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CORROSION-INHIBITED PHOSPHATE FIRE-FIGHTING SOLUTIONS AND COMPOSITIONS USEFUL FOR MANUFACTURING THEM

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13 Claims. (Cl. 252-2)

This patent application is a continuation-in-part of co-pending application S.N. 235,866, filed Nov. 6, 1962, now abandoned.

This invention relates to improved aqueous phosphate fire-fighting solutions, 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 fire-fighting solutions suitable for prolonged use in handling and storage equipment made of copper and/or copper alloys and to the compositions useful in manufacturing them.

One of the most valuable recent developments in the field of fire control, and more particularly, forest fire fighting, was that relating to the use of aqueous solutions of ammonium phosphate salts thickened with a viscosity modifying agent so that the solutions stick readily to surfaces with which they come into contact. These solutions 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 fire-fighting 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 fire-fighting 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 and thickening agents 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 fire-fighting solutions.

It is a still further object of the present invention to provide ammonium phosphate compositions which are useful in preparing aqueous ammonium phosphate fire-fighting solutions characterized by having a significantly reduced tendency to corrode copper metal and copper-containing alloys.

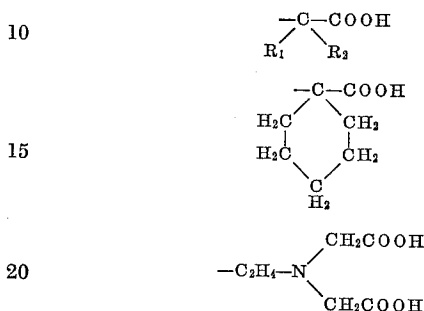
It has now been found that the normal or natural tendency of aqueous solutions of ammonium phosphate fire-fighting solutions can be significantly reduced and even practically eliminated by the presence (in solution) of an

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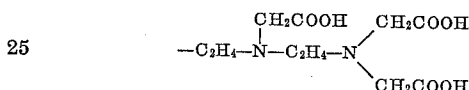
effective amount of a water-soluble amino polycarboxylic acid or salt thereof, said acid having the formula



wherein R is a member selected from the group consisting of the radicals



and



wherein R₁ is a member selected from the group consisting of hydrogen, lower alkyl (1-4 carbon atoms) and phenyl and R₂ is a member selected from the group consisting of hydrogen and lower alkyl (1-4 carbon atoms).

Amino polycarboxylic acid compounds illustrative of being suitable for use include:

- ethylene diamine tetraacetic acid
- nitrilo triacetic acid
- anthranilic-N,N-diacetic acid
- c-diethyl-nitrilo triacetic acid
- c-dimethyl-nitrilo triacetic acid
- c-dibutyl-nitrilo triacetic acid
- c-phenyl-nitrilo triacetic acid
- c-cyclohexylenyl-nitrilotriacetic acid
- c-methyl-nitrilo triacetic acid
- c-ethyl-nitrilo triacetic acid
- c-butyl-nitrilo triacetic acid
- diethylene triamine penta acetic acid

Any water-soluble salt of the amino polycarboxylic acids can, in general, be also employed in practicing the present invention. Although the sodium salts, including the acid-salts, are preferred, other alkali metal salts, such as the potassium, lithium and the like, as well as mixtures of the alkali metal salts, may be substituted therefor. Other water-soluble salts which can be employed in practicing the present invention include the ammonium salts and amine salts, particularly when the amine is a low molecular weight amine, i.e., having a molecular weight below about 200, and more particularly the alkyl amines, alkyleneamines and alkanolamines containing not more than 2 amine groups.

The water-soluble amino polycarboxylic acids or salts are effective in aqueous solutions of ammonium phosphates and thickening agents 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 solutions. Especially preferred aqueous ammonium phosphate fire-fighting compositions contain from about 5 to about 25 weight percent of 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-fighting solutions of this invention, the preferred pH of these solutions 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, solutions having pH's somewhat higher or lower than these preferred ranges can also be utilized to advantage in the practice of the present invention.

The various thickening agents which are useful in the aqueous ammonium phosphate fire-fighting solutions are selected from the class consisting of carboxy lower alkyl cellulose, such as carboxymethylcellulose, carboxyethylcellulose and carboxypropylcellulose, and the like which in addition include the water-soluble salts thereof such as the sodium, potassium and ammonium salts, algin which includes the water-soluble salts thereof such as the sodium, potassium and ammonium salts, guar gum, and hydratable clays, such as bentonites and attapulgitites and the like. In most cases, the thickening agents are used in minor amounts, that is, less than about 50 weight percent of the aqueous ammonium phosphate fire-fighting solution and preferably from about 0.5 to about 30 weight percent with from about 1 to about 15 weight percent being especially preferred.

Although the presence of even a very small amount of the water-soluble amino polycarboxylic acids or salts in the aqueous ammonium phosphate fire-fighting solutions described above has a corrosion-inhibiting effect upon them, as a general rule, aqueous phosphate fire-fighting solutions containing from about 0.04 to about 10, and preferably from about 0.10 to about 2 weight percent of one or more of the amino polycarboxylic acid compounds in the dissolved state should be utilized.

The corrosion-inhibited ammonium phosphate fire-fighting solutions of the present invention can also contain materials other than the phosphate salts, the thickening agents and the amino polycarboxylic acid 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; other complexing agents such as the alkali metal tripolyphosphate, pyrophosphates and trimetaphosphates, as well as the higher polyphosphates such as the hexametaphosphates; other corrosion-inhibiting ingredients; and inorganic and organic pigments and dyes; as well as many other materials.

The corrosion-inhibited phosphate fire-fighting solutions 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 solution. For example, the amino polycarboxylic acid compound can simply be dissolved by intermixing it into or with the otherwise completely formulated aqueous solutions, or at any other stage during the preparation of the fire-fighting solution. Via another method, the amino polycarboxylic acid compound can first be dissolved in water, and the resulting solution then intermixed subsequently with the ammonium phosphate fire-fighting solution.

Still another process for manufacturing the aqueous corrosion-inhibited phosphate fire-fighting solutions 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 and one or more of

the thickening agents described hereinbefore with one or more of the amino polycarboxylic acid (inhibitor) compounds, generally in a particulated, solid form. Preferably the inhibitor compound(s), ammonium phosphate salt(s) and the thickening agent will be present in this concentrate composition or mixture in amounts proportionate to those found in the fire-fighting solutions described hereinbefore, so that the final fire-fighting solution 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, at least one of the above-described thickening agents, and at least one of the amino polycarboxylic acid (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, and a weight ratio of phosphate salt to thickening agent, respectively, of from about 1:5 to about 50:1, and preferably from about 1:1 to about 20:1. These preferred concentrate compositions can also contain effective amounts of practically any other ingredients such 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 ammonium orthophosphate material, that is, at least about 50 weight percent, in addition to minor amounts, that is, less than 50 weight percent of the thickening agent, corrosion inhibitor, 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 fighting compositions, very little weighing and handling equipment is available that is capable of manufacturing the fire-fighting solutions 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 fighting solutions of the present invention), as a practical matter, such corrosion inhibited final fire-fighting solutions 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 monoammonium orthophosphate, 1.0 weight percent of nitrilotriacetic acid and 9.0 weight percent of sodium alginate.

(b) 90 weight percent of diammonium orthophosphate, 0.5 weight percent of tetrasodium ethylene diamine tetraacetate and 9.5 weight percent of sodium carboxymethylcellulose.

(c) 55 weight percent of an equimolar mixture of monoammonium orthophosphate and diammonium orthophosphate, 1.0 weight percent of ethylene diamine tetraacetic acid, 35 weight percent of sodium tripolyphosphate and 9 weight percent of sodium alginate.

(d) 89 weight percent of monoammonium orthophosphate, 0.25 weight percent of trisodium nitrilo triacetate and 10.75 weight percent of pentasodium amino tri(methylenephosphonate).

(e) 70 weight percent of diammonium orthophosphate, 20 weight percent of monoammonium orthophosphate, 9 weight percent of sodium carboxyethylcellulose and 1 weight percent of disodium ethylenediamine tetraacetate.

(f) 84 weight percent of diammonium orthophosphate, 15.50 weight percent of guar gum and 0.50 weight percent of tetrasodium ethylenediamine tetraacetate.

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

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to that in which more corrosive, less desirable sodium chloride is presently conventionally utilized. For example, these particulated, solid ammonium phosphate-amino polycarboxylic acid-thickening agent compositions can effectively de-ice airplane runways, 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 to 10 parts of crystalline technical grade diammonium orthophosphate, 1 part of carboxymethylcellulose and 0.5 part of ethylenediamine tetraacetic acid. The resulting mixture is then stirred until all of the diammonium orthophosphate has dissolved.

Into the resulting fire-fighting solution 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 13 mils per year.

By comparison, a composition which is prepared in the same way as this example but without the amino polycarboxylic acid, 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 amino polycarboxylic acids or salts which include nitrilo triacetic acid, anthranilic-N,N-di-acetic acid, c-cyclohexylenitrilo triacetic acid, c-phenyl-nitrilo triacetic acid, dimethyl-nitrilo triacetic acid, diethylene triamine penta acetic acid and the like, as well as various thickening agents which include hydratable clays such as bentonites and attapulgites and the like, algin, guar gum, carboxyethyl cellulose and the like.

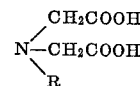
As being illustrative of an airplane attachment for extinguishing fires as well as the method for using such, reference is made to U.S. Patent 1,997,669.

We claim:

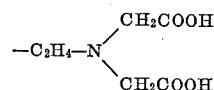
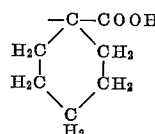
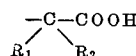
1. An aqueous ammonium orthophosphate fire-fighting

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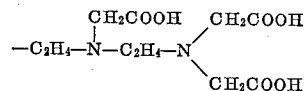
solution consisting essentially of, in addition to the ammonium orthophosphate dissolved therein in an amount of at least about 0.5 weight percent, a thickening agent in an amount of at least about 0.5 weight percent selected from the group consisting of carboxy, methyl cellulose, carboxy ethyl cellulose, carboxy propyl cellulose, algin, guar gum, bentonite clays and attapulgite clays and to decrease the normal corrosivity of said solution towards copper and copper containing alloys a corrosion inhibitor in an amount of at least about 0.04 weight percent selected from the group consisting of amino polycarboxylic acids having the formula



wherein R is a member selected from the group consisting of the radicals



and



wherein R₁ is a member selected from the group consisting of hydrogen, lower alkyl containing from 1 to 4 carbon atoms and phenyl and R₂ is a member selected from the group consisting of hydrogen and lower alkyl containing from 1 to 4 carbon atoms and their water-soluble salts selected from the group consisting of alkali metal salts, ammonium salts and amine salts of amines having a molecular weight below about 200 and containing not more than 2 amine groups.

2. An aqueous ammonium orthophosphate fire-fighting solution according to claim 1, wherein said ammonium orthophosphate is selected from the group consisting of monoammonium orthophosphate, diammonium orthophosphate and mixtures thereof, said thickening agent is in an amount of from about 0.5 to about 30 weight percent and said corrosion inhibitor is in an amount of from about 0.04 to about 10 weight percent.

3. An aqueous ammonium orthophosphate fire-fighting solution according to claim 1, wherein said ammonium orthophosphate is in an amount of from about 5 to about 25 weight percent, said thickening agent is in an amount of from about 1 to about 15 weight percent and said corrosion inhibitor is in an amount of from about 0.10 to about 2.0 weight percent.

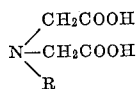
4. A corrosion-inhibited liquid ammonium orthophosphate fire-fighting solution as in claim 3, wherein said corrosion inhibitor is ethylene diamine tetraacetic acid.

5. A corrosion-inhibited liquid ammonium orthophosphate fire-fighting solution as in claim 3, wherein said corrosion inhibitor is a sodium salt of ethylene diamine tetraacetic acid.

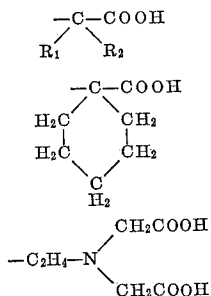
6. A concentrated ammonium orthophosphate fire-fighting composition suitable for use in the manufacture of aqueous copper corrosion-inhibited ammonium orthophosphate fire-fighting solutions, said composition consisting essentially of a water-soluble copper corrosion inhibitor

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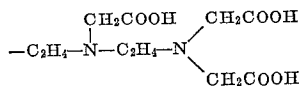
selected from the group consisting of amino polycarboxylic acids having the formula



wherein R is a member selected from the group consisting of the radicals



and



wherein R₁ is a member selected from the group consisting of hydrogen, lower alkyl containing from 1 to 4 carbon atoms and phenyl and R₂ is a member selected from the group consisting of hydrogen and lower alkyl containing from 1 to 4 carbon atoms and their water-soluble salts selected from the group consisting of alkali metal salts, ammonium salts and amine salts of amines having a molecular weight below about 200 and containing not more than 2 amine groups, a thickening agent selected from the group consisting of carboxy methyl cellulose, carboxy ethyl cellulose, carboxy propyl cellulose, algin, guar gum, bentonite clay and attapulgite clays, and a major portion of at least one ammonium orthophosphate salt; the weight ratio of said ammonium orthophosphate salt to said corrosion inhibitor in said composition being from about 3800:1 to about 10:1 and the weight ratio of said ammonium orthophosphate salt to said thickening agent in said composition being from about 1:5 to about 50:1.

7. A particulated, solid concentrate composition according to claim 6, wherein said ammonium orthophosphate is selected from the group consisting of monoammonium orthophosphate, diammonium orthophosphate and mixtures thereof, the weight ratio of said ammonium orthophosphate to said corrosion inhibitor in said composition being from about 750:1 to about 100:1 and the weight ratio of said ammonium orthophosphate to said thickening agent in said composition being from about 1:1 to about 20:1.

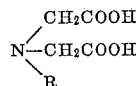
8. A particulated, solid concentrate composition as in claim 7, wherein said amino polycarboxylic acid is ethylene diamine tetraacetic acid.

9. A particulated, solid concentrate composition as in claim 7, wherein said amino polycarboxylic acid is nitrilo triacetic acid.

10. 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, a thickening agent selected from the group consisting of carboxy methyl cellulose, carboxy ethyl cellulose, carboxy propyl cellulose, algin, guar gum, bentonite clays and attapulgite clays, and as a copper corrosion inhibitor, a water-soluble

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alkali metal salt of an amino polycarboxylic acid having the formula



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wherein R is a member selected from the group consisting of the radicals

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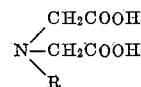
wherein R₁ is a member selected from the group consisting of hydrogen, lower alkyl containing from 1 to 4 carbon atoms and phenyl and R₂ is a member selected from the group consisting of hydrogen and lower alkyl containing from 1 to 4 carbon atoms, the weight ratio of said ammonium orthophosphate material to said corrosion inhibitor in said concentrate being from about 750:1 to about 100:1 and the weight ratio of said ammonium orthophosphate material to said thickening agent in said concentrate composition being from about 1:1 to about 20:1.

11. A particulated, solid concentrate composition as in claim 10, wherein said salt of said amino polycarboxylic acid is the sodium salt of ethylene diamine tetraacetic acid.

12. A particulated, solid concentrate composition as in claim 10, wherein said salt of said amino polycarboxylic acid is the sodium salt of nitrilo triacetic acid.

13. A method of retarding the corrosion of copper and copper-containing alloys upon contact with a normally corrosive aqueous ammonium orthophosphate fire-fighting solution, which method comprises effecting said contact when said aqueous ammonium orthophosphate fire-fighting solution contains said ammonium orthophosphate in an amount of at least about 0.5 weight percent and a corrosion inhibitor in an amount of at least about 0.04 weight percent selected from the group consisting of amino polycarboxylic acids having the formula

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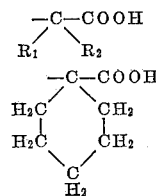


wherein R is a member selected from the group consisting of the radicals

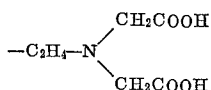
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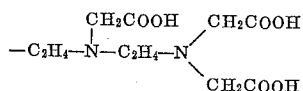
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and



wherein R_1 is a member selected from the group consisting of hydrogen, lower alkyl containing from 1 to 4 carbon atoms and phenyl and R_2 is a member selected from the group consisting of hydrogen and lower alkyl containing from 1 to 4 carbon atoms and their water-soluble salts selected from the group consisting of alkali metal salts, ammonium and amine salts of amines having a molecular weight below about 200 and containing not more than 2 amine groups.

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