Chem. Abstracts, 55:18548 (1961).
Shibasaki et al., Chem. Abstracts, 63:5227 (1965).

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252—146, 181, 396, 407