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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 and to the compositions useful for manufacturing them.

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 solution (often thickened with a viscosity modifying agent so that the solutions stick readily to surfaces with which they come into contact) are dropped by airplanes such as air-tankers 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.

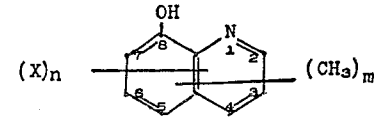
Aqueous solutions containing several weight percent of dissolved ammonium phosphate are considered to be corrosive toward copper metal or copper alloys such as brass and bronze and the like, and such are corrosive to the extent to cause great concern when the aqueous solutions are to come into physical 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 is a still further object of the present invention to provide ammonium phosphate compositions which are useful in preparing aqueous ammonium phosphate solutions characterized by having a significantly reduced tendency to corrode copper metal and copper-containing alloys.

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 a water-soluble 8-hydroxy quinoline compound including the halo and methyl substituted 8-hydroxy derivatives (all of which are hereinafter termed 8-hydroxy quinoline compounds) of the following formula:



wherein X is selected from the group consisting of chloro, bromo and iodo, *n* is an integer from 0 to 4 and *m* is an integer from 0 to 4, especially preferred halo and methyl substituted 8-hydroxy quinoline are the mono- and di-halo; and the mono- and di-methyl substituted derivatives. In addition, the water-soluble salts (addition compounds) can also be used such as the citrates, sulfates, benzoates, tartarates salts of the foregoing compounds as well as the water-soluble salts (chelated structures) such as the alkaline earth (calcium, magnesium, barium and the like), and the heavy metal salts, such as copper, zinc, nickel, iron, aluminum, lead and the like.

8-hydroxy quinoline compounds illustrative of being suitable for use include

8-hydroxy quinoline
5,7-dibromo, 8-hydroxy quinoline
5,7-dichloro, 8-hydroxy quinoline
2,4,5,7-tetramethyl, 8-hydroxy quinoline
2-methyl, 5,7-dichloro, 8-hydroxy quinoline
5-chloro, 7-iodo, 8-hydroxy quinoline
2,4-methyl, 8-hydroxy quinoline
5,7-dibromo, 2,4-dimethyl, 8-hydroxy quinoline
2,4,5,7-tetrachloro, 8-hydroxy quinoline

The compounds are effective in aqueous solutions of ammonium phosphates of normally useful concentrations and which in most cases are from 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 compositions contain from about 5 to about 25 weight percent of an ammonium orthophosphate. 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 8-hydroxy quinoline compounds in

the aqueous ammonium phosphate solutions described above has a corrosion-inhibiting effect upon them, as a general rule, aqueous phosphate compositions containing from about 0.005 to about 10 and even higher amounts can be used although such does not appear to appreciably improve the corrosion inhibition of the aqueous ammonium phosphate solutions over the use of lesser amounts. Preferably from about 0.05 to about 2 weight percent of one or more of the 8-hydroxy quinoline compounds in the dissolved state should be utilized.

The corrosion-inhibited ammonium phosphate solutions of the present invention can also contain materials other than the phosphate salts and the 8-hydroxy quinoline 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 contain ethylenediamine tetraacetic acid and various metal and ammonium nitrilotriacetates; any of the various thickening agents such as carboxymethylcellulose, algin, guar gum, pectates, such as lemon pectates and the like, hydratable clays such as bentonites, attapulgites and the like, and carbethoxyethylcellulose; other corrosion-inhibiting ingredients; and inorganic and organic pigments and dyes; as well as many other materials.

A particular advantage in the use of the 8-hydroxy quinoline compounds in ammonium phosphate solutions is that they are particularly effective in the presence of water-soluble fluosilicate compounds, such as sodium fluosilicate, ammonium fluosilicate, and potassium fluosilicate, which are useful as inhibitors for aluminum in contact with ammonium phosphate solutions and therefore provide ammonium phosphate solutions which are characterized by having a significantly reduced tendency to corrode not only copper-containing metals, but also aluminum-containing metals. In fact, in most cases, the combination of the 8-hydroxy quinoline compounds and the fluosilicate compounds function better as a corrosion inhibitor for copper and copper-containing alloys than the 8-hydroxy quinoline compound when used individually. Such fluosilicates are described and disclosed in U.S. Re. 25,394.

A further particular advantage in the use of the 8-hydroxy quinoline compounds in ammonium phosphate solutions is that they can also function as preservatives for such thickening agents which are usually present in the solutions as carboxymethyl cellulose and carboxyethyl cellulose and the like and which are subject to fungicidal degradation.

The corrosion-inhibited phosphate compositions of this invention can be manufactured via any of a number of manipulative methods without any noticeably detrimental effects upon the ultimate performance of the compositions. For example, the 8-hydroxy quinoline 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 8-hydroxy quinoline 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 8-hydroxy quinoline (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 8-hydroxy quinoline (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. 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. Especially preferred concentrate compositions contain a major amount of the ammonium orthophosphate material, that is, at least about 50 weight percent, in addition to the minor amounts, that is, less than 50 weight percent, of the corrosion inhibitor, thickener, and other desired additives. 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 amounts 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) 99.0 weight percent of diammonium orthophosphate and 1.0 weight percent of 8-hydroxyquinoline.

(b) 90.0 weight percent of monoammonium orthophosphate, 1.0 weight percent of 8-hydroxy quinoline sulfate and 9.0 weight percent of sodium alginate.

(c) 90 weight percent of diammonium orthophosphate, 0.5 weight percent of 5,7-dichloro 8-hydroxy quinoline 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 8-hydroxy quinoline benzoate, 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 2-methyl, 5,7-dichloro, 8-hydroxy quinoline and 10.75 weight percent of pentasodium aminotrimethylenephosphonate.

(f) 70 weight percent of diammonium orthophosphate, 20 weight percent of monoammonium orthophosphate, 9 weight percent of sodium carboxyethylcellulose and 1 weight percent of 8-hydroxy quinoline citrate.

(g) 84 weight percent of diammonium orthophosphate, 15.50 weight percent of guar gum and 0.50 weight percent of calcium 8-hydroxy quinoline.

(h) 90 weight percent of diammonium orthophosphate, 8 weight percent of sodium carboxymethylcellulose, 1 weight percent of 8-hydroxy quinoline and 1 weight percent of sodium fluosilicate.

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-8-hydroxy quinoline compositions can effectively de-ice

sidewalks, roadways and the like when they are simply spread over ice and/or snow on these substrates.

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 phosphate 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 example, which is illustrative of one of the preferred embodiments of the present invention, all parts given are by weight unless otherwise specified.

Example

Into a conventional iron storage tank fitted with a fairly efficient mixer are charged 89 parts of water and 11.5 parts of a pre-prepared blend made up of 10 parts of crystalline technical grade diammonium orthophosphate, 1 part of sodium alginate and 0.5 part of 8-hydroxy quinoline. 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 immersed in the composition 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 this example is thus found to be about 10 mils per year. When .15 part of sodium fluosilicate is added to the foregoing composition, the corrosion rate on copper by the composition of this example is found to be about 0.9 mil per year.

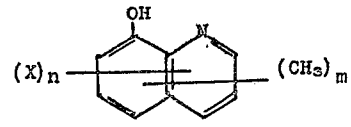
By comparison, a composition which is prepared in the same way as that in this example but without the 8-hydroxy quinoline or sodium fluosilicate, corrodes similar copper coupons at a rate of about 1,000 mils per year.

Good results comparable to the foregoing example can also be obtained using substantially equivalent amounts of other 8-hydroxy quinoline compounds which include the benzoate and sulfate salts, as well as the calcium, magnesium, copper, zinc and nickel salts of 8-hydroxy quinoline, 5,7-dibromo, 8-hydroxy quinoline, 2-methyl-5,7-dichloro, 8-hydroxy quinoline, 5-chloro, 7-iodo, 8-hydroxy quinoline and the like as well as substantially equivalent amounts of various thickening agents which include hydratable clays, algin, guar gum, pectates, carboxyethyl cellulose and the like.

As being illustrative of an airplane attachment for extinguishing fires as well as the method for using such, reference is made to U.S. Patent 1,997,669.

What is claimed is:

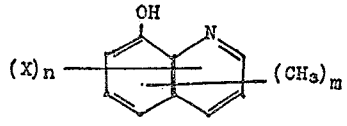
1. An aqueous ammonium orthophosphate composition consisting essentially of, in addition to the ammonium orthophosphate dissolved therein in an amount of at least about 0.5 weight percent of said composition, a water-soluble 8-hydroxy quinoline compound to effectively decrease the normal corrosivity of said composition toward copper and copper-containing alloys, said 8-hydroxy quinoline compound selected from the group consisting of a compound having the following formula



wherein X is selected from the class consisting of chloro, bromo and iodo, n is an integer from 0 to 4, and m is an integer from 0 to 4, and their water-soluble salts in an amount of at least about 0.005 weight percent of said composition.

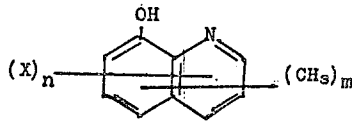
2. A corrosion-inhibited aqueous ammonium phosphate composition as in claim 1, wherein said water-soluble 8-hydroxy quinoline compound is 8-hydroxy quinoline.

3. A corrosion-inhibited liquid aqueous ammonium orthophosphate 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 as a copper corrosion inhibitor, from about 0.005 to about 10 weight percent of a water-soluble 8-hydroxy quinoline compound selected from the group consisting of a compound having the following formula



wherein X is selected from the class consisting of chloro, bromo and iodo, n is an integer from 0 to 4, and m is an integer from 0 to 4, and their water-soluble salts.

4. A corrosion-inhibited liquid aqueous ammonium orthophosphate composition consisting essentially of from about 5 to about 25 weight percent of an ammonium orthophosphate and as a copper corrosion inhibitor, from about 0.05 to about 2.0 weight percent of a water-soluble 8-hydroxy quinoline compound selected from the group consisting of a compound having the following formula

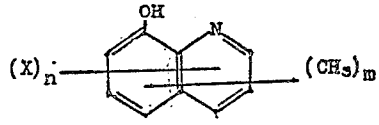


wherein X is selected from the class consisting of chloro, bromo and iodo, n is an integer from 0 to 4, and m is an integer from 0 to 4, and their water-soluble salts.

5. A corrosion-inhibited aqueous ammonium orthophosphate composition as in claim 1, additionally containing an effective corrosion-inhibiting amount of a water-soluble fluosilicate compound selected from the group consisting of sodium fluosilicate, potassium fluosilicate and ammonium fluosilicate.

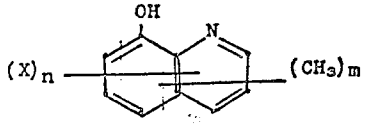
6. A concentrated ammonium orthophosphate composition suitable for use in the manufacture of aqueous copper corrosion-inhibited ammonium orthophosphate fire-fighting solutions, said composition consisting essentially of a water-soluble 8-hydroxy quinoline compound

as a copper corrosion inhibitor selected from the group consisting of a compound having the following formula



wherein X is selected from the class consisting of chloro, bromo and iodo, *n* is an integer from 0 to 4, and *m* is an integer from 0 to 4, and their water-soluble salts, and a major portion of at least one ammonium orthophosphate salt; the weight ratio of said ammonium orthophosphate salt to said 8-hydroxy quinoline compound in said composition being from about 3800:1 to about 10:1.

7. 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 as a copper corrosion inhibitor, a water-soluble 8-hydroxy quinoline compound selected from the group consisting of a compound having the following formula



wherein X is selected from the class consisting of chloro, bromo and iodo, *n* is an integer from 0 to 4, and *m* is an integer from 0 to 4, and their water-soluble salts, the weight ratio of said ammonium orthophosphate material to said 8-hydroxy quinoline compound in said concentrate composition being from about 750:1 to about 100:1.

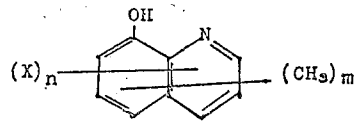
8. A particulated, solid concentrate composition as in claim 7, wherein said 8-hydroxy quinoline compound is 8-hydroxy quinoline.

9. A particulated, solid concentrate composition as in claim 7, wherein said 8-hydroxy quinoline compound is the sulfate salt of 8-hydroxy quinoline.

10. A particulated, solid concentrate composition as in claim 7, wherein said 8-hydroxy quinoline compound is the benzoate salt of 8-hydroxy quinoline.

11. A particulated, solid concentrate composition as in claim 7, wherein said 8-hydroxy quinoline compound is the calcium salt of 8-hydroxy quinoline.

12. A method of retarding the corrosion of copper and copper-containing alloys upon contact with a normally corrosive aqueous ammonium orthophosphate solution, which method comprises effecting said contact when said aqueous ammonium orthophosphate contains a water-soluble 8-hydroxy quinoline compound selected from the group consisting of a compound having the following formula



wherein X is selected from the class consisting of chloro, bromo and iodo, *n* is an integer from 0 to 4, and *m* is an integer from 0 to 4, and their water-soluble salts.

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