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CORROSION-INHIBITED PHOSPHATE SOLUTIONS AND COMPOSITIONS USEFUL FOR MANUFACTURING THEM

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This invention relates to improved aqueous solutions of phosphate salts, which solutions are characterized by having a significantly reduced tendency to corrode copper metal and copper-containing alloys. More specifically, the present invention relates to corrosion-inhibited ammonium phosphate solutions suitable for prolonged use in handling and storage equipment made of copper and/or copper alloys.

Aqueous ammonium phosphate solutions have many uses: One of the most valuable recent developments in the field of fire fighting, and more particularly, forest fire fighting, was that relating to the use of aqueous solutions of ammonium phosphate salts. Since the present invention is particularly valuable when practiced in connection with forest fire fighting, the present discussion will be directed toward this particular end use. However, it should be kept in mind that the invention is generally useful for inhibiting corrosion of copper by ammonium phosphate solutions. Ordinarily, the solutions (often thickened with a viscosity modifying agent so that the solutions stick readily to surfaces with which they come into contact) are dropped onto brush, trees and dry grass in the path of a fire in order to slow or stop the progress of the fire. The extensive use of such ammonium phosphate solutions for forest fire control has been slowed because of the concern by those in the field over the natural corrosivity of such aqueous ammonium phosphate solutions toward some of the vital parts of air-tankers and storage equipment.

While, ordinarily, aqueous solutions containing several weight percent of dissolved ammonium phosphate are not considered to be extremely corrosive toward copper metal or copper alloys such as brass and bronze and the like, they are, nevertheless, sufficiently corrosive to cause great concern when the aqueous solutions are to come into physical contact with vital aircraft parts, since failure of the aircraft parts due even to slow corrosion occurring over a prolonged period of time could result in the loss of the aircraft and crew. Thus, in order to be considered completely acceptable for use in forest fire fighting by the air-drop method, it is necessary that the corrosivity of aqueous ammonium phosphate solutions, particularly toward copper metals, be significantly reduced.

Consequently, it is an object of the present invention to provide aqueous solutions containing ammonium phosphate salts useful for forest fire fighting, the normal tendency of which to corrode copper and copper-containing alloys is significantly reduced or substantially eliminated.

It is another object of the present invention to provide novel methods of inhibiting the corrosion of copper equipment by aqueous ammonium phosphate solutions.

It has now been found that the normal or natural tendency of aqueous solutions of ammonium phosphate salts, such as, for example, monoammonium orthophosphate and diammonium orthophosphate to corrode copper equipment can be significantly reduced and even

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practically eliminated by the presence (in solution) of an effective amount of an inorganic water-soluble thiocyanate. The term "water-soluble inorganic thiocyanate" is intended to include all of those inorganic thiocyanate materials or compounds that are soluble at ambient temperatures in the aqueous ammonium phosphate solutions to be inhibited to at least the extent at which they can discernibly reduce copper corrosion (i.e., generally at least about 0.005 weight percent). It includes, for example, the alkali metal and alkaline earth metal thiocyanates such as sodium, potassium, lithium, calcium, magnesium and strontium thiocyanates as well as ammonium thiocyanate. Of these, generally sodium, potassium and/or ammonium thiocyanates are preferred. Actually, since the protection from corrosion that can be afforded copper equipment by practicing the present invention apparently results from the thiocyanate (anion) portion of the thiocyanate compound, the particular source from which the thiocyanate anions are derived in manufacturing the aqueous ammonium phosphate solutions is not at all critical, so long as a sufficient amount of thiocyanate anions are provided in the phosphate solutions to effectively decrease the normal corrosivity of the phosphate solutions toward equipment made of copper and copper-containing alloys.

The ammonium phosphate solutions in which these thiocyanate compounds perform particularly effectively are those that contain at least about 0.5 weight percent, and up to the level at about which the solutions are saturated therewith, but preferably between about 5 and about 25 weight percent of dissolved ammonium phosphate salts, including monoammonium orthophosphate and/or diammonium orthophosphate salts, and also including the diammonium and monoammonium mixed orthophosphate salts that also contain an alkali metal cation, such as monoammonium disodium orthophosphate, monoammonium dipotassium orthophosphate and the like, no matter from what source these materials were derived, or in what form the materials are initially introduced into the aqueous compositions. Generally, it is preferred that the inhibited aqueous phosphate solutions of this invention have a pH between about 3 and about 9. When monoammonium orthophosphate is the only ammonium phosphate salt present in the inhibited fire-control compositions of this invention, the preferred pH of these compositions is generally from about 3 to about 5. Similarly, when diammonium orthophosphate is the only ammonium phosphate salt contained therein, the preferred pH is from about 7 to 9. When mixtures of monoammonium orthophosphate and diammonium orthophosphate are utilized, pH's between these preferred ranges are generally more desirable. However, compositions having pH's somewhat higher or lower than these preferred ranges can also be utilized to advantage in the practice of the present invention.

Although the presence of even a very small amount of the water-soluble thiocyanate compounds in the aqueous ammonium phosphate solutions described above has a corrosion-inhibiting effect upon them, as a general rule, aqueous phosphate compositions containing at least about 0.01 and preferably at least about 0.04 weight percent of one or more of the thiocyanate compounds in the dissolved state should be utilized. Generally optimum corrosion-inhibiting effects can be attained by utilizing at least about 0.10 weight percent of the thiocyanate compound. Stated otherwise, the corrosion-inhibited aqueous

ammonium orthophosphate compositions of this invention should ordinarily contain from about 0.075 to about 7.5, and preferably from about 0.03 to about 1.5 weight percent of thiocyanate anions dissolved therein.

The corrosion-inhibited ammonium phosphate solutions of the present invention can also contain materials other than the phosphate salts and the thiocyanate compounds without detracting substantially from the benefits that can be obtained by practicing this invention. For example, the solutions can contain minor amounts of surfactants; inorganic and organic complexing agents such as the alkali metal tripolyphosphate, pyrophosphates and trimetaphosphates, as well as the higher polyphosphates such as the hexametaphosphates; and can also contain ethylenediamine tetraacetic acid and various alkali metal and ammonium salts thereof and the alkali metal and ammonium nitrilotriacetates. These compositions can also contain any of the various thickening agents such as carboxymethylcellulose, algin, guar gum and carboxyethylcellulose; other corrosion-inhibiting ingredients; and inorganic and organic pigments and dyes; as well as many other materials.

The corrosion-inhibited phosphate compositions of this invention can be manufactured via any of a number of methods without any noticeably detrimental effects upon the ultimate performance of the compositions. For example, the thiocyanate compound can simply be dissolved by intermixing it into or with the otherwise completely formulated aqueous compositions, or at any other stage during the preparation of the fire-control composition. Via another method, the thiocyanate compound can first be dissolved in water and the resulting solution then intermixed subsequently with the ammonium phosphate materials.

Still another process for manufacturing the aqueous corrosion-inhibited phosphate compositions described heretofore involves one of the preferred embodiments of the present invention. This preferred embodiment comprises preparing an intermediate "concentrate" mixture of one or more of the ammonium phosphate salts described heretofore with one or more of the thiocyanate (inhibitor) compounds, generally in a particulated, solid form. Preferably the inhibitor compound(s) and ammonium phosphate salt(s) will be present in this concentrate composition or mixture in amounts in direct proportion to their respective amounts found in the fire-control compositions described heretofore, so that the final fire-control composition can be manufactured by simply dissolving the concentrate in a sufficient amount of water. In other words, generally the preferred concentrate compositions of this invention will contain at least one of the above-described ammonium phosphate salts and at least one of the thiocyanate (inhibitor) compounds in a weight ratio of phosphate salt to inhibitor compound, respectively, of from about 3800:1 to about 10:1, and preferably from about 750:1 to about 100:1. It is still further preferred that these particulated, solid concentrate compositions contain a total of at least about 50 weight percent of one or more of the above-described ammonium orthophosphate salts. These preferred concentrate compositions can also contain effective amounts of practically any other ingredients that can be utilized in fire-fighting compositions, including a thickener if one is desired in the final fire-control compositions, as well as dyes, pigments, water-softening agents, and the like, all of which should preferably be present in the concentrate compositions in minor amounts, as compared to the ammonium phosphate salt(s) contained therein. Some of the advantages of these preferred concentrate compositions can readily be appreciated when it is realized that at most points from which aircraft are loaded for their various air-drops of fire-control compositions, very little weighing and handling equipment is available that is capable of manufacturing the fire-control compositions from the individual components. Thus, in the absence of the preferred con-

centrate compositions described above (which concentrate compositions need simply be dissolved in appropriate amount of water in order to be converted into the final, valuable fire-control compositions of the present invention), as a practical matter, such corrosion inhibited final aqueous fire-control compositions as those described heretofore could not be utilized.

Typical examples of the preferred concentrate compositions of this invention include:

(a) 99.0 weight percent of diammonium orthophosphate and 1.0 weight percent of sodium thiocyanate.

(b) 90.0 weight percent of monoammonium orthophosphate, 1.0 weight percent of ammonium thiocyanate and 9.0 weight percent of sodium alginate.

(c) 90 weight percent of diammonium orthophosphate, 0.5 weight percent of potassium thiocyanate and 9.5 weight percent of sodium carboxymethylcellulose.

(d) 55 weight percent of an equimolar mixture of monoammonium orthophosphate and diammonium orthophosphate, 1.0 weight percent of ammonium thiocyanate, 35 weight percent of sodium tripolyphosphate and 9 weight percent of sodium alginate.

(e) 89 weight percent of monoammonium orthophosphate, 0.25 weight percent of magnesium thiocyanate and 10.75 weight percent of pentasodium aminotrimethylene phosphonate.

(f) 70 weight percent of diammonium orthophosphate, 20 weight percent of monoammonium orthophosphate, 9 weight percent of sodium carboxyethylcellulose and 1 weight percent of sodium thiocyanate.

(g) 84 weight percent of diammonium orthophosphate, 15.50 weight percent of guar gum and 0.50 weight percent of ammonium thiocyanate.

These "concentrate" compositions are also useful as corrosion-inhibited de-icer compounds, wherein, either alone or in combination with additional corrosion inhibiting materials, they can be utilized in a manner similar to that in which more corrosive, less desirable, sodium chloride is presently conventionally utilized. For example, these particulated, solid ammonium phosphate-thiocyanate compounds can effectively de-ice sidewalks, roadways and the like when they are simply spread over ice and/or snow.

The concentrate compositions can be prepared via any of a number of convenient procedures, including simply blending or mixing together the appropriate amounts of the various dry ingredients. Although the size of the individual particles in these preferred concentrate compositions is not critical in so far as the practice of the present invention is concerned, it is generally preferred that they be of sufficiently small size to pass through a U.S. Standard 12 mesh screen. For optimum results, at least about 80 weight percent of these particles should be small enough to pass through a U.S. Standard 40 mesh screen. Although commercial grades of the various available phosphate and soluble thiocyanate salts do not necessarily meet these optimum standards of particle size, they can readily be utilized in the preparation of the compositions of this invention.

In the following examples, which are illustrative of some of the preferred embodiments of the present invention, all parts are by weight unless otherwise specified.

Example 1

Into a conventional aluminum storage tank fitted with a fairly efficient mixer are charged 8.34 parts of water and 1.2 parts of a pre-prepared blend made up of 84 parts of crystalline technical grade diammonium orthophosphate, 15 parts of sodium alginate and 1 part of sodium thiocyanate. The resulting mixture is then stirred until all of the diammonium orthophosphate has dissolved.

Into the resulting fire-control composition are immersed several clean, preweight soft copper (1" x 2" x 1/16") coupons. The coupons are continuously immersed and removed from the composition in a cycle adjusted to that

the coupons remain immersed in the composition for 30 seconds, and then remain out of the solution, exposed to the ambient air, for 30 seconds. This procedure is continued for a total of 72 hours, after which the coupons are removed from the fire-control composition, rinsed with distilled water and acetone and then reweighed. The loss in weight (in milligrams) is then appropriately inserted into the equation:

$$\frac{534W}{DAT} = \text{Corrosion in mils per year}$$

wherein:

W=weight lost during test in milligrams,

D=specific gravity of metal,

A=exposed surface area in square inches,

T=time of exposure to solution in hours,

in order to determine the corrosion that has taken place, expressed in terms of mils of penetration per year. The corrosion rate or rate of attack on copper by the composition of Example I is thus found to be about 1.0 mils per year.

By comparison, a composition which is prepared in the same way as that in Example I, above, but without the sodium thiocyanate, corrodes similar copper coupons at a rate of about 1,000 mils per year.

In a manner similar to that just described, other compositions containing various levels of inorganic thiocyanate compounds are tested. Results of these tests are given in Table 1, below:

TABLE 1.—CORROSION INHIBITED AMMONIUM PHOSPHATE SOLUTIONS

Example No.	Ammonium Phosphate	Parts	Thickener ¹	Inhibitor	Parts	Metal	Corrosion Rate (m.p.y.)
Control	Diammonium Orthophosphate	10	None	None		Copper	1,500
Do	do	10	CMC ²	do		Brass	7.3
Do	do	10	None	do		Bronze	1,300
Do	do	10	CMC ²	do		Copper	940
Do	do	10	None	do		do	15
II	Monoammonium Orthophosphate	5	do	Sodium Thiocyanate	0.05	do	1
III	do	5	do	do	0.05	Brass	2
IV	do	5	do	do	0.05	Bronze	2
V	do	5	CMC ²	Ammonium Thiocyanate	0.04	Copper	1
VI	do	10	Algin Gel	Sodium Thiocyanate	0.10	do	1
VII	do	10	CMC ²	Potassium Thiocyanate	0.05	do	6
VIII	do	10	CMC ²	Magnesium Thiocyanate	0.05	do	6
IX	do	10	CMC ²	Ammonium Thiocyanate	0.10	Bronze	2
X	Monoammonium Orthophosphate	5	CMC ²	Sodium Thiocyanate	0.05	Copper	0
XI	Diammonium Orthophosphate	5	CMC ²	do	0.05	do	1
XI	Monoammonium Orthophosphate	5	CMC ²	do	0.05	do	1
XI	Diammonium Orthophosphate	10	CMC ²	do	0.05	do	1
XII	Monoammonium Orthophosphate	1	CMC ²	do	0.05	do	5
XII	Tetrasodium Pyrophosphate	3	do	do	0.05	do	5
XIII	Diammonium Orthophosphate	5	None	do	0.10	do	0

¹ Thickener used at the 1 weight percent level, based on total weight of the composition.

² Carboxymethylcellulose.

What is claimed is:

1. An aqueous ammonium phosphate composition consisting essentially of, in addition to at least one inorganic ammonium orthophosphate selected from the group consisting of monoammonium orthophosphate and diammonium orthophosphate, an inorganic water-soluble thiocyanate compound; there being dissolved in said compositions from about 0.5 to about 25 weight percent of said inorganic ammonium orthophosphate, and from about 0.03 to about 7.5 weight percent of dissolved thiocyanate ion.

2. An aqueous composition as in claim 1, wherein said inorganic water-soluble thiocyanate compound is selected from the group consisting of ammonium, alkali metal and alkaline earth metal thiocyanates.

3. A corrosion-inhibited liquid aqueous ammonium phosphate composition consisting essentially of at least about 0.5 weight percent of an ammonium orthophosphate salt selected from the group consisting of monoammonium orthophosphate, diammonium orthophosphate

and mixtures thereof, and from about 0.075 to about 7.5 weight percent of dissolved thiocyanate ions.

4. A corrosion-inhibited liquid aqueous ammonium phosphate composition consisting essentially of water from about 5 to about 25 weight percent of an ammonium orthophosphate salt and from about 0.03 to about 1.5 weight percent of dissolved thiocyanate ions.

5. A concentrated ammonium phosphate composition suitable for use in the manufacture of aqueous corrosion-inhibited ammonium orthophosphate firefighting solutions, said composition consisting essentially of at least one ammonium orthophosphate salt selected from the group consisting of monoammonium orthophosphate and diammonium orthophosphate and a water-soluble inorganic thiocyanate compound; the weight ratio of said ammonium orthophosphate salt to said thiocyanate compound in said composition being from about 3800:1 to about 10:1.

6. A particulated solid concentrate composition consisting essentially of at least about 50 weight percent of an ammonium orthophosphate material selected from the group consisting of monoammonium orthophosphate, diammonium orthophosphate and mixtures thereof, and an inorganic thiocyanate compound selected from the group consisting of ammonium, alkali metal and alkaline earth metal thiocyanates; the weight ratio of said ammonium orthophosphate material to said thiocyanate compound in said concentrate composition being from about 750:1 to about 100:1.

7. A particulated, solid concentrate composition as in claim 6, wherein said thiocyanate compound is ammonium thiocyanate.

8. A particulated, solid concentrate composition as in claim 6, wherein said thiocyanate compound is sodium thiocyanate.

9. A particulated, solid concentrate composition as in claim 6, wherein said thiocyanate compound is potassium thiocyanate.

10. A particulated, solid concentrate composition as in claim 6, wherein said thiocyanate compound is magnesium thiocyanate.

11. A particulated, solid concentrate composition as in claim 6, wherein said thiocyanate compound is calcium thiocyanate.

12. A method of retarding the corrosion of copper and copper alloys upon contact with a normally corrosive aqueous ammonium orthophosphate solution consisting essentially of water and, dissolved therein, from about 0.5 to about 25 weight percent of ammonium orthophosphate

selected from the group consisting of monoammonium orthophosphate, diammonium orthophosphate and mixtures thereof, which method comprises effecting said contact when said aqueous ammonium orthophosphate solution contains dissolved therein from about 0.075 to about 7.5 weight percent of thiocyanate ions.

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