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**(54) Corrosion inhibiting method for closed cooling systems**

Verfahren zur korrosionsinhibierung für geschlossenen Kühlkreislaifer.

Procédé d'inhibition de la corrosion pour des systèmes de refroidissement fermés

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**Description**Field of the Invention

5 **[0001]** The invention relates to methods for the prevention of scale and corrosion on metal surfaces in contact with water based fluids, in particular aqueous fluids, having a conductivity of 100 micromhos or less in closed cooling or heating systems.

Technical Background

10 **[0002]** Closed recirculating water systems are used for a variety of heating and cooling systems. These systems range from those used in automobile and truck cooling systems, heating and cooling of buildings, the cooling of molten steel in continuous casting units, the cooling of industrial process equipment, and many other applications. In all of these systems, the prevention of scaling and the minimization of corrosion of metal parts in contact with the heating or cooling liquid are of paramount importance. While the liquids used in the heating or cooling systems are primarily aqueous, these fluids may contain in certain instances high levels of anti-freeze compounds such as ethylene glycol. In other instances, the cooling systems may be required to be relatively pure aqueous fluids such as in high heat flux or low conductivity systems which are employed in the steel industry.

15 **[0003]** Many corrosion and scale inhibitors have been used in the past. Many of the most successful materials have contained nitrites, molybdates, chromates, soluble oils, amines or phosphates. Each of these components have some environmental or safety consideration involving their use. For example nitrites are suspected carcinogens, molybdates and chromates are heavy metals, amines are reactive, and phosphates provide a nutrient source for algae when discharged.

20 **[0004]** In addition, many of these additives, and other additives of the prior art do not exhibit properties which modern systems now require. While prior art references teach the separate use of gluconate and sorbitol in coolant systems, there is no disclosure of utilizing these ingredients in combination with each other.

25 **[0005]** US-A-5 330 683 discloses the use of certain sorbitol, and gluconate mixtures which may optionally contain borates as effective corrosion and scale inhibitors for brine based refrigeration systems. Surprisingly, when the additives of the above patent were tested as corrosion and scale inhibitors for non-brine systems, they performed well, at lower dosages than those required in the above patent.

30 **[0006]** DE-A-39 04 733 discloses corrosion inhibitors for protecting metals being in contact with water, in particular in boiler water systems. The corrosion inhibitors disclosed therein consist of tannic acid, a sugar and an aldonic acid in a proportion (parts by weight) of 100:(100-500):(250-500). The corrosion inhibitors described in the above document are used in concentrations of 500 to 2000 ppm in the boiler water.

35 **[0007]** GB-A-2 027 002 refers to a process of inhibiting corrosion of ferrous metal in an aqueous medium by adding to the aqueous medium sorbitol in combination with benzotriazole or tolyltriazole and a water-soluble phosphate.

**[0008]** In "Surface and Coatings Technology", 34 (1988), 537-547, sodium, calcium and zinc salts of gluconic acid optionally in mixture with sodium tetraborate have been reported to be successful inhibitors against the corrosion of iron and mild steel in near-neutral media.

40 **[0009]** According to U. S-A-4 303 546 scale formation as well as corrosion are suppressed by adding aminomethylene phosphonic acids, hydroxyalkane diphosphonic acids, aminoalkane diphosphonic acids, polyhydroxy acids, their alkali metal salts or mixtures thereof to an aqueous heating medium of heating systems. Furthermore, pentoses and hexoses or polyvalent alcohols such as glycerol or sorbitol may be added to the aqueous systems to be treated according to this known process.

Summary of the Invention

45 **[0010]** It is an object of this invention to provide to the art a practical scale and corrosion inhibitor formulation for use in closed cooling or heating systems, in particular those where nitrites, phosphonates, phosphates, metal inhibitors and soluble oils must be avoided. The object of this invention is in particular to provide to the art a scale and corrosion control method that performs in normal closed cooling or heating systems, but which also offers protection to mild steel in contact with closed cooling or heating system liquids in critical systems including high heat flux and low conductivity systems.

50 **[0011]** Subject-matter of the present invention is according to a first aspect a method for the prevention of corrosion on metal surfaces in contact with a water based fluid having a conductivity of 100 micromhos or less in a closed cooling or heating system

which method comprise maintaining in the fluid

from 5 ppm to 4000 ppm, preferably von 40 ppm to 2000 ppm, of sorbitol,

from 5 ppm to 4000 ppm, preferably from 40 ppm to 2000 ppm, of an alkali metal gluconate, and up to 700 ppm, preferably from 5 ppm to 200 ppm, of borax as sodium tetraborate pentahydrate.

**[0012]** According to a preferred embodiment of the method of the invention the fluid contains at least one additional ingredient selected from the group consisting of inert fluorescent tracers, anti-foam compounds, biocide control agents, and yellow metal corrosion inhibitors.

**[0013]** A particular useful yellow metal corrosion inhibitor is selected from the group consisting of tolyltriazole, mercaptobenzotriazole, and benzotriazole.

**[0014]** The water based fluid in the method of the present invention preferably is water, most preferably deionized water.

**[0015]** The fluid used in the method of the present invention preferably is maintained at a pH of from 6.5 to 11.5, in particularly of from 7.5 to 9.5.

**[0016]** According to a further preferred embodiment of the method of the invention an inert fluorescent tracer is added to the fluid in proportion to the amount of sorbitol present.

**[0017]** According to another preferred embodiment of the method of the present invention a corrosion inhibitory package is added to the fluid, the package comprising in weight%:

26.5 % of 50 weight% of gluconic acid

19.0 % of 70 weight% of sorbitol

8.4 % of 50 % of NaOH

1 % of 50 weight% of sodium tolyltriazole

3,13 % of sodium tetraborate pentahydrate balance water.

**[0018]** According to a second aspect the present invention relates to a method for the prevention of scale and corrosion on metal surfaces in contact with aqueous fluids having a conductivity of 100 micromhos or less in closed cooling or heating systems which method comprises

adding to the aqueous fluid present in such cooling or heating system a concentrate composition comprising (in weight%):

a) 2-25 % of sorbitol

b) 2-25 % of an alkali metal gluconate;

c) 0-9 % of borax and

d) balance water

**[0019]** in an amount sufficient to maintain in the fluid from 5 ppm to 4000 ppm of sorbitol, from 5 ppm to 4000 ppm of an alkali metal gluconate and up to 700 ppm of borax as sodium tetraborate pentahydrate.

#### Detailed description of the invention

**[0020]** The closed cooling systems to which the corrosion and scale inhibitors used in this invention are applicable are those normally encountered in the heating and cooling systems of large buildings, machinery, and metals processing. These systems differ from open recirculating systems in that they are not exposed to the ambient air, and cooling is not achieved through evaporation as in the case of open recirculating systems. Typical closed cooling systems operate by picking up heat at a heat rich point, and releasing the heat at a heat deficient point, generally a heat exchanger. While the term cooling system is used herein, the invention is equally applicable to closed hot water heating systems such as those found in large buildings, and the term cooling system is meant to encompass heating systems as well.

**[0021]** As stated before, this invention finds particular utility in low conductivity water systems which without treatment are highly corrosive to mild steel as naturally occurring waters but do not accommodate conventional inhibitors because their conductivity contributions are too significant. Systems of this type include but are not limited to: hot water boiler coolant systems, chilled water systems, air compressors, heating and ventilating equipment systems (comfort systems), thermal storage, and ice systems and other systems where the presence of foreign materials in the event of leakage could cause severe contamination or scaling problems.

**[0022]** The coolant fluid in the closed system is generally pumped from point to point, although gravity may be used to move the fluid from an upper point to a lower point without the use of supplementary mechanical pumps. Coolant fluids are generally aqueous, and depending upon their ultimate use, may be simple well water containing high levels of dissolved hardness ions (calcium and magnesium), treated municipal drinking water, or ion-exchanged, low conductivity water. The fluids may on occasion be winterized in those locations requiring such treatment through the use of ethylene glycol or methanol anti-freeze additives. It is desirable in certain instances to use aqueous coolant fluids

having low levels of alkali or alkaline earth metals contained therein. In these cases, it may be desirable to use a distilled or deionized water as the basis for the aqueous coolant fluid.

**[0023]** Typical coolants to which this invention finds applicability are water based, have a conductivity of 100 micro-mhos or less and contain from 0.1 - 1000 ppm of hardness expressed as  $\text{CaCO}_3$ . Preferably, the coolants to which this invention finds applicability are water based and contain from 1.0 - 750 ppm of hardness expressed as  $\text{CaCO}_3$ . Most preferably, the coolants to which this invention finds applicability are water containing as little as 0.5 - 500 ppm of hardness expressed as  $\text{CaCO}_3$ .

**[0024]** The metals used in closed cooling systems are generally categorized as mild steel or galvanized steel, although special steel alloys may be used in certain high heat flux or low conductivity applications. Occasionally, so called yellow metals, copper, and brass may be present in the system and the selection of corrosion and scale inhibitors must be weighed with these metals in mind. Typically, most coolant systems which are the intended beneficiaries of the corrosion and scale protection agents of this invention are made of mixtures of various steel alloys including mild steel. When used with yellow metals, it is optional to add from 1-100 ppm of known copper corrosion inhibitors such as tolyltriazole, benzotriazole and mercaptobenzothiazole.

**[0025]** Typically, the pH values of the aqueous coolant fluids contained in the closed cooling systems of this invention are maintained in the range of 6.5 to 11.5 and preferably from 7.5 to 9.5.

**[0026]** The corrosion and scale inhibitor used in the method of this invention is a blend of sorbitol, an alkali metal gluconate, and optionally borax. If yellow metals are present in the system, typical copper corrosion inhibitors such as tolyltriazole may also be added.

**[0027]** Generally, the corrosion and scale inhibitors used in this invention are added in enough quantity to provide from 5 ppm to 4000 ppm of gluconate, from 5 ppm to 4000 ppm of sorbitol and from 0 to 700 ppm of sodium tetraborate pentahydrate in the coolant contained in the system. Preferably, from 40 ppm to 2000 ppm of gluconate is present and most preferably from 80 ppm to 200 ppm of gluconate is added. Preferably, from 40 ppm to 2000 ppm of sorbitol is present in the coolant liquid. Most preferably, from 80 ppm to 200 ppm of sorbitol is added to the coolant liquid.

**[0028]** Preferably from 5 ppm to 200 ppm of borax as sodium tetraborate pentahydrate is added. In the most preferred embodiment of this invention, from 10 ppm to 60 ppm of sodium tetraborate pentahydrate is added to the coolant liquid.

**[0029]** While the dosages to the coolant fluids given above are typical, they may vary depending upon the hardness present in the coolant. Dosages of active ingredients are typically lowered in the case of low conductivity systems containing little hardness, and increased for coolants containing hardness causing constituents.

**[0030]** While the dosages listed above are expressed as an amount to be added to the closed cooling system to which they are added, typical formulations may be manufactured which contain the corrosion and scale inhibitor ingredients of this invention so that the mixture may be preformulated and fed into the coolant system. Since all of the components of this invention are water soluble, they may be readily mixed together to form suitable inhibitor packages. A typical formulation for use in this invention may broadly comprise in percentages by weight:

|                    |       |
|--------------------|-------|
| Water              | 95-10 |
| Sodium Gluconate   | 2-25  |
| Sorbitol           | 2-25  |
| Sodium Tetraborate | 0-9   |

**[0031]** More preferably a formulation for use in this invention will comprise:

|                    |       |
|--------------------|-------|
| Water              | 90-15 |
| Sodium Gluconate   | 3-20  |
| Sorbitol           | 3-20  |
| Sodium Tetraborate | 0.5-7 |

**[0032]** Most preferably a formulation for use in this invention will comprise:

|                    |       |
|--------------------|-------|
| Water              | 85-25 |
| Sodium Gluconate   | 5-15  |
| Sorbitol           | 5-15  |
| Sodium Tetraborate | 1-5   |

**[0033]** A preferred corrosion inhibitory package used for the practice of this invention comprises in percentages by weight:

Compound A

**[0034]** 26.5% of 50 wt. % Gluconic Acid  
 19.0% of 70% wt. % Sorbitol  
 8.4% 50% NaOH  
 1% of 50 wt. % Sodium Tolyltriazole  
 3.13% Sodium Tetraborate 5H<sub>2</sub>O  
 balance ----- water

**[0035]** The gluconate used in this invention is an alkali metal gluconate salt. Preferably, sodium gluconate is employed although other alkali metal salts of gluconate may be utilized. Sodium gluconate is available commercially from the American International Chemical Inc as sodium gluconate. Additionally, gluconic acid may also be used in the preparation of the corrosion inhibitors of this invention, although, if the acid form is utilized, it is preferred to neutralize it with an alkali metal hydroxide either prior to addition to the formula, or after the other ingredients have been mixed so as to avoid the possibility of having a low pH in the coolant system that is being treated.

**[0036]** The sorbitol utilized as an ingredient in this invention is generally of a technical grade, although food grades may also be employed. A preferred sorbitol for use in this invention is available from ICI Americas Inc. under the tradename SORBO. The borate material utilized in this invention is generally categorized as borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. While the sodium salt is preferred, other alkali metal tetraborate salts can be used.

**[0037]** In the formulations of the corrosion and scale inhibitors of this invention, it will be readily apparent that other ingredients may also be added. Other ingredients which may find utility in the subject invention include anti-foam materials such as silicon oils, and hydrophobized silica. While the formulations of this invention when used properly do not promote foaming, process leaks may occur into the coolant system which may necessitate the inclusion of anti-foam type materials. Tracer type materials such as those described in US-A- 5,006,311, 5,132,096, 4,966,711 and 5,200,106 may also be included in the formulations. These typically inert tracer type materials may be added to help monitor or control the amount of active sorbitol, gluconate and borate in the coolant system. In the practice of this invention it is preferred to utilize an inert fluorescent indicator described and claimed in US-A-5,006,311 and US-A-5,132,096 rather than the transition metal tracers described in US-A-4,966,711 and US-A-5,200,106 above. In a most preferred application of this invention, an inert fluorescent tracer dye is added to the system in known concentration to the sorbitol, gluconate or borax, and is used to monitor the dosage of active treatment chemicals in the coolant system through the use of fluorescence spectroscopy.

**[0038]** While the gluconate/sorbitol/blends of this invention have been shown to not foster the growth of bacteria, mold, slime or algae in coolant systems, process leaks into the system may necessitate the inclusion of a microbiocide into the system. While prior art systems employing nitrite based corrosion inhibitors could not utilize the so called oxidizing biocides, oxidizing biocides may be used in the processes of the instant invention. Typical oxidizing biocides which are compatible with the gluconate/sorbitol/blends of this invention include chlorine, calcium hypochlorite, stabilized chlorine, sodium hypochlorite, and mixtures of sodium bromide with chlorine or hypochlorite. Non-oxidizing biocides may also be employed in conjunction with the formulations of this invention. Typical non-oxidizing biocides that may find utility in the corrosion and scale control formulations of this invention include: 2,2-dibromo-3-nitrilopropionamide, polyoxyethylene (dimethyliminio)ethylene (dimethyliminio)ethylene; 5-chloro-2-methyl-4-isothiazolin-3-one; 2-methyl-4-isothiazolin-3-one; glutaraldehyde, kathon<sup>\*\*</sup>, tetrabutylazine<sup>\*</sup>, and methylenebisthiocyanate. The examples of biocides given herein are meant to be representative and are no in way inclusive of the current commercially available oxidizing and non-oxidizing biocides which may find utility in the coolant system treatments of this invention.

**[0039]** Other additives that may be considered for addition to the coolant formulations of this invention include visible dyes for the purpose of visible leak detection and coolant source identification. Dyes of this type should be stable at the maximum temperatures to be encountered in the coolant system.

**[0040]** In order to show the efficacy of the corrosion inhibitors of this invention the following experiments were performed.

EXAMPLE 1

**[0041]** The corrosion inhibitors of this invention were evaluated against several commonly available commercial closed system cooling inhibitor formulations. The experiments were conducted in the following manner:

**[0042]** A liter of water containing the ingredients to be tested is placed into a one liter container. The container is then placed in a constant temperature bath. The corrosive water is agitated to 0,30 m/s (1 foot/second) using a magnetic stirrer. The constant temperature bath is heated to maintain 43°C (110°F) inside the container. The corrosion coupons are suspended in the container using an ordinary Teflon tape. the tape needs to be rolled into a string before it can be

<sup>\*\*</sup> a combination of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

<sup>\*</sup>2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine

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inserted into the small hole at one end of the corrosion coupon. The coupon is suspended in the corrosion cell by pinching the ends of the rolled Teflon tape against the outside wall of the corrosion cell with a rubber band. Excessive evaporation of the corrosive water is eliminated by covering the top of the corrosion cell with a plastic wrap, Saran brand wrap being preferred.

**[0043]** Coupons were prepared by polishing with sand paper to 600 grit finish.

Each coupon is weighed individually to 0.1 mg and, its dimensions measured by a caliper to the nearest 0.1mm. The surface areas measured averaged 21.82 cm<sup>2</sup> with a standard deviation of ± 0.5 cm<sup>2</sup>. Coupon surface is calculated by:

$$\text{Area (cm}^2\text{)} = 2(A)(B) + 2(A)(C) + 2(B)(C) - 2(\pi r^2)$$

where

A = length (cm)

B = width (cm)

C = thickness (cm)

$\pi = \text{pi} = 3.142$

r = Radius of the coupon hole

### Procedure

**[0044]** The test duration is 14 days, and the temperature of the corrosive water as well as the stirring action of the magnetic stirrer are checked daily. At the end of each test, the coupon is removed from the cell and cleaned of its corrosion products by an abrasive Nylon pad. After rinsing with deionized water, the coupon is dried and weighed. The corrosion rate is calculated using the following formula:

$$\text{MMPY (MPY)} = \{[(A') - (B')] \frac{365 \text{ days}}{\text{year (yr.)}} \times \frac{25.4 \text{ mm (1000 mils)}}{2.54 \text{ cm (inch)}} \times \frac{25.4 \text{ mm (1 inch)}}{2.54 \text{ cm}}\} / [(C')(D)(E)]$$

MMPY (MPY) is mm per year (mils per year) where

A' is the initial weight of the coupon in grams (g)

B' is the final weight of the coupon in grams (g)

C' is the test duration in days measured to the nearest hour (t)

D is the density of the coupon (value used is 7.87g/cm<sup>3</sup>)

E is the area of the coupon (cm<sup>2</sup>)

**[0045]** The following Examples reported in Table I were run using the procedure described above. All tests were run in water containing 0.24% CaCl<sub>2</sub> to simulate a corrosive environment. An additional test, not reported in the table was performed using a commercial formulation containing nitrite. The formulation precipitated in the high hardness water and the test was discontinued. Based on the results shown, a mixture of sorbitol and gluconate provided superior corrosion protection to mild steel over a blank containing no corrosion inhibitors or sorbitol by itself. Localized pitting corrosion obtained using gluconate alone was lowered using the sorbitol/gluconate blend. Borax helped to further lower localized pitting corrosion.

TABLE I

| EX. | pH   | ppm<br><u>Sorbitol</u> | ppm<br>Na<br><u>Gluconate</u> | ppm<br><u>NaNO<sub>2</sub></u> | ppm<br><u>IT</u> | ppm<br><u>Borax</u> | Length<br>of Test<br>(days) | pH<br>Final | Pitting<br>(mpy)<br>mmPy | Pitting<br>sites | mpy<br>(mpy) |
|-----|------|------------------------|-------------------------------|--------------------------------|------------------|---------------------|-----------------------------|-------------|--------------------------|------------------|--------------|
| 1   |      | 1005                   | 1005                          |                                | 38               | 238                 | 10                          | 7.3         | (130) 3,30               | 50               | 0.49(19.3)   |
| 2   | 10.7 | 1870                   | 1870                          |                                | 70               | 440                 | 12.1                        | 7           | (50) 1.27                | 30               | 0.30(12)     |
| 3   | 9.3  | 743                    | 1003                          |                                | 38               | 478                 | 12.07                       | 7.6         | (50) 1.27                | 300              | 0.30(11.9)   |
| 4   | 10.0 |                        | 1670                          |                                |                  |                     | 7.6                         | 7.23        | (94) 2.39                | 100              | 0.31(12.3)   |
| 5   | 10   |                        |                               |                                |                  |                     | 7.6                         | 7           |                          |                  | 0.91(36)     |
| 6   | 10   | 1550                   |                               |                                |                  |                     | 7.6                         | 5.25        |                          |                  | 0.45(17.8)   |
| 7   | 10   | 1550                   | 1670                          |                                |                  |                     | 7.6                         | 7.26        | (64) 1.63                | 100              | 0.32(12.7)   |
| 8   | 10   |                        |                               | 395                            |                  |                     | 7.6                         | 7.78        |                          |                  | 0.02 (0.74)  |

**EXAMPLE 2**

**[0046]** The corrosion inhibitors of this invention were evaluated in a pilot high heat flux recirculating cooling unit. This unit consisted of a 946 l (250 gallon) tank equipped with a heat exchanger to allow regulation of the temperature in the tank, a bottom outlet leading to an adjustable recirculating pump. After the pump, water passed through a 240 volt copper clad electrical heater having a high output and back to the top opening of the tank. Sufficient electrical energy could be added to the heater. Temperature and flow could be monitored at several points. Corraters were installed to measure corrosion rates, and corrosion coupons could be added to the system.

**Compound A**

**[0047]** 26.5% - 50 wt. % Gluconic Acid  
 19.0% of 70% wt. % Sorbitol  
 8.4% 50% NaOH  
 1% of 50 wt. % Sodium Tolytriazole  
 3.13% Sodium Tetraborate 5H<sub>2</sub>O  
 balance-----water

**Low Conductivity Applications**

**[0048]** The first two experiments were performed on low conductivity systems and the conditions were as follows:

|                        |                                                                 |
|------------------------|-----------------------------------------------------------------|
| Water                  | Deionized water                                                 |
| Conductivity           | ≤ 100 μmhos                                                     |
| Heat Flux              | (150,000 Btu/hr-ft <sup>2</sup> ) 406 950 kcal/h·m <sup>2</sup> |
| Heater voltage         | 132 Volts                                                       |
| Velocity               | (5 ft/sec) 1,5 m/s                                              |
| Flowrate               | 12 gpm                                                          |
| Bulk Water Temperature | (135° F) 57°C                                                   |
| Skin Temperature       | 111°C (231° F) - of heater                                      |
| Heater Material        | Mild Steel                                                      |
| Corraters              | Mild Steel, Copper                                              |
| Coupon                 | Mild Steel                                                      |

**[0049]** Initially, to the water was added 55 ppm of Compound A, the preferred material as described on page 9 of the specification, and stabilized chlorine to provide 5 ppm of total residual chlorine. Upon the initial addition of stabilized chlorine, the conductivity of the water increased by about 30 μmhos. 55 ppm of Compound A did not provide enough corrosion protection on mild steel when 5 ppm of total chlorine were maintained in the system. Over a period of 44 hours, the corrosion rate on mild steel increased to 0,12 mm/year (4.80 mpy). During this time, the conductivity of the water was 55-70 μmhos. Since the maximum allowed conductivity for the test had not been reached, the dosage of Compound A was increased during the experiment so that the conductivity was 90-100 μmhos.

**[0050]** The final dosage of Compound A was approximately 300 ppm and total chlorine was 3.04 ppm. It was apparent that as the product dosage was increased, mild steel corrosion decreased over time. Over the next 120 hrs., the corrosion rate on mild steel decreased from 0,12 to 0,05 mm/year (4.80 to 1.80 mpy) and still appeared to be decreasing over time as the test was ended. Copper corrosion remained at approximately 0,0025 mm/year (0.10 mpy). The corrosion rate on the mild steel coupon was determined to be 0,07 mm/year (3.12 mpy), which was approximately the average corrosion rate for mild steel during the period. The heat transfer surface (mild steel) had a yellowish color with some raised, brownish spots and the unheated surface had more of the raised deposits, which left pits on the heater material. The deposit on the heated and unheated areas were analyzed and the analytical results showed that the material was approximately 99% iron as Fe<sub>2</sub>O<sub>3</sub> and less than 1% carbonate as CO<sub>2</sub>. There was less than 1% dichloromethane extractables.

**[0051]** A second test was run under the same operating conditions with the treatment program slightly different. Initially, 157 ppm of Compound A and 34 ppm of a commercially available non-oxidizing biocidal product (45% glutaraldehyde) was added to the system. The conductivity of the water was added to the system. The conductivity of the water was approximately 23 μmhos which was all from Compound A. There was no apparent increase in the conductivity of the water upon the addition of the biocide. During the test, an increase in mild steel corrosion was not observed.

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After 52 hours, mild steel and copper corrosion rates remained at 0,0025 mm/year (0.10 mpy). The corrosion rate on the mild steel coupon was 0,0 mm/year (0.0 mpy). The heat transfer surface felt smooth, had a shiny appearance, and no major discoloration was observed.

**[0052]** The next three tests were performed on a simulated continuous caster cooling system. Conditions were as follows:

|                               |                                                                                            |
|-------------------------------|--------------------------------------------------------------------------------------------|
| Water (as CaCO <sub>3</sub> ) | 13 ppm Calcium<br>6 ppm Magnesium<br>18 ppm Alkalinity<br>13 ppm Chloride<br>6 ppm Sulfate |
| Heat Flux                     | (300,000 Btu/hr-ft <sup>2</sup> ) 813900 kcal/h-m <sup>2</sup>                             |
| Heater Voltage                | 187 Volts                                                                                  |
| Velocity                      | (21 ft/sec) 6,30 m/s                                                                       |
| Flowrate                      | 52 gpm                                                                                     |
| Bulk Water Temperature        | (120° F) 49°C                                                                              |
| Skin Temperature              | (185° F) 85°C                                                                              |
| Heater Material               | Copper                                                                                     |
| Corraters                     | Mild Steel, Copper                                                                         |
| Coupon                        | Mild Steel                                                                                 |

**[0053]** The initial dosage of Compound A was 183 ppm with stabilized chlorine added to provide chlorine present at 5 ppm. During the first 35 hrs. the product dosage did not provide enough protection against corrosion when maintaining this dosage of chlorine. Mild steel corrosion increased from 0,015 to 0,030 mm/year (0.6 to 1.20 mpy) during that period. As a result, dosage of Compound A was increased to 300 ppm over the next 60 hours. As Compound A was added, corrosion rate on mild steel increased for a short period of time and then continued to again increase. Copper corrosion remained at .10 mpy for the duration of the test, while mild corrosion was increasing over time. The copper surface of the heater was smooth and no deposition or discoloration was observed. The corrosion rate that was obtained on the mild steel coupon was about 1,08 mm/year (20 mpy).

**[0054]** The next test was run under the same conditions as the previous, however the initial dosage of Compound A was 800 ppm. At this dosage, mild steel corrosion was 0,0089 mm/year (0.35 mpy). Stabilized chlorine to provide 5 ppm of total chlorine was initially added to the system in the form of a sodium salt of sulfamic acid + chlorine containing 7.9% as available chlorine = stabilized chlorine. However, it was observed that at the dosage of Compound A in the system, a rapid degradation of total chlorine occurred. During the first seventeen hours, total chlorine decreased to 0.52 ppm. Subsequently, stabilized chlorine to provide about 4.5 ppm total chlorine was added to the system. Several hours following the addition of biocide, total chlorine was measured at 3.42 ppm. Mild steel corrosion remained at about 0,008 mm/year (0.33 mpy) for the duration of the test, while copper was maintained at 0,0018 mm/year (0.07 mpy). The corrosion rate on the mild steel coupon was 0,0076 mm/year (0.30 mpy) which was in better agreement with corrater readings. The final total chlorine content was measured at about 0.1 ppm. Corrosion rate on copper and mild steel remained the same. At the end of the test, the copper heater was smooth and no deposition nor discoloration was observed.

**[0055]** The next test ran under the same operating conditions with the treatment program slightly varied. Initially, 300 ppm of Compound A and 60 ppm of a 1.5% by weight aqueous solution of 2-methyl-4-isothiazolin-3-one was added to the system. The corrosion rate on mild steel using this treatment program was about 0,0089 mm/year (0.35 mpy). Throughout the test, the dosage of Compound A was incrementally increased to determine the reduction in mild steel corrosion. At 450 ppm, Compound A corrosion rate decreased slightly to about 0,0076 mm/year (0.30 mpy). At 600 ppm, the change was minimal, and at 800 ppm, mild steel corrosion decreased to about 0,0064 mm/year (0.25 mpy). With the addition of 53 additional ppm of the biocide, corrosion rates remained the same. Copper corrosion remained at 0,0013 mm/year (0.05 mpy) for the duration of the test. The copper heater surface remained smooth and there was no deposition or discoloration on the heat transfer surface. Corrosion rate on the mild steel coupon was 0.0358 mm/year (1.41 mpy) which did not agree with the corrater readings due to the short length of time that the coupon remained in the water.

**[0056]** According to the above results, 300 ppm of Compound A provided satisfactory corrosior protection to mild steel in the presence of 5 ppm total chlorine. At this level, the conductivity of water is about 100 µmhos which leaves little room for dosage increase in systems requiring low conductivity. With 45 ppm of glutaraldehyde as a biocidal

treatment, 150 ppm of Compound A is recommended. This dosage maintained the conductivity of water at about 25  $\mu$ mhos which allows room for dosage increase if needed.

[0057] In the high heat flux test described above, higher levels of treatment chemical are required when biocide is added. However, the treatment program provided satisfactory results by lowering corrosion rates.

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## Claims

1. A method for the prevention of corrosion on metal surfaces in contact with a water based fluid having a conductivity of 100 micromhos or less in a closed cooling or heating system which method comprises maintaining in the fluid from 5 ppm to 4000 ppm of sorbitol, from 5 ppm to 4000 ppm of an alkali metal gluconate, and up to 700 ppm of borax as sodium tetraborate pentahydrate.
2. A method of claim 1 which comprises maintaining in the fluid from 40 ppm to 2000 ppm of sorbitol from 40 ppm to 2000 ppm of an alkali metal gluconate, and from 5 ppm to 200 ppm of borax.
3. The method of claim 1 or 2 wherein the fluid contains at least one additional ingredient selected from the group consisting of: inert fluorescent tracers, anti-foam compounds, biocide control agents, and yellow metal corrosion inhibitors.
4. The method of claim 3 wherein the yellow metal corrosion inhibitor is selected from the group consisting of: tolyltriazole, mercaptobenzotriazole, and benzotriazole.
5. The method of any of claims 1 to 4 wherein the fluid is water.
6. The method of claim 5 wherein the fluid is deionized water.
7. The method of any of claims 1 to 6 wherein the fluid is maintained at a pH of from 6.5 to 11.5.
8. The method of claim 7 wherein the fluid is maintained at a pH of from 7.5 to 9.5.
9. The method of any of claims 3 to 8 wherein an inert fluorescent tracer is added to the fluid in proportion to the amount of sorbitol present.
10. The method of any of claims 3 to 9 wherein a corrosion inhibitory package is added to the fluid, the package comprising in weight%:
  - 26.5 % of 50 weight% of gluconic acid
  - 19.0 % of 70 weight% of sorbitol
  - 8.4 % of 50 % of NaOH
  - 1 % of 50 weight% of sodium tolyltriazole
  - 3,13 % of sodium tetraborate pentahydrate
  - balance water.
11. A method for the prevention of scale and corrosion on metal surfaces in contact with aqueous fluids having a conductivity of 100 micromhos or less in closed cooling or heating systems which method comprises adding to the aqueous fluid present in such cooling or heating system a concentrate composition comprising (in weight%):
  - a) 2-25 % of sorbitol
  - b) 2-25 % of an alkali metal gluconate;
  - c) 0-9 % of borax and
  - d) balance water

in an amount sufficient to maintain in the fluid from 5 ppm to 4000 ppm of sorbitol,

from 5 ppm to 4000 ppm of an alkali metal gluconate and  
up to 700 ppm of borax as sodium tetraborate pentahydrate.

5 **Patentansprüche**

1. Verfahren zur Verhinderung der Korrosion auf Metalloberflächen, die mit einer Flüssigkeit auf Wasserbasis in Kontakt stehen, die eine elektrische Leitfähigkeit von 100 Mikromhos oder weniger aufweist, in einem geschlossenen Kühl- oder Heizsystem, wobei das Verfahren umfaßt das Aufrechterhalten in der Flüssigkeit von  
10 5 ppm bis 4000 ppm Sorbit,  
5 ppm bis 4000 ppm eines Alkalimetallgluconats und  
bis zu 700 ppm Borax als Natriumtetraborat-pentahydrat.
2. Verfahren nach Anspruch 1, das umfaßt das Aufrechterhalten in der Flüssigkeit von  
15 40 ppm bis 2000 ppm Sorbit,  
40 ppm bis 2000 ppm eines Alkalimetallgluconats und  
5 ppm bis 200 ppm Borax.
3. Verfahren nach Anspruch 1 oder 2, worin die Flüssigkeit mindestens einen zusätzlichen Bestandteil enthält, der ausgewählt wird aus der Gruppe, die besteht aus inerten fluoreszierenden Tracern, Antischaum-Verbindungen, biociden Kontrollmitteln und Gelbmetall-Korrosionsinhibitoren.  
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4. Verfahren nach Anspruch 3, worin der Gelbmetall-Korrosionsinhibitor ausgewählt wird aus der Gruppe, die besteht aus Tolyltriazol, Mercaptobenzotriazol und Benzotriazol.  
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5. Verfahren nach einem der Ansprüche 1 bis 4, worin die Flüssigkeit Wasser ist.
6. Verfahren nach Anspruch 5, worin die Flüssigkeit entionisiertes Wasser ist.
- 30 7. Verfahren nach einem der Ansprüche 1 bis 6, worin die Flüssigkeit bei einem pH-Wert von 6,5 bis 11,5 gehalten wird.
8. Verfahren nach Anspruch 7, worin die Flüssigkeit bei einem pH-Wert von 7,5 bis 9,5 gehalten wird.
- 35 9. Verfahren nach einem der Ansprüche 3 bis 8, worin ein inerte fluoreszierender Tracer der Flüssigkeit zugesetzt wird proportional zur Menge des vorhandenen Sorbits.
10. Verfahren nach einem der Ansprüche 3 bis 9, worin der Flüssigkeit ein Korrosionsinhibitor-Paket zugegeben wird, das (in Gew.-%) umfaßt:  
40 26,5 % von 50 Gew.-% Gluconsäure  
19,0 % von 70 Gew.-% Sorbit  
8,4 % von 50 % NaOH  
1 % von 50 Gew.-% Natriumtolyltriazol  
3,13 % Natriumtetraborat-pentahydrat  
45 Rest Wasser.
11. Verfahren zur Verhinderung von Scale-Bildung und Korrosion auf Metalloberflächen im Kontakt mit wäßrigen Flüssigkeiten, die eine elektrische Leitfähigkeit von 100 Mikromhos oder weniger aufweisen, in geschlossenen Kühl- oder Heizsystemen, wobei das Verfahren umfaßt die Zugabe zu der wäßrigen Flüssigkeit, die in einem solchen Kühl- oder Heizsystem vorliegt, einer Konzentrat-Zusammensetzung, die (in Gew.-%)umfaßt:  
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a) 2-25 % Sorbit  
b) 2-25 % eines Alkalimetallgluconats  
c) 0-9 % Borax und  
55 d) Rest Wasser

in einer Menge, die ausreicht, um innerhalb der Flüssigkeit aufrechtzuerhalten  
5 ppm bis 4000 ppm Sorbit,

5 ppm bis 4000 ppm eines Alkalimetallgluconats und  
bis zu 700 ppm Borax als Natriumtetraborat-pentahydrat.

## 5 Revendications

1. Procédé pour éviter la corrosion sur des surfaces métalliques qui sont en contact avec un liquide à base d'eau, ce liquide ayant une conductivité de 100 micromhos ou moins dans un système fermé de refroidissement ou de chauffage,  
le procédé comprenant le maintien dans le fluide de  
5 ppm à 4000 ppm de sorbitol,  
5 ppm à 4000 ppm d'un gluconate d'un métal alcalin et  
jusqu'à 700 ppm de borax en tant que pentahydrate de sodium tétraborate
2. Procédé selon la revendication 1, qui comprend le maintien dans le liquide de  
40 ppm à 2000 ppm de sorbitol  
40 ppm à 2000 ppm d'un gluconate d'un métal alcalin et  
5 ppm à 200 ppm de borax.
3. Procédé selon la revendication 1 ou 2, dans lequel le liquide contient au moins un composant additionnel choisi du groupe consistant de traceurs inertes fluorescents, de composés anti-mousse, de moyens de contrôle biocide et d'inhibiteurs de corrosion d'un métal jaune.
4. Procédé selon la revendication 3, dans lequel l'inhibiteur de corrosion d'un métal jaune est choisi du groupe composé par le tolyltriazole, le mercaptobenzotriazole et le benzotriazole.
5. Procédé selon l'une des revendications 1 à 4, dans lequel le liquide est de l'eau.
6. Procédé selon la revendication 5, dans lequel le liquide est de l'eau dèionisée.
7. Procédé selon l'une des revendications 1 à 6, dans lequel le liquide est maintenu à un pH de 6,5 à 11,5.
8. Procédé selon la revendication 7, dans lequel le liquide est maintenu à un pH de 7,5 à 9,5.
9. Procédé selon l'une des revendications 3 à 8, dans lequel un traceur inerte fluorescent est ajouté au liquide proportionnellement à la quantité du sorbitol présent.
10. Procédé selon l'une des revendication 3 à 9, dans lequel un paquet d'inhibiteur de corrosion est ajouté au liquide, le paquet contenant en % en poids:  
26,5% de 50% en poids d'acide gluconique  
19,0% de 70% en poids de sorbitol  
8,4 % de 50% en poids de NaOH  
1 % de 50% en poids de tolyltriazole de sodium  
3,13% de pentahydrate de sodium tétraborate  
le restant est de l'eau.
11. Procédé pour éviter la formation de tartre et la corrosion sur des surfaces métalliques en contact avec des liquides aqueux ayant une conductivité de 100 micromhos ou moins, dans des systèmes fermés de refroidissement ou de chauffage, ledit procédé comprenant l'addition au liquide aqueux présent dans un tel système de refroidissement ou de chauffage d'un concentré d'une composition comprenant (en % en poids):  
a) 2-25% de sorbitol  
b) 2-25% d'un gluconate d'un métal alcalin  
c) 0,9% de borax et  
d) le restant est de l'eau

dans une quantité suffisante pour maintenir au sein du liquide de  
5 ppm à 4000 ppm de sorbitol,

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5 ppm à 4000 d'un gluconate d'un métal alcalin et  
jusqu'à 700 ppm de borax en tant que pentahydrate de sodium tétraborate.

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