

(19)



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European Patent Office
Office européen des brevets



(11)

EP 1 266 981 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:

18.12.2002 Bulletin 2002/51

(51) Int Cl.7: **C23F 11/00**

(21) Application number: **01915719.7**

(86) International application number:
PCT/JP01/02319

(22) Date of filing: **23.03.2001**

(87) International publication number:
WO 01/071061 (27.09.2001 Gazette 2001/39)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

Designated Extension States:

AL LT LV MK RO SI

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(30) Priority: **24.03.2000 JP 2000083529**

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(54) **ANTICORROSIVE AGENT FOR STAINLESS STEEL AND METHOD OF ANTICORROSIVE
TREATMENT OF STAINLESS STEEL**

(57) An anticorrosive agent for a stainless steel surface comprising a hydroxylamine salt; a method of anticorrosive treatment of a stainless steel surface which comprises contacting the stainless steel surface with an aqueous solution of a hydroxylamine salt and heating it.

The method can be employed for significantly improving the corrosion resistance of stainless steel under severe circumstances.

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Description

[Technical Field]

5 **[0001]** The present invention relates to an anticorrosive agent for a surface of a stainless steel article and an anticorrosive treatment using the same. Particularly, the invention relates to an anticorrosive agent for a surface of a stainless steel article and an anticorrosive treatment using the same which are effectively utilizable under severe conditions.

10 **[0002]** It is known that a surface of metal article can be converted to have a corrosion-resistant coating or increased corrosion resistance by treating the surface with an inorganic or organic corrosion inhibitor.

[0003] It is known that among metals a stainless steel containing chromium shows high resistance to corrosion. However, even such stainless steel is gradually corroded on its surface when it is kept under strong acidic or alkaline condition, or when it is placed under weak acidic or alkaline condition for a long period of time. The corrosion causes damage of the stainless steel. Further, if stainless steel is employed as material for making a reaction vessel (to be used for performing chemical reaction) or storage vessel, the corrosion products migrate into the material in the vessel as impurities.

15 **[0004]** A hydroxylamine salt ($\text{NH}_2\text{OH}\cdot\text{A}$, in which A is an acid such as H_2SO_4 , H_3PO_4 , or HCl) can be prepared, for example, by reacting sodium hydrogensulfite and sodium nitrate in an aqueous solution to obtain an aqueous sodium hydroxylamine disulfonate solution, and hydrolyzing the sodium hydroxylamine disulfonate. The hydroxylamine salt is stable in the solid form or in an aqueous solution. The hydroxylamine salt *per se* is generally employed as a starting material in chemical reactions. It is also used for leaving or preparing a highly chemically unstable free hydroxylamine which is of value as a chemical compound or for processing or washing electronic materials, when it is required.

20 **[0005]** As an anticorrosive treatment of iron or the like, there is known a phosphate treatment which is performed by treating a metal surface with an aqueous acidic phosphate solution. For instance, United States Patents No. 4,149,909, No. 4,865,653, and No. 5,597,465; Published EP Applications No. 0 695 817 A1 and No. 0 315 059 A1; WO 93/03198; and WO 93/20259 teach that a metal such as iron or zinc can be made to have improved corrosion resistance by placing the metal in contact with an aqueous iron phosphate or zinc phosphate solution, respectively, and forming on the metal surface a phosphate coat and that the formation of phosphate coat is enhanced by addition of several weight % of a hydroxylamine salt such as hydroxylamine sulfate into the aqueous phosphate solution.

25 **[0006]** The present invention provides an anticorrosive agent and an anticorrosive treating method which are effective to enhance corrosive resistance of stainless steel under severe conditions.

[Disclosure of Invention]

35 **[0007]** The present inventors have studied for discovering an anticorrosive agent and anticorrosive treating method which does not cause corrosion of stainless steel under severe acidic or alkaline conditions for long period of time. As a result, they have discovered that a surface of stainless steel is converted into a highly anticorrosive surface when it is heated in an aqueous hydroxylamine solution. The present invention has been made upon the discovery.

40 **[0008]** The present invention resides in an anticorrosive agent for stainless steel surface which comprises a hydroxylamine salt.

[0009] The invention further resides in a method for anti-corrosive treatment which comprises heating a stainless steel surface to a temperature of 50°C or higher in contact with the above-mentioned hydroxylamine salt anticorrosive agent.

45 **[0010]** Preferred embodiments of the hydroxylamine salt anticorrosive agent for stainless steel surface according to the invention are described below.

(1) The hydroxylamine salt is hydroxylamine sulfate or hydroxylamine phosphate.

(2) The anticorrosive agent comprising 0.2 to 50 wt.% of a hydroxylamine salt.

50 [Preferred Embodiments for Performing Invention]

[0011] The hydroxylamine salt anticorrosive agent of the invention generally is in the form of an aqueous solution. The concentration is in the range of 0.2 to 50 wt.%, preferably in the range of 5 to 20 wt.%. Examples of the hydroxylamine salts include hydroxylamine sulfate, hydroxylamine phosphate, and hydroxylamine hydrochloride. Particularly preferred are hydroxylamine sulfate and hydroxylamine phosphate. These hydroxylamine salts can be prepared by known methods, as described hereinbefore.

[0012] In the method, an article of stainless steel can be prevented from corrosion by keeping the article in contact with a heated aqueous solution of a hydroxylamine salt. The aqueous hydroxylamine salt solution is preferably heated

to a temperature of 50°C or higher. If the article of stainless steel is kept into contact with an heated hydroxylamine salt solution in an pressure-resistant reaction vessel such as an autoclave, the temperature can be 100°C or higher. Generally, the temperature is kept in the range of 60 to 160°C. The stainless steel article is kept in contact with the heated hydroxylamine salt solution, preferably for a period of 3 minutes or longer, more preferably 1 to 20 hours.

[0013] There are no limitations with respect to stainless steel which can be treated by the method of the invention. But, the method of the present invention is preferably applied to anticorrosive treatment of stainless steel containing chromium element and nickel element.

[0014] The anticorrosive treatment of the invention can effectively prevent corrosion of stainless steel under severe conditions and obviate migration of impurities of corrosion products. For instance, if a distillation apparatus made of stainless steel (employed for obtaining an aqueous hydroxylamine solution of increased purity, which is of value for preparing pharmaceutically active compound or of value as a detergent for washing electronic parts) is previously treated by the above-mentioned anticorrosive treatment, the corrosion of the apparatus by the highly corrosive hydroxylamine is effectively obviated, and migration of the impurities from the apparatus is effectively avoided.

[Example 1]

[0015] In a glass-made flask equipped with a reflux condenser, an aqueous hydroxylamine phosphate solution (concentration: 20 wt.%) was placed. A specimen of stainless steel having the below-mentioned alloy composition was placed in the aqueous hydroxylamine phosphate solution.

[0016] The flask was then placed on an oil bath heated to approx. 100°C, for 8 hours or 24 hours, for performing anti-corrosive treatment.

(1) SUS 304L Stainless steel (composition: Fe approx. 73%, Ni approx. 9%, Cr approx. 18%)

(2) SUS 316L Stainless steel (composition: Fe approx. 70%, Ni approx. 12%, Cr approx. 16%, Mo approx. 2%)

(3) SUS 310S Stainless steel (composition: Fe approx. 57%, Ni approx. 19%, Cr approx. 24%)

[0017] Thus treated specimen was weighed, and placed in an aqueous 10 wt.% sulfuric acid solution in a heat-resistant glass bottle. The glass bottle was placed in a thermostat heated to 80°C and kept for certain periods. Then, the glass bottle was taken out from the thermostat. The specimen was recovered from the sulfuric acid solution, washed with water, dried, and weighed. Both weights were compared for determining weight loss which was caused by corrosion of the stainless steel specimen.

[0018] For comparison, the equivalent stainless steel specimen having no corrosion-inhibiting treatment was subjected to the above-mentioned test for evaluating the resistance in the sulfuric acid solution.

[0019] The results are set forth in Tables 1 to 3.

Table 1

(for SUS 304L)			
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of 24 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	16.4526	17.9558	18.5543
1	--	--	18.2378
24	16.4523	17.9557	--
44	16.4521	17.9556	--
68	16.4518	17.9554	--
116	16.4517	17.9553	--
164	16.4513	17.9548	--
188	16.4513	17.9548	--
236	16.4514	17.9554	--
284	16.4516	17.9554	--
380	--	17.9546	--
529	--	17.9544	--

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Table 2

(for SUS 316L)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	18.2641	18.2103
24	18.1244	17.6733
44	18.0132	--

Table 3

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	17.3690	17.5489
1	--	17.4191
8	17.3690	--
23	17.3686	--
47	17.3687	--
71	17.3685	--
95	17.3688	--
119	17.3686	--
161	17.3684	--
209	17.3683	--
281	17.3685	--
329	17.3681	--
455	17.3679	--

[Example 2]

[0020] The procedures of Example 1 were repeated except for replacing the aqueous hydroxylamine phosphate solution with an aqueous hydroxylamine sulfate solution (concentration: 20 wt.%).

[0021] In the corrosion resistance-enhancing treatment, the treatment was additionally performed for 8 hours, 24 hours, or 72 hours.

[0022] The specimens having been subjected to anticorrosive treatment were examined in their anticorrosive performance in the same manner as in Example 1. The results are set forth in Tables 4 to 6.

Table 4

(for SUS 304L)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	15.5943	18.5543
1	--	18.2378
24	15.5944	--
44	15.5940	--
68	15.5937	--
116	15.5935	--
164	15.5931	--
188	15.5931	--
236	15.5935	--
284	15.5937	--
380	15.5930	--
529	15.5929	--

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Table 5

(for SUS 316L)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	18.2045	18.2103
24	18.0672	17.6733
44	17.9577	--

Table 6-1

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	17.7900	17.5489
1	--	17.4191
8	17.7901	--
24	17.7897	--
47	17.7897	--
71	17.7895	--
95	17.7898	--
119	17.7896	--
167	17.7892	--
215	17.7894	--
287	17.7895	--
335	17.7888	--
455	17.7889	--
628	17.7887	--

Table 6-2

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 24 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	17.9786	17.5489
1	--	17.4191
24	17.9787	--
44	17.9788	--
68	17.9785	--
116	17.9782	--
164	17.9784	--
236	17.9784	--
284	17.9779	--
335	17.9777	--

Table 6-3

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 72 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	17.5712	17.5489
1	--	17.4191
19	17.5713	--
67	17.5710	--

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Table 6-3 (continued)

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 72 hrs. treatment (weight g)	Specimen of no treatment (weight g)
115	17.5711	--
187	17.5711	--
235	17.5707	--
355	17.5707	--
528	17.5706	--

[Example 3]

[0023] In an autoclave, an aqueous hydroxylamine sulfate solution (concentration: 20 wt.%) was placed. A specimen of stainless steel (3) described in Example 1 was placed in the autoclave.

[0024] The autoclave was then placed on an oil bath heated to approx. 160°C, for 3 hours, for performing anti-corrosive treatment of the specimen.

[0025] The specimen was then placed in the aqueous sulfuric acid solution in the manner described in Example 1, to examine the corrosion resistance of thus treated specimen. The results are set forth in Table 7.

Table 7

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 3 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	17.1045	17.5489
1	--	17.4191
124	17.1041	--

[Example 4]

[0026] In an autoclave, an aqueous hydroxylamine sulfate solution (concentration: 5 wt.%) was placed. A specimen of stainless steel (1) or (3) described in Example 1 was placed in the autoclave.

[0027] The autoclave was then placed on an oil bath heated to approx. 160°C, for 8 hours, for performing anti-corrosive treatment of the specimen.

[0028] The specimen was then placed in the aqueous sulfuric acid solution in the manner described in Example 1, to examine the corrosion resistance of thus treated specimen. The results are set forth in Tables 8 to 9.

Table 8

(for SUS 304L)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	17.9588	18.5543
1	--	18.2378
124	17.9583	--

Table 9

(for SUS 310S)		
Time (hr.) in aq. H ₂ SO ₄	Specimen of 8 hrs. treatment (weight g)	Specimen of no treatment (weight g)
0	35.5074	17.5489
1	--	17.4191
124	35.5066	--

[0029] As is apparent from the results shown in Tables 1 to 9, the specimens of stainless steel having been treated with an aqueous hydroxylamine salt solution according to the present invention keep their weights even after they are

placed in a heated aqueous sulfuric acid solution for several ten hours or several hundred hours. In contrast, the equivalent specimens of stainless steel having been subjected to no anti-corrosive treatment loss their weights within one to 24 hrs. In the aqueous sulfuric acid solution, the untreated specimens show blacken surface or give bubble formation within a short period of time.

[0030] Accordingly, it is clear that the anticorrosive agent and anticorrosive treatment of the invention are effective for keeping stainless steel from corrosion.

[Industrial Utility]

[0031] The anticorrosive agent of the invention which comprises a hydroxylamine salt is of value to prominently enhance resistance to corrosion of stainless steel, particularly chromium-containing stainless steel. Further, the method of anticorrosive treatment according to the invention keeps stainless steel placed under severe conditions such as acidic or alkaline conditions for a long period of time from corrosion. This means that migration of impurities of corrosion products and their contamination is effectively avoided.

Claims

1. An anticorrosive agent for stainless steel surface which comprises a hydroxylamine salt.
2. The anticorrosive agent of claim 1, in which the hydroxylamine salt is hydroxylamine sulfate or hydroxylamine phosphate.
3. The anticorrosive agent for stainless steel surface which comprises an aqueous solution of 0.2 to 50 weight % of a hydroxylamine salt.
4. A method of anticorrosive treatment of stainless steel surface which comprises heating the stainless steel surface to a temperature of 50°C or higher in contact with the anticorrosive agent of any one of claims 1 to 3.
5. The method of anticorrosive treatment of stainless steel surface, in which the heating is performed at 50 to 200°C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/02319

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C23F11/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C23F11/00, 15/00, C23C22/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI (hydroxylamine, corrosion, stainless)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 53-55427, A (The Furukawa Electric Co., Ltd.), 19 May, 1978 (19.05.78), Claims (Family: none)	1-5
Y	WO, 96/32522, A (Holderchen Holding AG), 17 October, 1996 (17.10.96), Claim 2 & JP, 10-501849, A & EP, 755462, A	1-3
Y A	US, 4350606, A (Dionisio G. Cuisia, et al.), 21 September, 1982 (21.09.82), Claim 1 & JP, 57-63364, A	1-3 4-5
Y A	US, 4865653, A (Linda S. Kramer), 12 September, 1989 (12.09.89), Claim 1 & JP, 1-123080, A & EP, 315059, A	1-3 4-5
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 22 June, 2001 (22.06.01)		Date of mailing of the international search report 03 July, 2001 (03.07.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)