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CORROSION-INHIBITED PHOSPHATE SOLUTIONS
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This is a continuation-in-part of U.S. patent application Serial No. 235,864, filed November 6, 1962, now abandoned.

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 practically eliminated by the presence (in solution) of an effective amount of an inorganic water-soluble thiosulfate. The term "water-soluble inorganic thiosulfate" is intended to include all of those inorganic thiosulfate materials or compounds that are soluble in distilled water to the ex-

tent of at least about 0.005 weight percent. It includes, for example, the alkali metal and alkaline earth metal thiosulfates such as sodium, potassium, lithium, calcium, magnesium and strontium thiosulfates as well as ammonium thiosulfate. Of these, generally sodium, potassium and/or ammonium thiosulfate are preferred. Actually, since the protection from corrosion that can be afforded copper equipment by practicing the present invention apparently results from the thiosulfate (anion) portion of the thiosulfate compound, the particular source from which the thiosulfate anions are derived in manufacturing the inhibited aqueous ammonium phosphate solutions of the present invention is not at all critical, provided a sufficient amount of thiosulfate anions are provided in the phosphate solutions to effectively decrease the normal corrosivity of the phosphate solutions toward copper and copper-containing alloys.

The ammonium phosphate solutions in which these thiosulfate 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, 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. Especially preferred aqueous ammonium phosphate solutions contain from about 5 to about 25 weight percent of diammonium orthophosphate. Generally, it is preferred that the inhibited aqueous phosphate solutions of this invention have a pH above about 7.2, preferably above about 7.5. Also, the pH's of these compositions should ordinarily be below about 11. This includes solutions containing monoammonium orthophosphate as the only ammonium phosphate salt incorporated into the inhibited fire-control compositions of this invention, which compositions have pH's above about 7.2. When diammonium orthophosphate is the only ammonium phosphate salt contained therein, the preferred pH is from about 7.5 to about 10. When mixtures of monoammonium orthophosphate and diammonium orthophosphate are utilized, pH's within 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 thiosulfate compound(s) 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 from about 0.04 to about 10 weight percent of one or more of the thiosulfate 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 thiosulfate compound.

The corrosion-inhibited ammonium phosphate solutions of the present invention can also contain materials other than the phosphate salts and the thiosulfate 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 also can con-

tain ethylenediamine tetraacetic acid and various alkali metal and ammonium salts thereof and the alkali metal and ammonium nitrilotriacetates; any of the various thickening agents such as sodium or potassium carboxymethylcellulose, algin, guar gum and sodium or potassium 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 thiosulfate 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 thiosulfate 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 a "concentrate" mixture of one or more of the ammonium phosphate salts described heretofore with one or more of the thiosulfate (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 proportionate to those 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 thiosulfate (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, 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 concentrate 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 fire-control compositions as those described heretofore could not be utilized.

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

(a) 90.0 weight percent of diammonium orthophosphate, 1.0 weight percent of ammonium thiosulfate and 9.0 weight percent of sodium alginate.

(b) 99.0 weight percent of diammonium orthophosphate and 1.0 weight percent of sodium thiosulfate.

(c) 70 weight percent of diammonium orthophos-

phate, 20 weight percent of monoammonium orthophosphate, 0.5 weight percent of potassium thiosulfate 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 thiosulfate, 35 weight percent of sodium tripolyphosphate and 9 weight percent of sodium alginate.

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

(f) 65 weight percent of diammonium orthophosphate, 25 weight percent of monoammonium orthophosphate, 9 weight percent of sodium carboxyethylcellulose and 1 weight percent of sodium thiosulfate.

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

(h) 85 weight percent of diammonium orthophosphate, 5 weight percent of monoammonium orthophosphate, 0.5 weight percent of potassium thiosulfate and 9.5 weight percent of sodium carboxymethylcellulose.

(i) 85 weight percent of diammonium orthophosphate, 5 weight percent of monoammonium orthophosphate, 9 weight percent of sodium carboxyethylcellulose and 1 weight percent of sodium thiosulfate.

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-thiosulfate compounds can effectively de-ice sidewalks, roadways and the like when they are simply spread over ice and/or snow.

The concentrate compositions of this invention 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 phosphate and thiosulfate 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 given are by weight unless otherwise specified.

EXAMPLE I

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 thiosulfate. The resulting mixture is then stirred until all of the diammonium orthophosphate has dissolved.

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

from about 0.01 to about 10 weight percent of a water soluble inorganic thiosulfate compound dissolved therein selected from the group consisting of ammonium, alkali metal and alkaline earth metal thiosulfates.

5 4. A liquid aqueous diammonium orthophosphate solution as in claim 3, wherein said inorganic water soluble thiosulfate is ammonium thiosulfate.

5 5. A liquid aqueous diammonium orthophosphate solution as in claim 3, wherein said inorganic water soluble thiosulfate is sodium thiosulfate.

10 6. A liquid aqueous diammonium orthophosphate solution as in claim 3, wherein said inorganic water soluble thiosulfate is potassium thiosulfate.

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
II	do	5	None	Sodium thiosulfate	0.25	do	15
III	do	5	do	do	0.25	Brass	17
IV	do	5	do	do	0.25	Bronze	18
V	do	5	CMC ²	Potassium thiosulfate	0.25	Copper	14
VI	do	10	Algin gel	Ammonium thiosulfate	0.20	do	18
VII	do	10	CMC ²	Magnesium thiosulfate	0.20	do	18
VIII	do	10	CMC ²	Ammonium thiosulfate	0.50	do	12
IX	do	10	CMC ²	Lithium thiosulfate	0.40	do	16
X	do	10	CMC ²	Potassium thiosulfate	0.40	Bronze	17
XI	Diammonium orthophosphate	10	CMC ²	Sodium thiosulfate	1	Copper	12
	Monoammonium orthophosphate	1					
	Diammonium orthophosphate	10					
XII	Monoammonium orthophosphate	1	CMC ²	do	0.50	do	14
	Tetrasodium pyrophosphate	3					
XIII	Diammonium orthophosphate	5	None	do	1	do	10

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

² Carboxymethylcellulose.

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

By comparison, a composition which is prepared in the same way as that in Example I, above, but without the sodium thiosulfate, 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 thiosulfate compounds are tested. Results of these tests are given in Table 1, below:

What is claimed is:

1. A liquid aqueous ammonium phosphate solution having a pH above about 7.2 and in contact with a material selected from the group consisting of copper and copper alloys; said solution consisting essentially of at least about 0.5 weight percent of an ammonium phosphate salt dissolved therein selected from the group consisting of monoammonium orthophosphate, diammonium orthophosphate and mixtures thereof and from about 0.01 to about 10 weight percent of a water soluble inorganic thiosulfate compound dissolved therein.

2. A liquid aqueous ammonium phosphate solution as in claim 1, wherein said solution contains dissolved therein between about 5 and about 25 weight percent of said ammonium phosphate salt and the weight ratio of said ammonium phosphate salt to said thiosulfate compound in said solution is from about 3800:1 to about 10:1.

3. A liquid aqueous diammonium orthophosphate solution having a pH between about 7.2 and about 11 and in contact with a material selected from the group consisting of copper and copper alloys; said solution consisting essentially of from about 5 to about 25 weight percent of diammonium orthophosphate dissolved therein and

7. A liquid aqueous diammonium orthophosphate solution as in claim 3, wherein said inorganic water soluble thiosulfate is magnesium thiosulfate.

45 8. A liquid aqueous diammonium orthophosphate solution as in claim 3, wherein said inorganic water soluble thiosulfate is calcium thiosulfate.

9. A liquid aqueous diammonium orthophosphate solution as in claim 3, wherein said solution also contains a thickening material selected from the group consisting of sodium carboxymethylcellulose, potassium carboxymethylcellulose, algin, guar gum, sodium carboxyethylcellulose and potassium carboxyethylcellulose.

10. A liquid aqueous diammonium orthophosphate solution as in claim 9, wherein said thickening agent is sodium carboxymethylcellulose.

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