(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 185 355 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
**18.08.2004 Bulletin 2004/34**

(21) Application number: **00925982.1**

(22) Date of filing: **13.04.2000**

(51) Int Cl.[7]: **B01D 53/26**, B01D 53/28, B01D 53/14, C23F 11/167, C23F 11/08, C09K 5/00

(86) International application number:
**PCT/US2000/009985**

(87) International publication number:
**WO 2000/067878 (16.11.2000 Gazette 2000/46)**

(54) **ANTI-CORROSION SOLUTIONS FOR AIR DEHUMIDIFICATION SYSTEMS**

KORROSIONSSCHUTZLÖSUNGEN FÜR ENTFEUCHTUNGSSYSTEME

SOLUTIONS ANTICORROSION POUR SYSTEMES DE DESHUMIDIFICATION DE L'AIR

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE**

(30) Priority: **06.05.1999 US 132931 P**
**28.07.1999 US 362260**

(43) Date of publication of application:
**13.03.2002 Bulletin 2002/11**

(73) Proprietor: **FMC CORPORATION**
**Philadelphia, PA 19103 (US)**

(72) Inventor: **VERMA, Shyam, Kumar**
**Gastonia, NC 28054 (US)**

(74) Representative: **Patentanwälte**
**Schaad, Balass, Menzl & Partner AG**
**Dufourstrasse 101**
**Postfach**
**8034 Zürich (CH)**

(56) References cited:
**EP-A- 0 807 695**
**WO-A-93/09198**
**WO-A-97/49842**
**FR-A- 2 505 861**
**US-A- 4 089 650**
**US-A- 5 292 455**
**US-A- 6 024 892**

- **PATENT ABSTRACTS OF JAPAN vol. 1998, no. 02, 30 January 1998 (1998-01-30) & JP 09 280683 A (NIPPON CHEM IND CO LTD), 31 October 1997 (1997-10-31)**
- **PATENT ABSTRACTS OF JAPAN vol. 003, no. 023 (C-038), 26 February 1979 (1979-02-26) & JP 53 146942 A (NITTO CHEM IND CO LTD;OTHERS: 01), 21 December 1978 (1978-12-21)**



EP 1 185 355 B1

Printed by Jouve, 75001 PARIS (FR)

## Description

### FIELD OF THE INVENTION

**[0001]** This invention relates generally to anti-corrosion solutions for air dehumidification systems, and in particular to air dehumidification solutions which include a phosphonate anti-corrosion agent.

### BACKGROUND OF THE INVENTION

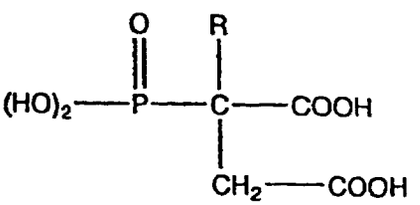
**[0002]** Alkali metal halide solutions and similar solutions, such as calcium chloride solutions, or their mixtures, are widely used in dehumidification processes and systems. In a typical air dehumidification system, humidified air to be conditioned is directed into a cooling system. The humidified air initially enters an air conditioning region where the air is cooled and then contacted with an absorbent solution of alkali metal halide, such as lithium chloride, alkaline earth metal halide, such as calcium chloride, or mixtures thereof. The absorbent solution removes water vapor from humidified stream of air by chemical absorption to provide an air stream with the desired relative humidity. Diluted solution is then routed to a regeneration region where the diluted solution is concentrated and thereafter directed back to the air conditioning region of the system.

**[0003]** Under poor environmental conditions, contaminants, such as carbon dioxide, sulfur oxide compounds ($SO_x$), nitric oxides ($NO_x$) or acidic vapors, can be present in the air stream to be treated. These conditions can adversely affect, that is reduce the pH of the absorbent solution, resulting in an acidic solution. Under acidic conditions, the absorbent solution becomes increasingly corrosive towards the metallic materials of the machine, such as carbon steel which is used to construct dehumidification equipment. US-A-5292455 relates to a method of inhibiting corrosion of metal surfaces in contact with calcium chlorine brines.

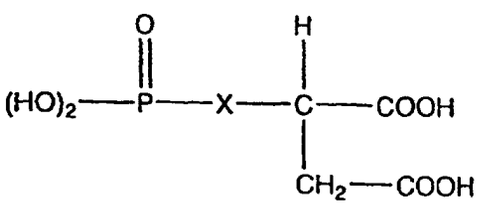
**[0004]** In current practice in the industry, molybdate, chromate or silicate anions or their salts are used as corrosion inhibiting additives. JP-A-09 280 683 and PATENT ABSTRACTS OF JAPAN (vol. 1998, no.02) relates to an absorbing solution containing Li iodide and Li molybdenate. US-A-6 024 892 relates to an absorbent solution for closed or open systems. Because the dehumidification systems are open systems, new environmentally friendly and improved corrosion inhibitors are in demand for these systems. Use of chromate is limited due to environmental concerns. While more environmentally acceptable, simple alkali metal molybdate salts have limited solubility in aerated solutions. Silicates also exhibit limited solubility in this solution.

### SUMMARY OF THE INVENTION

**[0005]** The present invention provides absorbent solutions which include one or more phosphonocarboxylic acid corrosion inhibiting agents useful for air dehumidification applications, wherein said phosphonocarboxylic acids include compounds of the formula

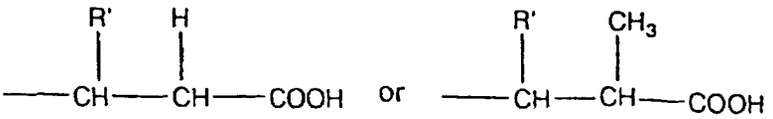


or

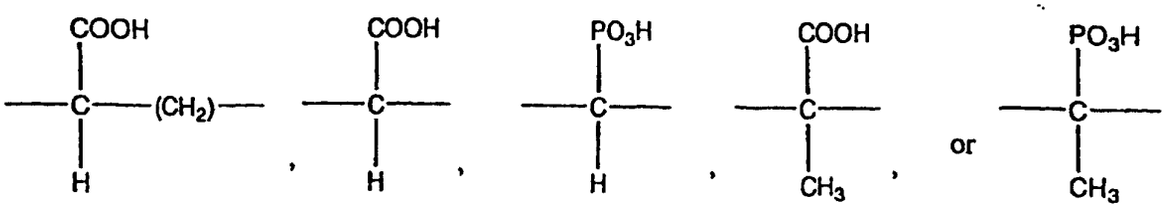


in which:

R is hydrogen, alkyl, alkenyl, or alkinyl radical having up to 4 carbon atoms, aryl, cycloalkyl or aralkyl radical or the radical



R' is hydrogen, alkyl radical having up to four carbon atoms or carboxyl radical;
and
X is



The solutions can offer comparable or improved anti-corrosion protection as compared to conventionally used corrosion inhibitors during repeated dehumidification cycles in closed or open systems. In addition, the solutions of the invention can be more environmentally acceptable. Still further, the phosphonates can be used in relatively small quantities, typically ranging from about 0.0005 to about 0.20 percent by weight and still provide high levels of corrosion protection even for dehumidification solutions having high concentrations of halide.

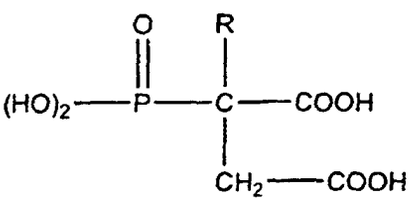
**[0006]** The solutions of the invention can also include one or more buffering agents to provide pH stable absorbent solutions useful for air dehumidification applications. The absorbent solutions can include inorganic buffers, such as boron-containing buffering agents. The absorbent solutions alternatively can include organic biological buffers, such as amino polyols and/or organic sulfonic acid buffering agents. The absorbent solutions can also include mixtures of the inorganic and/or organic buffering agents. The resultant solutions can exhibit stabilized pH through repeated fluid dehumidification cycles, even for fluid streams contaminated with carbon dioxide, sulfur oxide compounds ($SO_x$), nitric oxides ($NO_x$), acidic vapors, and the like.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

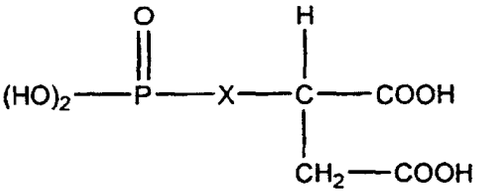
**[0007]** The present invention will be described more fully hereinafter in connection with illustrative embodiments of the invention which are given so that the present disclosure will be thorough and complete and will fully convey the scope of the invention to those skilled in the art. However, it is to be understood that this invention may be embodied in many different forms and should not be construed as being limited to the specific embodiments described and illustrated herein. Although specific terms are used in the following description, these terms are merely for purposes of illustration and are not intended to define or limit the scope of the invention.

**[0008]** Exemplary phosphonate corrosion inhibiting agents include without limitation phosphonocarboxylic acids, aminophosphonates, acylation products of phosphorous acid, phosphonoacetic acids, and the like and mixtures thereof.

**[0009]** Exemplary phosphonocarboxylic acids include, for example, compounds of the formula

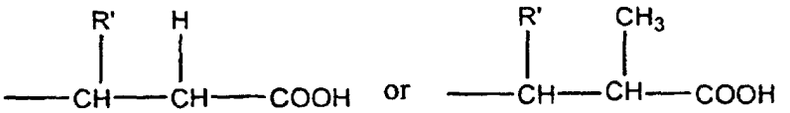


or

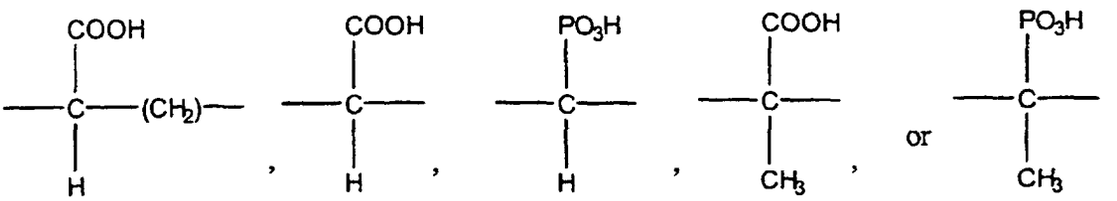


in which:

R is hydrogen, alkyl, alkenyl, or alkinyl radical having up to 4 carbon atoms, aryl, cycloalkyl or aralkyl radical or the radicals

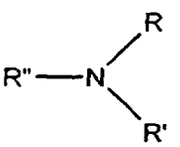


R' is hydrogen, alkyl radical having up to four carbon atoms or carboxyl radical; and
X is



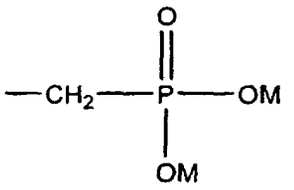
**[0010]** Suitable phosphonocarboxylic acids include without limitation α-methylphosphonosuccinic, phosphonosuccinic acid, 1-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, α-allylphosphonosuccinic acid, α-p-chlorophenyl-phosphonosuccinic acid, α-propargylphosphonosuccinic acid, α-benzyl-phosphonosuccinic acid, α-cyclohexylphosphonosuccinic acid, 2-phosphono-3-(α-methyl-carboxymethyl)-hexane-1,2,4-tricarboxylic acid, 2,2-diphosphono-butane-3,4-dicarboxylic acid, and the like and mixtures thereof.

**[0011]** Exemplary aminophosphonates include, for example, compounds having a methyl phosphonic acid or alkali metal or ammonium salt thereof bonded to a nitrogen atom. Such compounds can be generally described by the formula

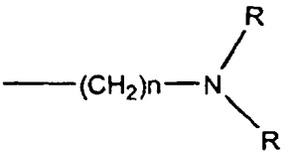


wherein:

R is

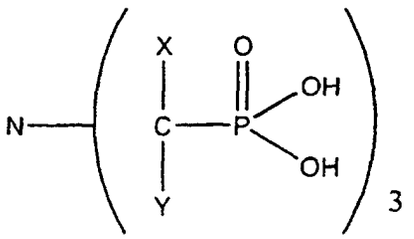


R' is R or $-CH_2CH_2OH$; and
R" is R, $-CH_2CH_2OH$ or



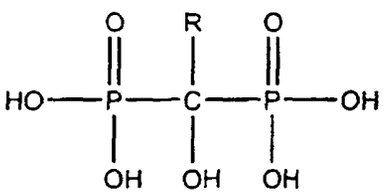
wherein M is hydrogen, $NH_4$, alkali metal, or a combination thereof and n is 1, 2 or 3.

**[0012]** Other exemplary aminophosphates include without limitation amino tri(lower alkyidenephosphonic acids) or their water soluble salts, as defined by the formula



wherein X and Y represent hydrogen or lower alkyl having 1 to 4 carbon atoms. Illustrative compounds include amino tri(methylphosphonic acid) $N(CH_2P(O)(OH)_2)_3$; amino(triethylidenephosphonic acid) $(N((CH_3)CHP(O)(OH)_2)_3$; amino tri(isopropylidenephosphonic acid) $(N((CH_3)(CH_3)CP(O)(OH)_2)_3$, and the like and mixtures thereof.

**[0013]** Exemplary acylation products of phosphorous acid include, for example, compounds of the formula



wherein R is alkyl having 1 to 5 carbon atoms; alkali metal, ammonium and ethanolamine salts thereof; and mono- and dialkyl esters thereof with methanol, ethanol, propanol or butanol.

**[0014]** Exemplary phosphonates include, but are not limited to, 2-hydroxyphosphonoacetic acid (HPA), tris-amino phosphonic acid (AMP), 1,1-hydroxyethylidine diphosphonic acid (HEDP), ethylene diamine tetramethylenephosphonic acid (ENTP), hexamethylene diamine tetramethylenephosphonic acid (HMTP), diethylene triamine penta-methylenephosphonic acid, 2-phosphono-1,2,4-butanetricarboxylic acid (PBTC), and the like, and mixtures thereof.

**[0015]** These and other phosphonates are well known in the art and are described in U.S. Patent Nos. 3,214,454; 3,278,446; 3,336,221; 4,026,815; 3,959,360; 3,366,675; and 4,689,200, the entire disclosure of each of which is hereby incorporated by reference. The phosphonates can be present in an amount from about 0.0005 to about 0.20 percent by weight, preferably about 0.0025 to about 0.050 percent by weight, based on the total weight of the solution.

**[0016]** The phosphonate corrosion inhibiting agents are added to absorbent solutions which include at least one alkali metal halide, such as lithium chloride, alkaline earth metal halide, such as calcium chloride, or a mixture thereof,

in conventional amounts. An exemplary alkali metal halide solution includes alkali metal halide in an amount from about 10 to about 45 weight percent, preferably about 20 to about 40 weight percent, based on the total weight of the solution.

**[0017]** Advantageously the solution further includes at least one buffering agent to stabilize pH of the dehumidification solution through repeated fluid dehumidification cycles, even for fluid streams contaminated with carbon dioxide, sulfur oxide compounds ($SO_x$), nitric oxides ($NO_x$), acidic vapors, and the like. The absorbent solutions can include inorganic buffers, such as boron-containing buffering agents. The absorbent solutions alternatively can include organic biological buffers, such as amino polyols and/or organic sulfonic acid buffering agents. The absorbent solutions can also include mixtures of the inorganic and/or organic buffering agents.

**[0018]** The boron-containing inorganic buffering agent is selected from boron-containing compounds capable of providing boron ions in the absorbent solution. Exemplary boron-containing inorganic buffering agents include, but are not limited to, lithium tetraborate and metaborate, sodium and potassium borates, boric acid, and the like, and mixtures thereof.

**[0019]** Exemplary amino polyols include, but are not limited to, $C_1$ to $C_3$ linear or branched amino polyols, in which one or more carbon atoms thereof can include $C_1$ to $C_6$ alkyl substituents, which substituents in turn can further include one or more hydroxy and/or amino groups. Exemplary amino polyols include, but are not limited to, amino methyl propane, amino methyl propanol, mixtures thereof and the like.

**[0020]** Exemplary organic sulfonic acid buffering agents include, but are not limited to, compounds of the formula R-$SO_3$H, wherein R can be $C_1$ to $C_{10}$ linear, branched or cyclic alkyl substituents, which substituents can include one or more hydroxyl and/or amino groups and/or $C_5$ to $C_{10}$ heterocyclic rings containing O and/or N atoms. Exemplary organic sulfonic acids include, but are not limited to, amino propane sulfonic acid, the buffers Tris, Bis-tris and Bis-tris propane, commercially available for example from ICN Pharmaceuticals, as well as mixtures thereof and the like.

**[0021]** Mixtures of inorganic and organic buffers as described herein can also be used.

**[0022]** The inorganic buffering agent can be present in an amount sufficient to provide boron in solution in amounts ranging from about 0.03 to about 1.0 percent by weight, preferably about 0.03 to about 0.3 percent by weight, based on the total weight of the solution. The organic buffering agent can be present in amounts ranging from about 0.7 to about 10.0 percent by weight, preferably about 0.7 to about 5.0 percent by weight, also based on the total weight of the solution. Such solutions can provide substantial buffering capacity and also provide some corrosion resistance, for example for carbon steel at absorbent solution temperatures of up to about 300°F under aerated conditions. Thus despite the presence of contaminates such as carbon dioxide, sulfur dioxide, nitric oxide, acidic vapors, and the like, the solutions are capable of stabilizing the pH thereof, for example from about 7 to about 9.5, through repeated fluid dehumidification cycles.

**[0023]** The solutions of the invention can also include other corrosion inhibitors that are commonly used in the industry, such as, but not limited to, alkali metal salts of molybdate, chromate and silicate anions, and mixtures thereof, although such agents are not required. The solutions can also include other corrosion inhibiting agents such as heteropoly complex anions of transition metal elements, preferably phosphomolybdates, as described, for example, in PCT Publication WO 97/49842, the entire disclosure of which is hereby incorporated by reference.

**[0024]** The heteropoly complex anions of transition metal elements useful in the invention can be generally described as coordination-type salts and free acids with a complex and high molecular weight anion. The heteropoly complex anions include as a ligand or complexing agent at least one transition metal atom which, as an ion in solution, exhibits corrosion inhibiting properties. The heteropoly complex anions useful in the invention also are preferably substantially completely soluble in alkali metal halide solutions, such as lithium chloride solutions, so as to maximize the concentration of the corrosion inhibiting ions in solution. The heteropoly anions contain complexed transition metal atoms (such as Mo). Therefore, the dissolved heteropoly anions can provide a higher level of transition metal anion (Mo anion) in a solution, as compared to simple transition metal oxides, such as molybdates like lithium molybdate.

**[0025]** Such complexes can be generally represented by the following formulas:

$$[X_aM_bO_c]^{-n},$$

$$[X_aZ_dM_bO_c]^{-n},$$

$$[X_aZ_dM_bO_cH_e]^{-n},$$

$$[X_aM_bO_c(OH)_f]^{-n},$$

and

$$[X_aZ_dM_bO_c(OH)_f]^{-n},$$

wherein:

X and Z are central heteroatoms from Groups I-VIII of the Periodic Table of Elements;
the value of a varies and is 1 or 2;
the value of d varies and is an integer from 0 to 4;
$M_bO_c$, $M_bO_cH_e$, and $M_bO_c(OH)_f$ are oxoanions in which M is a transition metal element; the value of b varies, depending upon the number of transition metal atoms present in the oxoanion and can be an integer from 5 to 22, preferably 6 to 12; the value of c varies, depending upon the number of oxygen atoms present in the oxoanion attached to the transition metal and also capable of forming unique structural groups with the central atoms, and is an integer from 20 to 70, preferably from 24 to 40; the value of e varies (for example in the reduced heteropolyanion, the value of e varies depending upon the reduction of the heteropolyanion) and is an integer from 0 to 6; and the value of f varies and is an integer from 0 to 3; and
n is the charge of the anion and is the sum of the charges on X, Z, M, O, H, and OH.

**[0026]** Although the above formulas are general representations of the heteropoly complex anions useful in the invention, as will be appreciated by the skilled artisan, other compounds can also be included. Also as these formulas represent, in some heteropoly complex anions, H atoms in addition to the O atoms have been reported. Any of the various heteropoly complex anions known in the art can be used in the invention, including compounds described by G.A. Tsigdinos, Topics Curr. Chem., vol. 76, 5-64 (1978) and D.L. Kepert, Comprehensive Inorganic Chemistry (A.F. Trofman et al.) Oxford:Pergamon Press, vol. 4, pp. 607 (1973), the entire disclosure of each of which is incorporated herein by reference.

**[0027]** With regard to the central or heteroatom X, over 40 different elements (both metals and nonmetals) from Periodic Groups I-VIII can function as central atoms in distinct heteropoly complex anions. For example, X can be an elements selected from Groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, and VA of the Periodic Table of Elements. Exemplary central atoms include, but are not limited to, ions of phosphorus, silicon, manganese, arsenic, boron, iron, tellurium, copper, zinc, aluminum, tin, zirconium, titanium, vanadium, antimony, bismuth, chromium, gallium, germanium, and the like.

**[0028]** M is a 2-18 hexavalent transition metal element atom, which surrounds one or more central atoms X. The transition metal atom M is selected from those elements which as ions in solution provide corrosion inhibiting effect in absorption refrigeration systems. Preferably the transition metal element M in the oxoanion is derived from molybdate or tungstate. Other transition metal elements can also be present, as represented in the formula as Z, such as but not limited to, an element selected from Groups IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, and VA of the Periodic Table of Elements. Exemplary elements include without limitation manganese, cobalt, nickel, copper, zinc, vanadium, niobium, tantalum, gallium, germanium, arsenic, antimony, bismuth, tellurium, and the like and other transition elements.

**[0029]** Exemplary heteropoly complex anions include, but are not limited to, phosphomolybdates, such as but not limited to, $[PMo_{12}O_{40}]^{-3}$, wherein $P^{+5}$ is the central atom or heteroatom, $[PMo_{10}V_2O_{40}]^{-5,}$ and the like; silicon molybdates, such as but not limited to, $[SiMo_{11}NiO_{40}H_2]^{-6}$, wherein $Si^{+4}$ is the central atom; manganese molybdates, such as but not limited to, $[MnMo_9O_{32}]^{-6}$, wherein $Mn^{+4}$ is the central atom; silicon tungstates, such as but not limited to, $[SiW_{12}O_{40}]^{-4}$, wherein $Si^{+4}$ is the central atom; tellurium molybdates, such as but not limited to, $[TeMo_6O_{24}]^{-6}$, wherein $Te^{+6}$ is the central atom; arsenic molybdates, such as but not limited to, $[As_2Mo_{18}O_{62}]^{-6}$, wherein $As^{+5}$ is the central atom; manganese niobiates, such as but not limited to, $[MnNb12O_{36}]^{-12}$, wherein $Mn^{+4}$ is the central atom; and the like, and mixtures thereof. Currently preferred heteropoly complex anions are phosphomolybdates.

**[0030]** The heteropoly complex anions which have been structurally characterized can be divided into the broad groups, depending upon the heteroatom [X], transition metal atom [M] stoichiometry, and upon the coordination number of the heteroatom (that is, the number of points at which M is attached to the heteroatom in the complex). The heteropoly complex anions can be classified according to the ratio of the number of the central atoms to the peripheral molybdenum or other such atoms. For example, the different types of known heteropoly complex anions of molybdate show the following X:M ratio with one or more central atoms: X:M = 1:12, 1:11, 1:10, 1:9, 1:6, 2:10, 2:17, 2:5, 4:12, 1m:6m (m unknown) and 1:1 heteropoly complex anions. The known tungstates include all of the above in addition to 2:18, 2:17 and 2:4:18.

**[0031]** Such complexes can be present in an amount from about 0.02 to about 0.3 percent by weight, preferably about 0.05 to about 0.2 percent by weight, based on the total weight of the solution.

**[0032]** The present invention will be further illustrated by the following non-limiting examples.

EXAMPLE 1

**[0033]** Corrosion tests were run on carbon steel coupons with lithium chloride solutions containing $Li_2MoO_4$ as a corrosion inhibiting agent, with and without buffer. The results are set forth below in Tables 2.

TABLE 2

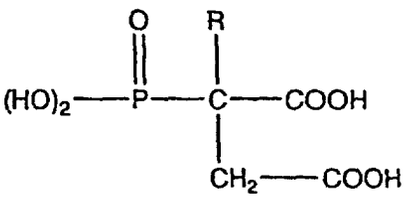
| Corrosion Rate of Carbon Steel in 25 wt.% LiCl Solution (110°F, Aerated, Ambient Pressure) | |
|---|---|
| Additive | Corrosion Rate (mils per year)* |
| None | 10.6 |
| $Li_2MoO_4$ (250 ppm) | 5.2 |
| PBTC (200 ppm) and Buffer** | 2.6 |

* = 30 days

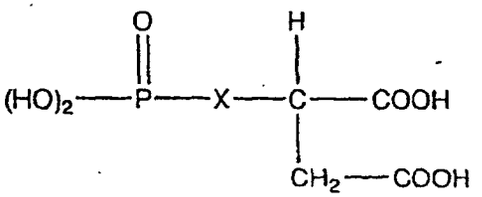
** = B = 0.2 percent

## Claims

**1.** An absorbent solution for dehumidifying humidified fluid streams, comprising at least one halide of an alkali metal, at least one halide of an alkaline earth metal, or a mixture thereof, in an amount ranging from 10 to 45 weight percent, and at least one phosphonocarboxylic acid corrosion inhibiting agent,
wherein said phosphonocarboxylic acids include compounds of the formula

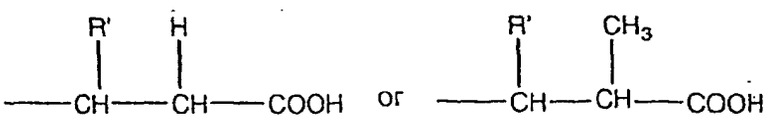


or

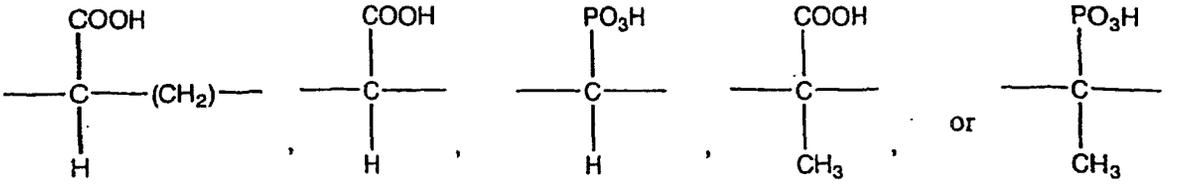


in which:

R is hydrogen, alkyl, alkenyl, or alkinyl radical having up to 4 carbon atoms, aryl, cycloalkyl or aralkyl radical or the radical



R' is hydrogen, alkyl radical having up to four carbon atoms or carboxyl radical;
and
X is




2. The solution of Claim 1, wherein said phosphonocarboxylic acid comprises a compound selected from the group consisting of α-methylphosphonosuccinic, phosphonosuccinic acid, 1-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, α-allylphosphonosuccinic acid, α-p-chlorophenyl-phosphonosuccinic acid, α-propargylphosphonosuccinic acid, α-benzyl-phosphonosuccinic acid, α-cyclohexylphosphonosuccinic acid, 2-phosphono-3-(α-methyl-carboxymethyl)-hexane-1,2,4-tricarboxylic acid, 2,2-diphosphono-butane-3,4-dicarboxylic acid, and mixtures thereof.

3. The solution of Claim 1, wherein said phosphonocarboxylic acid is 2-phosphono-1,2,4-butanetricarboxylic acid (PBTC).

4. The solution of Claim 1, wherein said solution comprises said phosphonocarboxylic acid in an amount ranging from about 0.0005 to about 0.2 percent by weight based on the total weight of the solution.

5. The solution of Claim 4, wherein said solution comprises said phosphonocarboxylic acid in an amount ranging from about 0.0025 to about 0.05 percent by weight based on the total weight of the solution.

6. The solution of Claim 1, wherein said at least one halide of an alkali metal, at least one halide of an alkaline earth metal, or mixture thereof comprises lithium chloride.

7. The solution of Claim 1, further comprising at least one inorganic or organic buffering agent or a mixture thereof capable of stabilizing the pH of said solution during repeated dehumidification cycles.

8. The solution of Claim 7, wherein said inorganic buffering agent is a boron-containing buffering agent.

9. The solution of Claim 8, wherein said boron-containing buffering agent is selected from the group consisting of lithium tetraborate compounds, lithium metaborate, sodium borate, potassium borate, boric acid, and mixtures thereof.

10. The solution of Claim 9, wherein said boron-containing buffering agent is a lithium tetraborate compound.

11. The solution of Claim 7, wherein said organic buffering agent is selected from the group consisting of amino polyols, organic sulfonic acids, and mixtures thereof.

12. The solution of Claim 11, wherein said organic buffering agent is selected from the group consisting of amino methyl propane, amino propane sulfonic acid, amino methyl propanol, Tris-, Bis-Tris, Bis-Tris propane and mixtures thereof.

13. The solution of Claim 12, wherein said organic buffering agent is selected from the group consisting of Tris, Bis-Tris, Bis-Tris propane, and mixtures thereof.

14. The solution of Claim 7, wherein said solution comprises inorganic buffering agent in an amount from about 0.03 to about 1.0 percent by weight based on the total weight of the solution.

15. The solution of Claim 14, wherein said solution comprises inorganic buffering agent in an amount from about 0.03 to about 0.3 percent by weight based on the total weight of the solution.

16. The solution of Claim 7, wherein said solution comprises organic buffering agent in an amount from about 0.7 to about 10.0 percent by weight based on the total weight of the solution.

17. The solution of Claim 16, wherein said solution comprises organic buffering agent in an amount from about 0.7 to about 5 percent by weight based on the total weight of the solution.

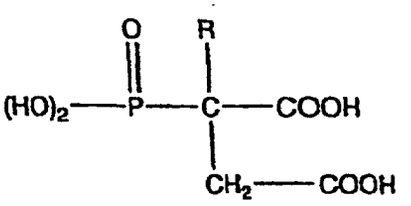
18. The solution of Claim 1, wherein said solution further comprises at least one corrosion inhibiting heteropoly complex anion of a transitional metal element.

19. The solution of Claim 1, wherein said solution is devoid of alkali metal salts of molybdate and chromate anions.

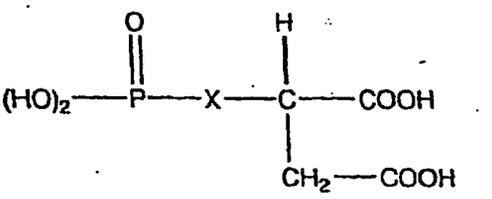
20. A process for dehumidifying humidified fluid streams, comprising circulating in a dehumidification machine a solution for dehumidifying humidified fluid streams comprising at least one halide of an alkali metal, at least one halide of an alkaline earth metal, or a mixture thereof, in an amount ranging from 10 to 45 weight percent and at least one phosphonocarboxylic acid corrosion inhibiting agent,
wherein the phosphonocarboxylic acid corrosion inhibiting agent is 2-phosphono-1,2,4-butanetricarboxylic acid (PBTC).

**Patentansprüche**

1. Eine absorbierende Lösung zum Entfeuchten befeuchteter Fluidströme, welche wenigstens ein Alkalimetallhalogenid, wenigstens ein Erdalkalimetallhalogenid oder eine Mischung davon in einer Menge im Bereich von 10 bis 45 Gewichtsprozent und wenigstens ein Phosphonocarbonsäure-Korrosionsschutzmittel enthält, in der die Phosphonocarbonsäuren Verbindungen der Formeln

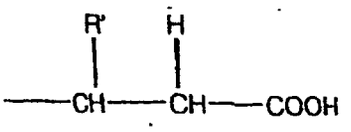



oder

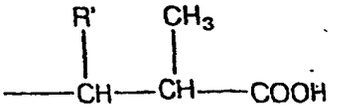



beinhalten, in denen:

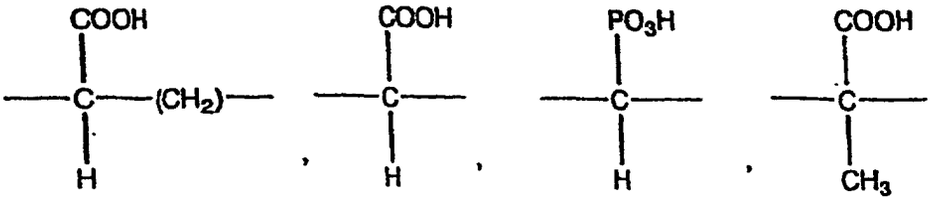
R ein Wasserstoff, ein Alkyl-, Alkenyl- oder AlkinylRest mit bis zu 4 Kohlenstoffatomen, ein Aryl-, ein Cycloalkyl- oder ein Aralkyl-Rest ist, oder der Rest



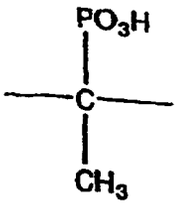

oder



R' Wasserstoff, ein Alkyl-Rest mit bis zu vier Kohlenstoffatomen oder ein Carboxyl-Rest ist und X



oder



ist.

2. Die Lösung nach Anspruch 1, in der die Phosphonocarbonsäure eine Verbindung enthält, die ausgewählt ist aus der Gruppe bestehend aus α-Methylphosphonobernsteinsäure, Phosphonobernsteinsäure, 1-Phosphonopropan-2,3-dicarbonsäure, 2-Phosphonobutan-1,2,4-tricarbonsäure, α-Allylphosphonobernsteinsäure, α-p-Chlorophenylphosphonobersteinsäure, α-Propargylphosphonobernsteinsäure, α-Benzylphosphonobersteinsäure, α-Cyclohexylphosphonobersteinsäure, 2-Phosphono-3-(α-methyl-carboxymethyl)-hexan-1,2,4-tricarbonsäure, 2,2-Diphosphonobutan-3,4-dicarbonsäure und Mischungen davon.

3. Die Lösung von Anspruch 1, in der die Phosphonocarbonsäure 2-Phosphono-1,2,4-butantricarbonsäure (PBTC) ist.

4. Die Lösung nach Anspruch 1, in der die Lösung die Phosphonocarbonsäure in einer Menge im Bereich von ca. 0.0005 bis ca. 0.2 Gewichtsprozent bezogen auf das Gesamtgewicht der Lösung enthält.

5. Die Lösung nach Anspruch 4, in der die Lösung die Phosphonocarbonsäure in einer Menge im Bereich von ca. 0.0025 bis ca. 0.05 Gewichtsprozent bezogen auf das Gesamtgewicht der Lösung enthält.

6. Die Lösung nach Anspruch 1, in der das wenigstens eine Alkalimetallhalogenid, das wenigstens eine Erdalkalimetallhalogenid oder die Mischung davon Lithiumchlorid beinhaltet.

7. Die Lösung nach Anspruch 1, weiter beinhaltend wenigstens ein anorganisches oder organisches Pufferagens oder eine Mischung davon, welches fähig ist, den pH der Lösung während wiederholter Entfeuchtungszyklen zu stabilisieren.

8. Die Lösung nach Anspruch 7, in der das anorganische Pufferagens ein borhaltiges Pufferagens ist.

9. Die Lösung nach Anspruch 8, in der das borhaltige Pufferagens ausgewählt ist aus der Gruppe bestehend aus

Lithiumtetraboratverbindungen, Lithiummetaborat, Natriumborat, Kaliumborat, Borsäure und Mischungen davon.

**10.** Die Lösung nach Anspruch 9, in der das borhaltige Pufferagens eine Lithiumtetraboratverbindung ist.

**11.** Die Lösung nach Anspruch 7, in der das organische Pufferagens ausgewählt ist aus der Gruppe bestehend aus Aminopolyolen, organischen Sulfonsäuren und Mischungen davon.

**12.** Die Lösung nach Anspruch 11, in der das organische Pufferagens ausgewählt ist aus der Gruppe bestehend aus Aminomethylpropan, Aminopropansulfonsäure, Aminomethylpropanol, Tris, Bis-Tris, Bis-Tris-Propan und Mischungen davon.

**13.** Die Lösung nach Anspruch 12, in der das organische Pufferagens ausgewählt ist aus der Gruppe bestehend aus Tris, Bis-Tris, Bis-Tris-Propan und Mischungen davon.

**14.** Die Lösung nach Anspruch 7, in der die Lösung anorganisches Pufferagens in einer Menge von ca. 0.03 bis ca. 1.0 Gewichtsprozent bezogen auf das Gesamtgewicht der Lösung enthält.

**15.** Die Lösung nach Anspruch 14, in der die Lösung anorganisches Pufferagens in einer Menge von ca. 0.03 bis ca. 0.3 Gewichtsprozent bezogen auf das Gesamtgewicht der Lösung enthält.

**16.** Die Lösung nach Anspruch 7, in der die Lösung organisches Pufferagens in einer Menge von ca. 0.7 bis ca. 10.0 Gewichtsprozent bezogen auf das Gesamtgewicht der Lösung enthält.

**17.** Die Lösung nach Anspruch 16, wobei die Lösung organisches Pufferagens in einer Menge von ca. 0.7 bis ca. 5 Gewichtsprozent bezogen auf das Gesamtgewicht der Lösung enthält.

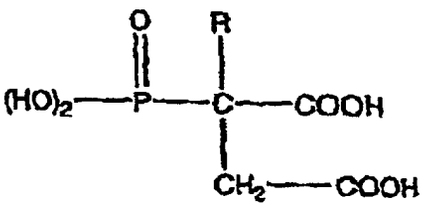
**18.** Die Lösung nach Anspruch 1, wobei die Lösung weiter wenigstens ein vor Korrosion schützendes Heteropolykomplex-Anion eines Übergangsmetallelementes enthält.

**19.** Die Lösung nach Anspruch 1, wobei die Lösung frei von Alkalimetallsalzen von Molybdat- und Chromat-Anionen ist.

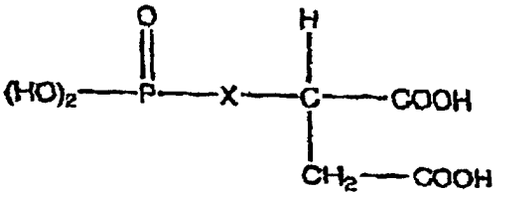
**20.** Ein Verfahren zum Entfeuchten befeuchteter Fluidströme beinhaltend, dass eine Lösung zum Entfeuchten befeuchteter Fluidströme, welche wenigstens ein Alkalimetallhalogenid, wenigstens ein Erdalkalimetallhalogenid oder eine Mischung davon in einer Menge im Bereich von 10 bis 45 Gewichtsprozent und wenigstens ein Phosphonocarbonsäure-Korrosionsschutzmittel enthält, in einer Entfeuchtungsmaschine zirkuliert wird, wobei das Phosphonocarbonsäure-Korrosionsschutzmittel 2-Phosphono-1,2,4-butantricarbonsäure (PBTC) ist.

**Revendications**

**1.** Solution absorbante permettant de déshumidifier des courants de fluides humidifiés, comprenant au moins un halogénure d'un métal alcalin, au moins un halogénure d'un métal alcalino-terreux, ou un de leurs mélanges, en quantité allant de 10 à 45 pour cent en poids, et au moins un agent inhibiteur de corrosion de type acide phosphonocarboxylique, dans laquelle lesdits acides phosphonocarboxyliques comprennent des composés de formule

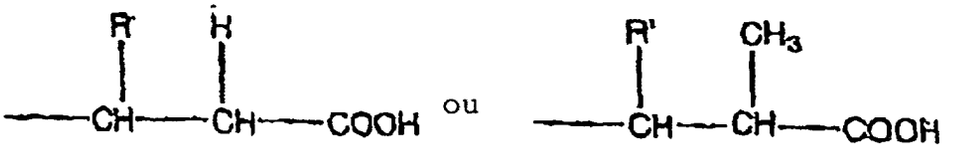



ou

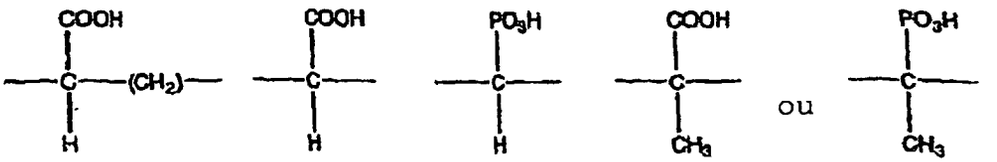


dans lesquelles :

R est un atome d'hydrogène, un radical alkyle, alcényle ou alcinyle comportant jusqu'à 4 atomes de carbone, un radical aryle, cycloalkyle ou aralkyle, ou le radical



R' est un atome d'hydrogène, un radical alkyle comportant jusqu'à quatre atomes de carbone ou un radical carboxyle ; et
X est



2. Solution selon la revendication 1, dans laquelle ledit acide phosphonocarboxylique comprend un composé choisi dans le groupe constitué par l'acide α-méthylphosphonosuccinique, l'acide phosphonosuccinique, l'acide 1-phosphonopropane-2,3-dicarboxylique, l'acide 2-phosphonobutane-1,2,4-tricarboxylique, l'acide α-allylphosphonosuccinique, l'acide α-p-chlorophénylphosphonosuccinique, l'acide α-propargylphosphonosuccinique, l'acide α-benzylphosphonosuccinique, l'acide α-cyclohexylphosphonosuccinique, l'acide 2-phosphono-3-(α-méthylcarboxyméthyl)hexane-1,2,4-tricarboxylique, l'acide 2,2-diphosphonobutane-3,4-dicarboxylique, et leurs mélanges.

3. Solution selon la revendication 1, dans laquelle l'acide phosphonocarboxylique est l'acide 2-phosphono-1,2,4-butanetricarboxylique (PBTC).

4. Solution selon la revendication 1, dans laquelle ladite solution comprend ledit acide phosphonocarboxylique en quantité allant d'environ 0,0005 à environ 0,2 pour cent en poids par rapport au poids total de la solution.

5. Solution selon la revendication 4, dans laquelle ladite solution comprend ledit acide phosphonocarboxylique en quantité allant d'environ 0,0025 à environ 0,05 pour cent en poids par rapport au poids total de la solution.

6. Solution selon la revendication 1, dans laquelle ledit au moins un halogénure d'un métal alcalin, ledit au moins un halogénure d'un métal alcalino-terreux, ou leur mélange, comprend du chlorure de lithium.

7. Solution selon la revendication 1, comprenant en outre au moins un agent tampon minéral ou organique, ou un de leurs mélanges, capable de stabiliser le pH de ladite solution durant les cycles de déshumidification répétés.

8. Solution selon la revendication 7, dans laquelle ledit agent tampon minéral est un agent tampon boré.

**9.** Solution selon la revendication 8, dans laquelle ledit agent tampon boré est choisi dans le groupe constitué par les composés tétraborate de lithium, le métaborate de lithium, le borate de sodium, le borate de potassium, l'acide borique, et leurs mélanges.

**10.** Solution selon la revendication 9, dans laquelle ledit agent tampon boré est un composé tétraborate de lithium.

**11.** Solution selon la revendication 7, dans laquelle ledit agent tampon organique est choisi dans le groupe constitué par les aminopolyols, les acides sulfoniques organiques, et leurs mélanges.

**12.** Solution selon la revendication 11, dans laquelle ledit agent tampon organique est choisi dans le groupe constitué par l'aminométhylpropane, l'acide aminopropanesulfonique, l'aminométhylpropanol, le Tris, le Bis-Tris, le Bis-Tris-propane, et leurs mélanges.

**13.** Solution selon la revendication 12, dans laquelle ledit agent tampon organique est choisi dans le groupe constitué par le Tris, le Bis-Tris, le Bis-Tris-propane, et leurs mélanges.

**14.** Solution selon la revendication 7, dans laquelle ladite solution comprend un agent tampon minéral à raison d'environ 0,03 à environ 1,0 pour cent en poids par rapport au poids total de la solution.

**15.** Solution selon la revendication 14, dans laquelle ladite solution comprend un agent tampon organique à raison d'environ 0,03 à environ 0,3 pour cent en poids par rapport au poids total de la solution.

**16.** Solution selon la revendication 7, dans laquelle ladite solution comprend un agent tampon organique à raison d'environ 0,7 à environ 10,0 pour cent en poids par rapport au poids total de la solution.

**17.** Solution selon la revendication 16, dans laquelle ladite solution comprend un agent tampon organique à raison d'environ 0,7 à environ 5 pour cent en poids par rapport au poids total de la solution.

**18.** Solution selon la revendication 1, dans laquelle ladite solution comprend en outre au moins un anion hétéropolycomplexe d'un élément de métal de transition inhibant la corrosion.

**19.** Solution selon la revendication 1, dans laquelle ladite solution est dépourvue de sels de métaux alcalins d'anions molybdate et chromate.

**20.** Procédé permettant de déshumidifier des courants de fluides humidifiés, comprenant la circulation, dans une machine de déshumidification, d'une solution permettant de déshumidifier des courants de fluides humidifiés, comprenant au moins un halogénure d'un métal alcalin, au moins un halogénure d'un métal alcalino-terreux, ou un de leurs mélanges, en quantité allant de 10 à 45 pour cent en poids, et au moins un agent inhibiteur de corrosion de type acide phosphonocarboxylique, dans lequel l'agent inhibiteur de corrosion de type acide phosphonocarboxylique est l'acide 2-phosphono-1,2,4-butanetricarboxylique (PBTC).