

(19)



(11)

EP 1 950 327 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

30.07.2008 Bulletin 2008/31

(51) Int Cl.:

C23G 1/08 (2006.01)

C23G 1/24 (2006.01)

C02F 1/68 (2006.01)

C02F 1/70 (2006.01)

C02F 5/10 (2006.01)

F28F 13/18 (2006.01)

(21) Application number: **07101166.2**

(22) Date of filing: **25.01.2007**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI
SK TR**

Designated Extension States:

AL BA HR MK

(72) Inventor: **Wijnia, Christiaan, Reinder**
4571 CX Axel (NL)

(74) Representative: **Beetz, Tom et al**
De Vries & Metman
Overschiestraat 180
1062 XK Amsterdam (NL)

(71) Applicant: **PURAC Biochem BV**
4206 AC Gorinchem (NL)

(54) **Method for derusting metallic surfaces**

(57) The invention pertains to a method for derusting a metallic surface by bringing the surface in contact with an aqueous solution of a buffer having a pH between 5.1 and 6.5, wherein the buffer comprises lactic acid and the

sodium, potassium and/or ammonium salt of lactic acid. A preferred combination is a lactic acid-ammonium lactate buffer.

EP 1 950 327 A1

Description

[0001] The invention relates to a novel method for derusting metallic surfaces.

[0002] Rust forming on metal surfaces is a common problem in industry. As a result of the formation of rust deposits, pit corrosion occurs inside steel pipes. Pit corrosion can damage, and causes leakage in pipes. Therefore, cooling installations frequently have to shut down and as a direct result, also the plant for intensive inspection. This all is very time consuming and very expensive. It is known to use lactic acid for rust removal, but this product has the disadvantage that when applied during longer periods itself causes corrosion.

[0003] Throughout the years many methods have been proposed to tackle these problems. Notwithstanding these many published methods the following problems have not fully been solved. Thus removal of rust in production plant installations often require considerable shut down times, derusting compositions may be environmental hazardous, or such compositions may be expensive. Further, derusting usually is accompanied with damaging the metallic surface.

[0004] Some of these problems have been solved in WO 2005/033365. This patent application discloses on page 3 the use of solutions of citric acid, or other organic hydroxy acids, for derusting steel parts. In particular citric acid is preferred, optionally in a mixture with a citrate such as ammonium citrate. An ammonium salt of said acid may further be used as buffer for these acid solutions. Such solutions should have a pH between 2.5 and 5 in order to obtain sufficient derusting, and further contain tin sulfate for reducing iron (III) to iron (II) ions. Instead of citric acid also mixtures of lactic acid or tartaric acid in combination with tin sulfate were exemplified. When citric acid is used also the combination citric acid-ammonium citrate-tin sulfate is described. The metal parts are thereby immersed in the derusting solution for about 15 minutes and then rinsed with a basic solution. It was found that this solution is less suitable for plant installations, which cannot be immersed therein but through which the solution must be pumped for a considerable longer time than used in WO 2005/033365. When used in that manner unacceptable damaging of steel pipes and the like may occur. Furthermore, it is disadvantageous that citric acid is a solid, making dosing and dissolving in cooling water difficult, particularly leading to difficulties at effective pH control.

[0005] It is therefore an object of the invention to provide a method that is devoid of the above disadvantages and nevertheless is environmental friendly and cheap. To this end the invention pertains to a method for derusting a metallic surface by bringing the surface in contact with an aqueous solution of a buffer having a pH between 5.1 and 6.5, wherein the buffer comprises lactic acid and the sodium, potassium and/or ammonium salt of lactic acid.

[0006] Thus according to the present invention it was found that considerable higher pH values can be used for derusting when the organic acid is lactic acid buffered with a sodium, potassium, or an ammonium salt, or a mixture thereof. These higher pH values have the considerable advantage that virtually no decomposition of the metallic surface can occur, whereas derusting properties are still satisfactory. This effect was not obtained when a citric acid-ammonium citrate buffer was used, since this was found to be insufficiently active for effective derusting such surfaces at these higher pH levels.

[0007] The present invention is of particular importance for removing rust within steel pipes as used in plant installations such as cooling installations. Pit corrosion in such pipes can cause serious damage and leakage of the pipes. Prevention is thus of utmost importance to prevent shut down of the installations and intensive inspection.

[0008] In such applications, apart from using citric acid, the use of aqueous lactic acid solutions was common and very effective, however, at the cost of surface damage at the inside of the pipes. Furthermore, the use of lactic acid as such does not prevent bacteria growth.

[0009] The above given novel method does not have any of these disadvantages.

[0010] The lactic acid is buffered with its sodium, potassium, and or ammonium salt. In view of effectiveness and price, a buffer system comprising lactic acid and ammonium lactate is preferred. Such systems do not longer require the presence of zinc sulfate, which is further advantage of the present method.

[0011] The invention can be performed in the pH range 5.1 to 6.5, but at the higher pH values the derusting process is much slower. For that reason it is preferred to perform the process at a pH between 5.1 and 5.7.

[0012] The method can be used at ambient temperature but when more quicker removal of rust is required the temperature of the aqueous acid solution may be raised to 70 °C, and if necessary to even higher temperatures until the boiling point of water.

[0013] The method of the invention is of particular interest for plant cooling systems through which the aqueous acid solution is pumped for usually 4 to 12 hours. When higher temperatures are used the circulation time can be shortened, which is favorable for shortening the shut down time.

[0014] The invention is further illustrated by the following examples, which show the benefits of this invention. Materials

- 50% (w/w) hydrolyzed L(+)-lactic acid (Prepared from PURAC HS 90, lot no. 2040800104)
- NaOH pellets, 98%
- 25% (w/w) ammonia
- citric acid

EP 1 950 327 A1

- Steel (already partly corroded) ASTM steel panels (101.5 X 150 mm)
- Demineralized tap water
- Acetone
- Hard water (50 °German hardness or °dH)

[0015] Six steel ASTM panels, which were already rusted, were brushed in order to remove the loose rust particles. After the panels were brushed, they were weighed and photographed. After the panels were photographed, they were placed on a construction wherein on a horizontal bar steel wires having the same length were connected. At the end of every steel wire, a paperclip was placed. The paperclip was used as a locking mechanism for the panel. By this way the panels could hang freely into the test solution.

[0016] At $t = 0$ hours the panels were partly submerged into a stirred 5% or 10 % (w/w) sodium lactate solution at different concentration and temperatures. The glass beakers, containing the partly submerged panels, were covered with aluminum foil. This simulates a closed system in the daily practice. At certain time intervals (see results) the panels were lifted out of the test solutions, immediately rinsed with demi-water (to remove the acid), rinsed with acetone, dried with an air hose, weighed, and finally photographed. At every time interval the time was stopped, until the panels were partly submerged in the test solutions again. After 48 hours the test was stopped.

[0017] Ammonium lactate solution was prepared from commercially available ammonium lactate to obtain a 10.0% (w/w) ammonium lactate solution. This concentration corresponds to a calculated concentration of lactic acid of 8.4% The solution was than brought to pH 5.7 by addition of 0.7% sodium hydroxide.

[0018] As comparison (di)ammonium citrate was prepared from citric acid as follows. The weight in amount of citric acid was based on the theoretically starting amount of L(+)-lactic acid in the used ammonium lactate solution. This is 8.4 % (w/w) acid. The citric acid was partly neutralized by adding 6.8% of ammonia, 25% to give pH 5.7. As a result, the calculated concentration of ammonium citrate in this solution was 10% as well.

Example 1

[0019] The derusting performance of sodium lactate and ammonium lactate was compared with ammonium citrate at pH 5.1 and pH 5.7. 10% (w/w) solutions, pH 5.7, of respectively ammonium lactate (NH_4L) and sodium lactate (NaL), and 8.4% (w/w) solution, pH 5.7, of NH_4L and ammonium citrate (NH_4C) were prepared in hard water (50 °dH). These solutions were tested for their derusting performance at 50 °C. The test was repeated with 5% (w/w) NH_4L and NaL solutions at pH 5.1. Results are given in Tables 1. The corrosion as function of the pH was also determined and the results are depicted in Table 2.

Table 1 (derusting)

Test solution	pH at T = 0	pH after 24 hours	Weight difference of panels after 24 hours (g)
10% NaL	5.7	6.89	0.5302
10% NH_4L	5.7	6.92	1.9900
5% NaL	5.1	5.53	0.3961
5% NH_4L	5.1	5.99	0.9046
10% NH_4L	5.7	6.92	0.8193*
10% NH_4C (comparison)	5.7	5.83	0.2966*
* weight difference of panels after 2 hours (g)			

[0020] Table 1 shows that both sodium lactate and ammonium lactate are effective in derusting steel panels, the latter being more effective than sodium lactate. Ammonium citrate is not effective at this pH. The prior art pH conditions (pH 3-5) lead to substantial more corrosion than the instant invention operating at higher pH. This is demonstrated by the experiments of Example 2.

Example 2

[0021] Two solutions of sodium lactate (NaL) at pH 3 and pH 5.7 were determined for their corrosion on two types of steel coupons (C-15 and C-1010). These types of steel are considered as standard types of steel. Two coupons of each

type of steel were (water-free) abraded with grit paper P 220, then with P 400 and acetone. The coupons were then submerged in the test solutions of 5% (w/w) NaL at pH 3 and pH 5.7. The samples were placed in a stove at 50 °C for 56 hours. After certain time intervals the coupons were rinsed with water and acetone. After the coupons were dried, the coupons were photographed and weighed (back). After 56 hours the test was stopped. The results are depicted in Table 2.

Table 2 (corrosion)

Steel type	pH	Weight difference of panels after 56 hours (g)
C-15	3	0.1694
C-15	5.7	0.0240
C-1010	3	0.2074
C-1010	5.7	0.0098

[0022] Table 2 shows that the pH conditions (pH 3-5) according to the prior art lead to substantial more corrosion than the instant invention operating at higher pH.

Claims

1. A method for derusting a metallic surface by bringing the surface in contact with an aqueous solution of a buffer having a pH between 5.1 and 6.5, wherein the buffer comprises lactic acid and the sodium, potassium and/or ammonium salt of lactic acid.
2. The method according to claim 1 wherein the buffer is a mixture of lactic acid and ammonium lactate.
3. The method according to claims 1-3 wherein the pH of the buffer is between 5.1 and 5.7.
4. The method according to claims 1-3 wherein the aqueous solution of the buffer is pumped through a system comprising metallic surfaces.
5. The method according to claims 1-4 wherein the metallic surface is steel.
6. The method according to claims 1-5 wherein the aqueous solution has a temperature from ambient temperature to 60 °C.
7. The method according to claims 1-6 for use in derusting metallic parts of cooling system.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 10 1166

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2006/039983 A (CHEMETALL GMBH [DE]; FISCHER PETER [CH]; BRUNNER HANSPETER [CH]) 20 April 2006 (2006-04-20) * page 1, lines 2-4,10,11 * * page 3, line 15 - page 4, line 8 * * page 4, lines 12-29 * * page 5, lines 1-5 * * page 6, lines 6-15 * * page 7, lines 7-15,18-20 * * page 9, lines 22-26 * * page 10, lines 1-4 * * claims 1,2 *	1-7	INV. C23G1/08 C23G1/24 C02F1/68 C02F1/70 C02F5/10 F28F13/18
A	DE 694 237 C (VER FUER CHEMISCHE UND METALLU) 27 July 1940 (1940-07-27) * page 1, column 1, lines 1-5,21-27 * * page 1, column 2, lines 50-53 * * page 2, column 1, line 52 - column 2, line 68 * * claim 1 *	1-7	
A	DE 742 477 C (PAUL EFFING) 4 December 1943 (1943-12-04) * page 1, column 1, lines 1-7 * * page 1, column 2, lines 26-42 * * page 2, column 1, lines 1-18 * * claims 1,5 *	1-7	TECHNICAL FIELDS SEARCHED (IPC) C23G C02F F28F B08B C11D
A	US 4 476 930 A (WATANABE DAVID J [US]) 16 October 1984 (1984-10-16) * column 1, lines 7-18 * * column 2, lines 39-63 * * column 6, lines 49-51 * * column 8, line 60 - column 9, line 4 * * examples 1-49 * * claim 1 *	1-7	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 4 July 2007	Examiner HANDREA-HALLER, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

2
EPO FORM 1503 03-82 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 10 1166

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	DE 197 21 422 A1 (ZIMZIK HENRY [DE]) 8 October 1998 (1998-10-08) * page 1, column 1, lines 1-10,33-47 * * claims 1,6 *	1-7	
A	WO 02/08127 A (RHODIA CONS SPEC LTD [GB]; FIDOE STEPHEN DAVID [GB]; TALBOT ROBERT ERI) 31 January 2002 (2002-01-31) * page 5, line 24 - page 6, line 11 * * claims 18-24 *	1-7	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 4 July 2007	Examiner HANDREA-HALLER, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

2

EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 07 10 1166

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-07-2007

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2006039983	A	20-04-2006	NONE	
DE 694237	C	27-07-1940	NONE	
DE 742477	C	04-12-1943	NONE	
US 4476930	A	16-10-1984	NONE	
DE 19721422	A1	08-10-1998	NONE	
WO 0208127	A	31-01-2002	AU 7080101 A	05-02-2002
			BR 0112574 A	01-02-2005
			CA 2416465 A1	31-01-2002
			CN 1458907 A	26-11-2003
			DK 200300053 A	13-03-2003
			GB 2379440 A	12-03-2003
			MX PA03000570 A	05-04-2004
			NO 20030230 A	12-03-2003
			RU 2281919 C2	20-08-2006
			US 2003226808 A1	11-12-2003

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2005033365 A [0004] [0004]