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(54) Titre : NETTOYANT LIQUIDE POUR METAUX POUR SYSTEME AQUEUX

(54) Title: LIQUID METAL CLEANER FOR AN AQUEOUS SYSTEM

(57) **Abrégé/Abstract:**

The invention relates to a composition useful for cleaning metal surfaces immersed in an aqueous system. The composition comprises as a mixture: an organic carboxylic acid; an alkanolamine; an amino polycarboxylic acid or alkali metal salt; and a sulfur-containing polymer.

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(54) Title: LIQUID METAL CLEANER FOR AN AQUEOUS SYSTEM (57) Abstract The invention relates to a composition useful for cleaning metal surfaces immersed in an aqueous system. The composition comprises as a mixture: an organic carboxylic acid; an alkanolamine; an amino polycarboxylic acid or alkali metal salt; and a sulfur-containing polymer.		

LIQUID METAL CLEANER FOR AN AQUEOUS SYSTEM

FIELD OF THE INVENTION

The invention relates to a liquid composition useful for
5 cleaning metal surfaces immersed in an aqueous system. The
composition comprises as a mixture: a carboxylic acid; an
alkanolamine; a chelating agent or alkali metal salt thereof;
and preferably a sulfur-containing polymer.

10 BACKGROUND OF THE INVENTION

Cooling systems remove waste heat from industrial
processes through a heat transfer mechanism. Since water is
the medium for removing heat from the system, metal parts in
the cooling system can become corroded. Such metal parts in
15 the cooling system may include chiller systems, heat
exchangers, auxiliary equipment and system piping.

Corrosion of metal parts results from the oxidation of
the metal when exposed to an oxidizing compound. Corrosion is
an electrochemical process in which a difference in
20 electrical potential (voltage) develops between two metals or
between different parts of a single metal. This potential can
be measured by connecting the metal to a standard electrode
and determining the voltage. The potential generated can be
expressed as positive or negative. A corrosion cell is then
25 produced in which the current passing through the metal
causes reactions at the anode (area of lower potential) and
cathode (area of higher potential).

The following shows the sequence of events as metal
becomes oxidized: (1) Fe^0 is lost from the anode to the bulk
30 water solution and becomes oxidized to Fe^{2+} . (2) Two
electrons are released through the metal to the cathode. (3)
Oxygen in the water solution moves to the cathode and forms
hydroxyl ions at the surface of the metal producing ferrous
hydroxide.

WO 98/21304

PCT/US97/14149

Ferrous hydroxide precipitates quickly on the metal surface as a white floc and is further oxidized to ferric hydroxide. When these reaction products remain at the cathode, a barrier is formed that physically separates the O₂ in the water from the electrons at the metal surface. This process is called polarization and protects the metal from further corrosion by minimizing the potential between the anode and the cathode. Removal of this barrier, called depolarization, through lowering of the pH or by increasing the velocity of the water produces further metal oxidation and the detrimental corrosion products of ferric or iron oxide, and rust.

Prefilming or passivation of equipment is a common practice in extending the life of equipment in aqueous systems. When equipment is new, a chemical corrosion inhibitor is added initially to form an impervious film to halt corrosion. Once the protective film is formed, a small amount of a corrosion inhibitor is continuously required to maintain the film and inhibit corrosion. However, changes in a cooling system environment such as low pH excursions, process leakage, microbiological deposition, organic and inorganic fouling can cause disruption and penetration of the protective film allowing production of corrosion products.

The corrosion can manifest itself in various forms such as uniform attack, pitting or tuberculation to name a few. Significant amounts of rust reduce heat transfer efficiency and can accelerate corrosion rates by the formation of concentration cells under the corrosion deposit. This can negatively affect the overall operation of a cooling system resulting in reduced operating efficiency, increased maintenance costs and down time as well as shortened equipment life. Once iron oxide is present in significant

WO 98/21304

PCT/US97/14149

amounts, cleaning of the equipment to remove the corrosion products is necessary.

The current practice for years in iron oxide removal was to shut down the system and add an acid cleaner containing
5 hydrochloric, sulfuric, sulfamic, gluconic or citric acids, reducing the pH to 3.0 to 3.5, and circulating the solution for several hours with heat. This process can be very corrosive to the base metal of equipment causing increased metal loss once the iron oxide is removed. Holes in the metal
10 of critical equipment can be created quickly, resulting in process leakage and/or reduced operating efficiency. In addition, the handling of large amounts of strong acids can be hazardous for plant employees. Another method for removing corrosion from metals exposed to an aqueous system,
15 is to circulate high concentrations of a chelant like ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) to sequester and bind iron. This can be cost-prohibitive since it can result in large amounts of chelant consumed in heavily fouled systems as it functions
20 stoichiometrically.

Just recently, several neutral-type on and off-line treatments were brought to the marketplace. These methods usually involve a much longer treatment time and may utilize tannins or similar-type compounds which can ultimately be
25 used by microbes as a nutrient source creating a deposition problem. These compounds generally have only a 50% rate of conversion of insoluble Fe^{3+} to a more soluble form, Fe^{2+} resulting in less than efficient cleaning. Moreover, a neutralizer or acid addition step requiring additional
30 chemical cost and handling is generally necessary with the neutral cleaners to aid in iron oxide removal and pH control.

U.S. Patent 3,527,609 discloses a two stage method of removing iron oxide: (1) adding an alkali metal salt or

WO 98/21304

PCT/US97/14149

ammonium salt of amino polycarboxylic acid to a recirculating system while adjusting pH to 8-11 then (2) acidifying system water to pH to 4-5.5 with sulfuric acid to remove iron oxide. U.S. Patent 5,466,297 explains a method for removing iron oxide and recycling ferrous/ferric compounds with the use of a citric acid-tannin and erythorbic acid blend while adjusting the pH of the cooling water system to a range of 1-5. Canadian Patent 1,160,034 teaches a method of removing iron oxide by adding 3-300 ppm of a sulfated glyceryl trioleate and 2-hepto-1-(ethoxy propionic acid) imidazoline into an acid cleaner. The multi-component product is then applied to maintain a pH of 1-6 to clean rust and other deposits in a cooling system.

15 SUMMARY OF THE INVENTION

This invention relates to a metal cleaner for an aqueous system comprising as a mixture:

- (1) a carboxylic acid;
- (2) an alkanolamine;
- 20 (3) a chelating agent or an alkali metal salt thereof; and preferably
- (4) a sulfur-containing polymer.

The metal cleaner is a liquid blend of components that displays excellent performance in removing metal oxides in aqueous systems including industrial, commercial and marine applications. Aqueous systems that may benefit from treatment with this metal cleaner include open and closed recirculating cooling water systems as well as diesel engine cooling systems.

Iron oxides are effectively removed on-line or off-line, depending on the severity of the iron fouling, without subjecting the system metallurgy to acidic, corrosive pH

WO 98/21304

PCT/US97/14149

levels. Additionally, the iron oxide that is removed is preferably dispersed and suspended in the bulk water so that redeposition on equipment surfaces is not likely to occur. The composition preferably contains a surfactant and solvent
5 for penetrating, removing and dispersing organic contamination in the aqueous system as well.

The invention also relates to a method of removing corrosion products, such as rust and iron oxide deposits from metal surfaces which come into contact with an aqueous
10 system. Examples of such metal surfaces include chiller systems, heat exchangers, auxiliary equipment and system piping using a unique cleaning formulation.

BEST MODE AND OTHER EMBODIMENTS OF THE INVENTION

15 The carboxylic acid used in the metal cleaner may be a mono-, di-, or polycarboxylic acid having a least two carbon atoms. Examples include, but are not limited to, acrylic acid, polyacrylic acid, polymethacrylic acid, acetic acid, hydroxyacetic acid, gluconic acid, formic acid and citric
20 acid. Citric is the preferred carboxylic acid due to its commercial availability and economic feasibility.

The amine can be, for example, morpholine, cyclohexylamine, an ethylamine, or an alkanolamine. The preferred amine is an alkanolamine. Preferably, the
25 alkanolamine is an ethanalamines such as monoethanolamine, diethanolamine, or triethanolamine. Triethanolamine is the preferred alkanolamine due to the resultant amine-citrate salt formed by its neutralization with citric acid. The amine-citrate shows improved performance when compared to a
30 salt formed by the neutralization of citric acid with sodium hydroxide.

The preferred chelating agents are amino polycarboxylic acids or alkali metal or ammonium salt thereof. Examples of

WO 98/21304

PCT/US97/14149

such chelating agents are ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), pentasodium diethylenetriaminepentaacetic and their salts. Alkali metal salts are preferred. The most preferred chelating agent is
5 the sodium salt of EDTA.

The addition of a sulfur-containing polymer is highly preferred because this component retards the redeposition of corrosion products by dispersing them or suspending them in water. The sulfur-containing polymer can be any sulfonated
10 polymer with a molecular weight between 100 and 50,000. The preferred polymer is AQUATREATTM AR-540 available from Alco Chemical.

The amounts of the various components in the metal cleaner are as follows:

15

(a) from about 1 to about 40 parts of carboxylic acid, preferably from about 10 to about 20 parts;

20

(b) from about 15 to about 25 parts of an amine, preferably an alkanolamine, preferably from about 15 to about 20 parts;

25

(c) from about 1 to about 20 parts of a chelating agent, or an alkali metal or ammonium salt thereof, preferably from about 2 to about 5 parts; and

(d) from about 0.5 to about 15 parts of a sulfonated polymer, preferably from about 1 to about 10 parts;

30

where all parts are based upon the total weight of the metal cleaner including water.

WO 98/21304

PCT/US97/14149

Preferably the weight ratio of carboxylic acid to alkanolamine is from 3:1 to 1:3, preferably 1:1.3. The weight ratio of chelating agent to alkanolamine is from 1:2 to 1:6. The weight ratio of the sulfonated polymer to alkanolamine is from 1:4 to 1:6. Preferably the weight ratio of carboxylic acid to alkanolamine is from 3:1 to 1:3, preferably 1:1.3. The weight ratio of chelating agent to alkanolamine is from 1:3 to 1:10. The weight ratio of the sulfonated polymer to alkanolamine is from 1.0:1.5 to 1.0:20.0.

The formulation may also contain one or more surfactants. The surfactant may be anionic, cationic, amphoteric, nonionic and/or mixtures, except that mixtures of cationic and anionic surfactants should be avoided, and are used in amounts of 1 to 5 weight percent, based upon the weight of the metal cleaner. Additionally, the formulation may contain 0.1 to 1.0 weight percent, based upon the weight of the metal cleaner, of a corrosion inhibitor for soft metals, sodium hydroxide to provide product neutrality and 0.1 to 1.0 weight percent, based upon the weight of the metal cleaner, of an antifoam to inhibit any foam generated by the surfactants.

The metal cleaner is typically used by pumping it into the water system to be cleaned, for instance a cooling tower, where it is recirculated with the recirculating water of the cooling tower at a typical velocity of about 3 ft/second to 7 ft/second. The temperature of the metal to be cleaned is usually similar to the temperature of the water in the system to be cleaned, usually about 35-55°C except if the metal is part of a heat exchanger in which case the metal could reach a temperature of 80-95°C. The cleaner is formulated to be effective at these temperatures as well. Of course, higher temperatures result in quicker removal and cleaning. The

WO 98/21304

PCT/US97/14149

cleaner will by itself as long as the pH is less than about 7.5.

5 An effective amount of the metal cleaning composition needed to remove iron oxide deposition continuously in lightly fouled on-line systems ranges from 50-10,000 ppm. The effective amount of the iron oxide remover necessary to clean heavily fouled systems in a practically short time ranges from 0.5 - 20%, preferably 1 - 10%.

10 The effective amount of the iron oxide remover necessary to clean heavily fouled systems in a practically short time ranges from 0.5 - 20%, preferably 1 - 10% (10,000 - 100,000 ppm). Depending on system metallurgy and operating conditions, these higher concentrations may be used on-line or off-line. By off-line it is meant circulating the cooling
15 water in the system to be cleaned without the heat load, so that in an open, recirculating system it is unnecessary to pass it through a cooling tower, or to reduce solids content by blowdown except as dictated by the cleaning process. This is usually done when the system is failing due to the heavy
20 deposit or corrosion problems. The high concentration cleaning usually last for 24 hours to two weeks depending on the severity of the problem and whether heat, which will shorten the required time, is available.

EXAMPLES

Experiments were run to determine efficacy of the iron oxide removal formulations. The letter examples represent
5 blanks or comparisons while the numbered examples are tests within the scope of this invention. Examples D-F and 7-12 show the effectiveness of the cleaners in on-line cleaning at a 10% concentration over a 14 day period at a temperature of about 23°C to about 27°C. The metal cleaning formulations
10 used in Examples F-E to 7-12 were as follows:

- A = Blank (no metal cleaner).
- 15 B = comparison cleaner, DREWGARD® metal cleaner, which is a blend of TEA, soy amine, and surfactants having a pH=12.
- C = blend of 15% citric acid, 20% TEA, 3% EDTA and surfactants having a pH = 8.96.
- 20 1 = blend of 23% citric acid, 20% AMP-95¹, 5% EDTA + surfactants having a pH = 5.5
- 2 = blend of 15% citric acid, 13% AMP-95, 5% EDTA +
25 surfactants having a pH = 5.5
- 3 = blend of 15% citric acid, 20% TEA, 5% EDTA and surfactants having a pH = 6.3
- 30 4 = blend of 15% citric acid, 20% TEA, 5% EDTA and surfactants having a pH = 5.5

¹2-amino-methyl-proponal (95% active).

WO 98/21304

PCT/US97/14149

5 = blend of 3.6% Citric Acid, 25% EDTA having a pH =
 5.9

6 = blend of 15% Citric Acid, 20% TEA, EDTA,
5 copolymer + surfactants having a pH = 6.1

 The experimental protocol was such that mild steel C-
1010 coupons were rusted for a period of two to four weeks to
develop a thick and heavy iron oxide deposit. After rusting,
10 the coupons were dried at 25°C for one week to strongly bind
the iron oxide to the metal substrate. The rusted coupons
were then employed in iron oxide removal evaluations using a
laboratory shaker. At that time, the coupons were suspended
in flasks containing tap water and a molybdate-based
15 corrosion inhibitor. Then the respective metal cleaning
treatments (A-C and 1-6) were added to the flasks and the
flasks were placed in the laboratory shaker. The speed of the
shaker was set to 150-160 rpm. Various test conditions were
used to evaluate the effectiveness of the metal cleaners.
20 The results are summarized in Table I.

 After the cleaning period, the cleaning solutions were
filtered through a 0.45 micron filter and analyzed to measure
the dissolved filterable iron (dfe). The % iron oxide removal
was also determined by weight reduction. Each sample was
25 tested five times to determine statistically significant
results.

TABLE I

EXAMPLES D-F and 7-12
ON-LINE CLEANER AT A 10% DOSAGE OVER 14 DAYS
AT ABOUT 23°C AND 27°C

5

EXAMPLE	METAL CLEANER	DOSAGE	pH (i)	pH (f)	dfe (ppm)	% Iron Oxide Removal
D	A	0	7.85	7.71	0.1	1.7
E	B	10.0%	5.90	7.50	NA	5.1
F	C	10.0%	8.96	8.95	3.2	3.2
7	1	10.0%	4.94	7.69	NA	38.3
8	2	10.0%	4.96	8.17	NA	30.9
9	3	10.0%	6.11	7.65	3806. 0	17.2
10	4	10.0%	5.10	7.13	6600. 0	66.0
11	5	10.0%	5.60	7.62	5287. 0	30.1
12	6	10.0%	6.31	7.21	5024. 0	64.7

Examples A-F and 7-12 show the effectiveness of the cleaners in on-line cleaning at a 10% concentration over a 14 day period at a temperature of about 23°C to about 27°C. The results indicate that a significant improvement in metal cleaning is achieved when cleaners within the scope of the subject invention are used. Comparisons F shows that the pH of the cleaner is significant. Also note that in Example 10 and 12, 66% and 64.75 iron removal was achieved. This is several times the amount removed when compared to the existing available technology as seen by the competitive product (B). Not only was iron oxide removal better, but more importantly, the iron oxide removed is completely dispersed in the water as indicated by the dissolved iron levels (DFE) and not removed as chips. The dissolved iron

TABLE II
EXAMPLES K-M and 15-16
ON-LINE CLEANER AT A 10% DOSAGE OVER 24 HOURS AT ABOUT 66°C

5

EXAMPLE	METAL CLEANER	DOSAGE	pH (i)	pH (f)	DFE (ppm)	% Iron Oxide Removal
K	G	0	7.96	8.53	< 0.1	5.2
L	H (no TEA)	10.0%	5.88	8.81	NA	16.4
M	I	10.0%	7.88	9.09	621	7.9
N	J	10.0%	5.73	8.52	1465	15.9
15	13	10.0%	5.14	7.37	4313	71.1
16	14	10.0%	5.12	7.09	5003	75.9

The laboratory study at higher temperatures simulated the procedure used to clean diesel engine jackets and loops in marine applications. Cleaning is accelerated and more complete with the use of formulations of this invention as shown by the high iron oxide removal percentages (> 71%). Comparison Example L shows the need for TEA in the formulation.

15

EXAMPLES R-S and 20-22

Examples R-S and 20-22 show the effects of using the metal cleaner at a 1% dosage. The formulation for the metal cleaners used in Examples R-S and 20-22 are as follows:

20 O = blank (no metal cleaner).

P = Comparison Product which is a blend of 7% phosphonate, surfactants, sodium sulfite, and caustic having a pH of 6.3).

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WO 98/21304

PCT/US97/14149

- Q = Competitive Product L with TEA added in place of the caustic to a pH of 6.3.
- 17 = blend of 15% Citric Acid, 20% TEA, EDTA, and
5 surfactants having a pH = 5.5.
- 18 = blend of 15% Citric Acid, 20% TEA, EDTA, and surfactants having a pH = 6.3.
- 10 19 = blend of 15% citric acid, 20% TEA, EDTA, polymer + surfactants having a pH = 6.5.

The results are summarized in Table III.

TABLE III

EXAMPLES R-T and 20-22
ON-LINE CLEANING AT A 1% DOSAGE OVER 14 DAYS
AT ABOUT 23°C TO ABOUT 27°C

5

EXAMPLE	METAL CLEANER	DOSAGE	pH (i) ²	pH (f) ³	DFE (ppm)
R	O	0	7.89	7.49	0.1
S	P	1.0%	6.32	7.08	255
T	Q	1.0%	6.31	7.92	397
20	17	1.0%	5.14	7.14	1490
21	18	1.0%	6.34	7.99	765
22	19	1.0%	6.34	7.97	830

The results indicate that a significant amount of iron
10 is dissolved with the citric acid/alkanolamine blends at 1%
concentration when compared to the blank and the competitive
product. An amount of alkanolamine was added to the
competitive product in an effort to enhance performance and
to verify the effectiveness of the TEA in removing iron. The
15 data shows that the dissolved iron level was increased by
over 55% with the use of TEA. The data also confirms the
synergistic behavior between citric acid and TEA for
solubilizing iron since the dissolved iron levels were
approximately 3-6 times that of the competitive product.

20

² i = initial³ f = final

CLAIMS

We claim:

1. A process for removing corrosive deposits from a metal surface exposed to an aqueous system where said process comprises:

contacting an effective amount of a metal cleaner in the range of 0.5 to 20 weight percent of the aqueous system to a metal surface exposed to the aqueous system where the pH of said metal cleaner is 5.0 to 7.5 and said metal cleaner comprises:
 - (a) from about 1 to about 40 parts by weight of citric acid;
 - (b) from about 15 to about 25 parts by weight of an alkanolamine;
 - (c) from about 1 to about 20 parts by weight of EDTA, alkali metal salts thereof, or ammonium salts thereof, and
 - (d) water,where said parts by weight are based upon 100 parts of metal cleaner, and whereby corrosive deposits are removed from said metal surface.
2. The process of claim 1 wherein the metal cleaner is present in the range of 1 to 10 weight percent.
3. The process of claim 1 or 2 where the process is carried out a temperature of 20° C to 100° C.
4. The process of claim 1 or 2 where the metal cleaned is selected from the group consisting of iron and steel.
5. The process of claim 4 where the corrosive deposit removed from the metal is iron oxide or rust.

6. The process of claim 1 or 2 where the process is carried out on-line.
7. The process of claim 1 or 2 where the process is carried out off-line.
8. The process of claim 1 or 2 which additionally contains a sulfur-containing polymer.
9. The process of claim 1 or 2 where the alkanolamine is triethanolamine.
10. The process of claim 1 or 2 wherein the metal cleaner comprises:
 - (a) from about 10 to about 20 parts by weight of the citric acid;
 - (b) from about 15 to about 20 parts by weight of triethanolamine;
 - (c) from about 1 to about 20 parts by weight of the ethylenediaminetetraacetic acid;
 - (d) from about 0.5 to about 15 parts by weight of a sulfonated polymer;
 - (e) water; and
 - (f) a surfactant in the amount of 1 to 5 weight percent, based on the weight of the metal cleaner.