

# PATENT SPECIFICATION

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## (54) CORROSION INHIBITOR

(71) We, DREW CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of One Drew Chemical Plaza, Boonton, New Jersey 07005, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to corrosion inhibition, and more particularly, to a new and improved corrosion inhibiting composition which is particularly suitable for aqueous systems.

U.S. Patent No. 3,992,318 discloses a three component corrosion inhibitor which includes a phosphonate, phosphate and polymer of acrylic or methacrylic acid.

Applicant has found that improved corrosion inhibition, at alkaline pH, can be obtained by replacing the polymer of acrylic or methacrylic acid with a homopolymer of maleic acid and/or maleic anhydride.

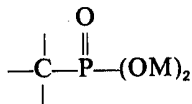
In accordance with the present invention, there is provided a corrosion inhibiting composition which includes corrosion inhibiting amounts of the following components:

- (a) at least one water soluble phosphonic acid or salt thereof;
- (b) at least one water soluble polyphosphate or alkali metal phosphate; and
- (c) a homopolymer of maleic acid or maleic anhydride or mixture thereof.

As used herein the term "water soluble" means that the compound is soluble in the amount required for corrosion inhibition. Accordingly, the compound can be sparingly soluble in water so long as the compound is sufficiently water soluble to provide, in solution, a corrosion inhibiting amount thereof.

The term "corrosion inhibiting amount" as used herein means that the component is present in an amount such that the composition inhibits corrosion and maintains such corrosion inhibition in an aqueous system.

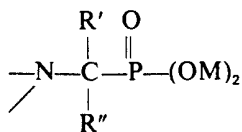
The phosphonic acid or salt thereof component of the present invention is a compound characterized by the following group:



wherein each M is independently either hydrogen or a cation; e.g., a metal ion, including alkali metals, such as sodium, lithium, and potassium, alkaline earth metals, such as calcium and magnesium, aluminum, zinc, cadmium, and manganese; nickel, cobalt, cerium; lead, tin; iron, chromium and mercury; an ammonium ion; or an alkyl ammonium ion derived from amines having a low molecular weight, such as below 300, and more particularly, the alkyl amines, alkylene amines and alkanol amines containing no more than two amine groups, such as ethyl amine, diethyl amine, propyl amine, propylene diamine, hexyl amine, 2 - ethylhexylamine, N - butylethanol amine and triethanol amine.

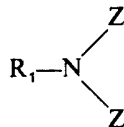
It is to be understood that as used herein the term "phosphonic acid" generically includes the phosphonic acid and the salts thereof.

As one type of phosphonic acid suitable for the purposes of the present invention, there may be mentioned the aminomethylene phosphonic acids which are characterized by the following grouping:

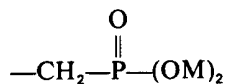


wherein M is as hereinabove defined and R' and R'' are each individually hydrogen or hydrocarbon (preferably C<sub>1</sub>—C<sub>5</sub> alkyl).

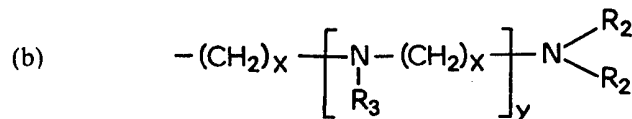
The aminomethylene phosphonic acids are preferably characterized by the following structural formula:



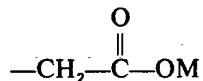
wherein Z is



and R<sub>1</sub> is



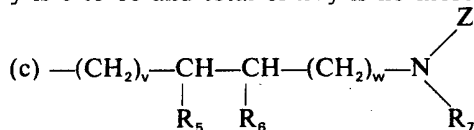
wherein each R<sub>2</sub> is independently either Z, hydrogen,



or CH<sub>2</sub>CH<sub>2</sub>OH and R<sub>3</sub> is either hydrogen, Z or C<sub>1</sub>—C<sub>20</sub> alkyl.

x is 1 to 20

y is 0 to 18 and total of x+y is no more than 20.



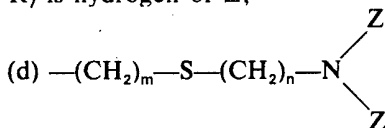
wherein R<sub>5</sub> is hydrogen or hydroxyl;

R<sub>6</sub> is hydrogen or alkyl, preferably an alkyl group containing 1 to 6 carbon atoms and R<sub>5</sub> and R<sub>6</sub> together with the two carbon atoms to which they are attached can form a cycloalkyl ring, preferably having from 4 to 6 carbon atoms.

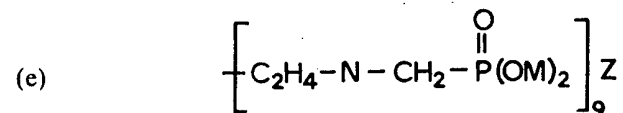
v is 0 to 20;

w is 0 to 20, and the total of v+w is no more than 20;

R<sub>7</sub> is hydrogen or Z;



wherein m and n are each 1 to 3.



wherein q is 1 to 20.

or



least 300, with the number average molecular weight generally not exceeding 5000; however, higher molecular weights can be employed, most generally, the number average molecular weight is from 500 to 2000.

The three components of the composition of the present invention are incorporated therein in corrosion inhibiting amounts; i.e., the three components are present in the composition in an amount which is effective to prevent corrosion upon addition of the composition to a system subject to corrosion. In general, the weight ratio of phosphonate to phosphate (calculated as  $\text{PO}_4$ ) in the composition ranges from about 0.1:1 to about 10:1, and preferably from about 0.5:1 to about 3:1. In general, the homopolymer of maleic acid or maleic anhydride is present in the composition in a polymer to phosphate (calculated as  $\text{PO}_4$ ) ratio of from about 0.01:1 to about 10:1 and preferably in an amount from about 0.1:1 to about 1:1, all by weight. It is to be understood that although the hereinabove described amounts of components employed in the composition of the present invention are preferred, the overall scope of the invention is not limited to such amounts. The choice of optimum amounts of the various components is deemed to be within the scope of those skilled in the art from the teachings herein.

The composition of the present invention, including the hereinabove described three components, is generally employed in combination with a liquid vehicle, preferably water. It is to be understood, however, that the composition can also be employed in solid form, or the components can be individually added to the aqueous system. In general, the composition is employed using water as a vehicle, and with the components being added to water to provide a concentration of the three components in the water from about 1 to about 80%, and preferably from about 10 to about 40%, all by weight. The composition may also include other water treatment components, such as, defoamers, dispersants and biocides, and accordingly, the addition of such components is within the spirit and scope of the present invention.

The composition of the present invention containing corrosion inhibiting amounts of the hereinabove described three components is added to a system subject to corrosion in a corrosion inhibiting amount; i.e., in an amount which is effective to prevent corrosion in the system. This amount will vary depending upon the system to which the composition is added and is influenced by factors, such as area subject to corrosion, processing conditions (pH, temperature), water quantity, etc. In general, the composition of the present invention is added to the system to provide at least 1 ppm of the phosphate component, and preferably from about 5 to about 25 ppm of the phosphate component. In general, the phosphate component is not added in an amount in excess of about 50 ppm. (The phosphate content is in parts by weight, calculated as  $\text{PO}_4$ ).

The corrosion inhibitor of the present invention is generally and preferably employed in aqueous systems in which corrosion is a problem, and in particular, in aqueous cooling systems. The overall scope of the invention, however, is not limited to such uses, and other uses should be apparent from the teachings herein.

The corrosion inhibiting composition of the present invention has been found to be particularly effective in that such a composition is capable of providing improved corrosion inhibition in alkaline systems, and in particular in systems where the pH is 8.5 or greater as compared to compositions in which acrylic or methacrylic acid polymers are employed in combination with a phosphate and phosphonate.

The invention will be further described with respect to the following examples; however, the scope of the invention is not to be limited thereby.

#### EXAMPLES

The following components are employed for testing corrosion efficiency at an alkaline pH:

Composition (Parts by Weight)	A	B
Sodium hexametaphosphate	15	15
Amino(trimethylene phosphonic acid)	4	0
Ethane-1-hydroxy-1,1-diphosphonic acid	0	4
Hydrolysed polymaleic anhydride	1	1

Compositions A & B are tested for corrosion inhibiting efficiency in standard "synthetic cooling water" at a pH of 8.5—9.0 and at an active solids basis of 20 ppm. The corrosion rates for compositions A & B are 8.7 and 10.7 mils per year.

Composition A is further tested in standard "synthetic cooling water" containing 2 ppm of hydrogen sulfide at a pH of 8.5—9.0 and active solids basis of 20 ppm. The determined corrosion rate is 6.9 mils per year.

WHAT WE CLAIM IS:—

- 5 1. A corrosion inhibitor, comprising: 5  
corrosion inhibiting amounts of (a) a water soluble polyphosphate or alkali metal phosphate; (b) a water soluble phosphonic acid or salt thereof; and (c) a homopolymer of maleic acid or maleic anhydride or mixtures thereof.
- 10 2. The corrosion inhibitor of Claim 1 wherein the weight ratio of phosphonate to phosphate, calculated as  $PO_4$ , is from 0.1:1 to 10:1. 10
3. The corrosion inhibitor of Claim 1 or 2 wherein the weight ratio of said polymer to phosphate, calculated as  $PO_4$ , is from 0.01:1 to 10:1.
- 15 4. The corrosion inhibitor of any one of the preceding claims wherein the phosphonate is at least one of ethane - 1 - hydroxy - 1,1 - diphosphonic acid, amino tri(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), hexamethylene diamine tetra(methylene phosphonic acid), and water soluble salts thereof. 15
5. The corrosion inhibitor of any one of the preceding claims wherein the phosphate is at least one of sodium hexametaphosphate and tetrapotassium pyrophosphate. 20
6. The corrosion inhibitor of any one of the preceding claims wherein the phosphonate is amino(trimethylene phosphonic acid).
7. The corrosion inhibitor of any one of the preceding claims wherein the phosphate is sodium hexmetaphosphate.
- 25 8. A process for inhibiting corrosion in an aqueous system, comprising: 25  
adding to the aqueous system corrosion inhibiting amounts of components (a), (b) and (c) of any one of the preceding claims.
9. The process of Claim 8 wherein component (a) is added in an amount of from 1 to 50 ppm.
- 30 10. The process of Claim 8 or 9 wherein the aqueous system is at a pH of at least 8.5. 30
11. A corrosion inhibitor according to Claim 1 described with reference to the examples.

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