



11 Publication number:

0 652 305 A1

(2) EUROPEAN PATENT APPLICATION

(21) Application number: 94117381.7 (51) Int. Cl.6: C23F 11/12, C23F 11/08

② Date of filing: 03.11.94

③ Priority: 04.11.93 US 145556

Date of publication of application:10.05.95 Bulletin 95/19

Designated Contracting States:

DE FR GB IT

DESIGNATION

DESIGNAT

71 Applicant: NALCO CHEMICAL COMPANY
One Nalco Center
Naperville
Illinois 60563-1198 (US)

Inventor: Sotoudeh, Kaveh 1004 Bainbridge Drive Naperville, Illinois 60565 (US)

Representative: Ruschke, Olaf et al Ruschke & Partner Pienzenauerstrasse 2 D-81679 München (DE)

64 Closed cooling system corrosion inhibitors.

Novel closed cooling system corrosion preventatives are disclosed. The ingredients include sorbitol, an alkali metal gluconate, and borax. Optionally, yellow metal corrosion inhibitors such as tolyltriazole may be incorporated into the formulation. The mixture is particularly effective in high heat flux and low conductivity closed cooling systems.

BACKGROUND OF THE INVENTION

Introduction:

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.

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.

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 seperate use of gluconate and sorbitol in coolant systems, there is no disclosure of utilizing these ingredients in combination with each other.

In my copending application serial 08/079,702 filed June 17, 1992, the disclosure of which is hereinafter incorporated by reference, I have disclosed 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 my earlier filed application were tested as corrosion and scale inhibitors for non-brine systems, they performed well, at lower dosages than those required in my earlier filed application.

Objects of the Invention:

30

It is an object of this invention to provide to the art a practical scale and corrosion inhibitor formulation for use in closed system cooling and heating systems.

It is a further object of this invention to provide to the art an effective scale and corrosion control formulation for use in closed cooling and heating systems where nitrites, phosphonates, phosphates, metal inhibitors and soluble oils must be avoided.

It is a still a further object of this invention to provide to the art a scale and corrosion control formulation that would perform in normal closed system cooling systems, but which would also offer protection to mild steel in contact with closed cooling system liquids in high heat flux and low conductivity systems.

It is an additional object of this invention to provide a closed cooling system corrosion and scale inhibitor that would be satisfactory for use in critical systems including high heat flux and low conductivity systems. Further objects will appear hereinafter.

The Invention:

45 The Cooling Systems

The closed cooling systems to which the corrosion and scale inhibitors of this invention are applicable are those normally encountered in the heating and cooling systems of large buildings, machinery, metals processing and the like.

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.

As stated before, this invention finds particular utility in the treatment of high heat flux cooling systems. These systems are often designed to handle high temperature gradients and are often prone to scaling due to the great amount of heat being dissipated into the cooling system at any one time. Among the various

types of systems of this type that the corrosion and scale inhibitor of this invention find utility are those in: blast furnace tuyeres, electromagnetic stirrers, mold coolants, electric arc furnace cooling roofs, blast furnace hearth staves, electrode cooling, and basic oxygen furnace hood cooling systems.

Likewise, the corrosion and scale inhibitors of this invention are also find 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.

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 aquous coolant fluid.

Typical coolants to which this invention finds applicability are water based and contain from 0.1-1000 ppm of hardness expressed as Ca(CO3). Preferably, the coolants to which this invention finds applicability are water based and contain from 1.0-750 ppm of hardness expressed as Ca(CO3). Most preferably, the coolants to which this invention finds applicability are water containing as little as 0.5-500 ppm of hardness expressed as Ca(CO3).

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 1-100ppm of known copper corrosion inhibitors such as tolyltriazole, benzotriazole and mercaptobenzothiazole

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.

The Corrosion and Scale Inhibitors of this Invention

The corrosion and scale inhibitor of this invention is a blend of sorbitol and alkali metal gluconate. Optionally, alkali metal borate may be added. If yellow metals are present in the system, typical copper corrosion inhibitors such as tolyltriazole may also be added.

Generally, the corrosion and scale inhibitors of this invention are added in enough quantity to provide from 5 ppm to 4000 ppm of gluconate and from 5 ppm to 4000 ppm of sorbitol 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. Optionally, from 0 to 700 ppm of borate as sodium tetraborate pentahydrate may be added to the system and preferably from 5 ppm to 200 ppm of borate is added. In the most preferred embodiment of this invention, from 10 ppm to 60 ppm of borate as sodium tetraborate is added to the coolant liquid.

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.

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

More preferably a formulation for use in this invention will comprise:

10		90-15
10	Sodium Gluconate	3-20
	Sorbitol	3-20

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

0.5-7

Sodium Tetraborate

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

Compound A

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 5H₂O balance ------ water

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.

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, $Na_2B_4O_7$. While the sodium salt is preferred, other alkali metal tetraborate salts can be used.

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, hydrophobized silica, and the like. 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 U.S. Patents 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 U.S. 5,006,311 and U. S. 5,132,096 rather than the transition metal tracers described in U.S. 4,966,711 and U. S. 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.

20

25

30

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**, tetrabuthylazine*, methylenebisthiocyanate, and the like. 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.

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.

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

EXAMPLE 1

15

20

25

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:

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 1 foot/second using a magnetic stirrer. The constant temperature bath is heated to maintain 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 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 prefered.

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 $21.82~\text{cm}^2$ with a standard deviation of \pm 0.5 cm². Coupon surface is caluculated by:

```
Area (cm<sup>2</sup>) = 2(A)(B) + 2(A)(C) + 2(B)(C) - 2(2\pi r^2)

40

where A = length (cm)

B = width (cm)

C = thickness(cm)

\pi = pi = 3.142

r = Radius of the coupon hole
```

Procedure

55

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:

** a combination of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

^{* 2-(}tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine

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

5

10

where A' is the initial weight of the coupon in grams

B' is the final weight of the coupon in grams

C' is the test duration in days measured to the nearest hour

D is the density of the coupon (value used is 7.87g/cc)

E is the area of the coupon (cm²)

The following Examples reported in Table I were run using the procedure described above. All tests were run in water containing 0.24% CaCl₂ 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.

20

25

30

35

40

45

50

	хаш	19.3	12	11.9	12.3	36	17.8	12.7	0.74
5	Pitting Sitem	50	30	300	100			100	
10	pH Pitting <u>Final mpy</u>	130	20	50	94			64	
15	pH <u>Final</u>	7.3	7	7.6	7.23	7	5.25	7.26	7.78
20	Length of Test <u>(days)</u>	10	12.1	12.07	7.6	7.6	7.6	7.6	7.6
25 2 5	ppm Borax	238	440	478					
30	TI	38	70	38					
	ppm <u>NaNO</u> 2								395
35	ppm Na <u>Gluconate</u>	1005	1870	1003	1670			1670	
40	ppm Sorbitol	1005		743			1550	1550	
45	ਮੁਰ		10.7	9.3	10.0	10	10	10	10
50	EX.	7	2	Э	4	S	9	7	80

EXAMPLE 2

55

The corrosion inhibitors of this invention were evaluated in a pilot high heat flux recirculating cooling unit. This unit consisted of a 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

5

10

30

26.5% - 50 wt. % Gluconic Acid 19.0% of 70% wt. % Sorbitol 8.4% 50% NaOH 1% of 50 wt. % Sodium Tolyltriazole 3.13% Sodium Tetraborate 5H₂O balance-----water

15 Low Conductivity Applications

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

20	Water	Deionized water
	Conductivity	≦ 100 µmhos
	Heat Flux	150,000 Btu/hr-ft ²
	Heater voltage	132 Volts
0.5	Velocity	5 ft/sec
25	Flowrate	12 gpm
	Bulk Water Temperature	135° F
	Skin Temperature	231 ° F - of heater
	Heater Material	Mild Steel
	Corraters	Mild Steel, Copper

Coupon

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 μ mhos. 55 ppm of Compound A did not 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 4.80 mpy. During this time, the conductivity of the water was 55-70 μ mhos. 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 μ mhos.

Mild Steel

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 4.80 to 1.80 mpy and still appeared to be decreasing over time as the test was ended. Copper corrosion remained at approximately 0.10 mpy. The corrosion rate on the mild steel coupon was determined to be 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_20_3 and less than 1% carbonate as CO_2 . There was less than 1% dichloromethane extractables.

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 commerically available non-oxidizing biocidal product (45% gluteraldehyde) was added to the system. The conductivity of the water was added to the system. The conductivity of the water was approximately 23 μ mhos 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. After 52 hours, mild steel and copper corrosion rates remained at 0.10 mpy.

The corrosion rate on the mild steel coupon was 0.0 mpy. The heat transfer surface felt smooth, had a

shiny appearance, and no major discoloration was observed.

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

5

10

15

20

55

Water (as CaCO ₃)	13 ppm Calcium 6 ppm Magnesium 18 ppm Alkalinity 13 ppm Chloride 6 ppm Sulfate
Heat Flux Heater Voltage Velocity Flowrate Bulk Water Temperature Skin Temperature	300,000 Btu/hr-ft ² 187 Volts 21 ft/sec 52 gpm 120° F 185° F
Heater Material Corraters Coupon	Copper Mild Steel, Copper Mild Steel

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 0.6 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 20 mpy.

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 0.35 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 0.33 mpy for the duration of the test, while copper was maintained at 0.07 mpy. The corrosion rate on the mild steel coupon was 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.

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 0.35 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 0.30 mpy. At 600 ppm, the change was minimal, and at 800 ppm, mild steel corrosion decreased to about 0.25 mpy.

With the addition of 53 additional ppm of the biocide, corrosion rates remained the same. Copper corrosion remained at 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 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.

According to the above results, 300 ppm of Compound A provided satisfactory corrosion protection to mild steel in the presence of 5 ppm total chlorine. At this level, the conductivity of water is about 100 μ mhos 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 µmhos which allows room for dosage increase if needed.

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.

Claims

1. A method for the prevention of corrosion on the metal surfaces in contact with a coolant fluid in a closed cooling system which comprises maintaining in the coolant fluid from 5 ppm to 4000 ppm of sorbitol and from 5 ppm to 4000 ppm of an alkali metal gluconate.

2. The method of claim 1 wherein the coolant fluid is water.

- 3. The method of claim 1 or 2 wherein the closed cooling system is a low conductivity cooling system.
- 4. The method of claim 1 or 2 wherein the closed cooling system is a high heat flux cooling system. 15
 - 5. The method of claim 1 wherein up to 700 ppm of borax as sodium tetraborate pentahydrate is added to the cooling system.
- 6. A method for the prevention of corrosion on metal surfaces in contact with an aqueous coolant fluid in a closed cooling system which comprises maintaining in the coolant fluid from 40 ppm to 2000 ppm of an alkali metal gluconate, from 40 ppm to 2000 ppm of sorbitol and from 5 ppm to 200 ppm of borax.
 - 7. The method of claim 6 wherein the closed cooling system is a high heat flux cooling system.

8. The method of claim 6 wherein the closed cooling system is a low conductivity cooling system.

- The method of any of claims 6 8 wherein the coolant fluid contains at least one additional ingredient selected from the group consisting of: inert fluroscent tracers, anti-foam compounds, biocide control agents.
- 10. The method of any of claims 6 9 wherein an effective amount of yellow metal corrosion inhibitor from the group consisting of tolyltriazole, mercaptobenzotriazole, and benzotriazole is added to the closed cooling system.
- 11. The method of any of claims 6 10 wherein the coolant fluid contains from .1 ppm to 1000 ppm of hardness expressed as CaCO₃.
- 12. The method of any of claims 6 11 wherein the coolant fluid is maintained at a pH of from 6.5 to 11.5.
- 13. A method for the prevention of corrosion on metal surfaces in contact with an aqueous coolant fluid present in a closed cooling system which comprises maintaining in the aqueous coolant fluid from 40 to 2000 ppm of an alkali metal gluconate, from 40 ppm to 2000 ppm sorbitol, from 5 ppm to 200 ppm of borax (as sodium tetraborate pentahydrate) and maintaining such coolant fluid at a pH of 7.5 to 9.5.
- 14. The method of claim 13 wherein an inert fluroscent tracer is added to the aqueous coolant fluid in proportion to the amount of sorbitol present.
- 15. The method of claim 13 or 14 wherein the aqueous coolant fluid is deionized water.
- 16. The method of any of claims 13 -15 wherein an effective amount of an oxidizing biocide is added to the coolant fluid to prevent microbiological growth.
- 17. The method of any of claims 13 -16 wherein an effective amount of an antifoam agent is added to the coolant fluid to prevent foaming. 55
 - 18. A composition for controlling scale and corrosion on the surfaces of metal in contact with aqueous coolant fluids in closed cooling systems which comprises adding to such system an effective amount of

25

30

40

45

50

5	 a composition comprising: a. to 2-25% sorbitol; b. to 2-25% alkali metal gluconate; and, c. to 0-9% borax. d. balance water.
10	19. A method for the prevention of scale and corrosion on the surfaces of metal in contact with aqueous coolant fluids in closed cooling systems which comprises adding to the aqueous coolant fluid present in such cooling system an effective amount of the composition of claim 18.
15	
20	
25	
30	
35	
40	
45	
50	
55	

EUROPEAN SEARCH REPORT

Application Number EP 94 11 7381

		DERED TO BE RELEVA	NT	
Category	Citation of document with i of relevant pa	ndication, where appropriate, ssages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,P, X	US-A-5 330 683 (SUF	·	1,5,6, 10-13,19	C23F11/12 C23F11/08
	* column 3; claims	1-19 *		
Y	DE-A-39 04 733 (KUR	RITA WATER INDUSTRIES)	1-4, 7-12, 14-19	
Y	* table 2, comparat	ive examples *	5,6,13	
Y	GB-A-2 027 002 (CHE	EMED CORP.)	1-4, 7-12, 14-19	
	* page 1, line 3 -	line 12; claim 1 *		
Y	GB-A-910 138 (IMPER INDUSTRIES) * claims 1,9 *	RIAL CHEMICAL	5,6,13	
A	WERKSTOFFE UND KORF February 1989, page 89-0560,	ROSION, vol. 40, no. 2 RA46, abstract no.	, 6,13	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
:	Weinheim, DE;			C23F
A	EP-A-0 451 434 (DEN * claim 1 *	NAC N.V.)	1-9	
A	FR-A-2 054 945 (ESS ENGINEERING CO.)	SO RESEARCH AND		
A	GB-A-2 162 507 (MIS	SAWA HOME K.K.)		
A	PATENT ABSTRACTS OF vol. 7, no. 185 (C- 1983	F JAPAN -181) (1330) 17 August		
		(SEIWA KOGYO K.K.) 31		
	abscrace	-/		
	The present search report has	been drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	22 December 1	994 Tor	rfs, F
Y: pai do A: tec O: no	CATEGORY OF CITED DOCUMP rticularly relevant if taken alone rticularly relevant if combined with an cument of the same category chnological background n-written disclosure ermediate document	E: earlier paten after the fili nother D: document ci L: document ci	ted in the application ted for other reasons	ished on, or



EUROPEAN SEARCH REPORT

Application Number / EP 94 11 7381

Category	Citation of document with in of relevant par	dication, where appropriate, sages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL6)		
A	EP-A-0 112 756 (BP	CHEMIE S.A.)				
A	EP-A-0 470 553 (BAS	F CORP.)				
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)		
	The present search report has b	een drawn up for all claims				
	Place of search	Date of completion of the search		Examiner		
	THE HAGUE	22 December 19	94 To:	rfs, F		
X : par Y : par do:	CATEGORY OF CITED DOCUMENT ticularly relevant if taken alone ticularly relevant if combined with and tument of the same category	E : earlier patent after the filing other D : document cite L : document cite	document, but put gdate d in the applicatio d for other reasons	olished on, or On		
O: no	hnological background n-written disclosure ermediate document	& : member of the same patent family, corresponding document				