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FIRE RETARDANT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

The corrosivity of liquid fire-retardant compositions is reduced by using an aqueous mixture of ammonium sulfate and diammonium phosphate in a weight ratio of sulfate to phosphate of from about 1:1 to about 5:1, said mixture having a pH of between about 6.5 and about 7.5.

This invention relates to improved fire extinguishing compositions. More particularly, it relates to inorganic fire retardant compositions characterized by fire extinguishing effectiveness combined with reduced corrosivity.

BACKGROUND

The use of inorganic fire extinguishing compositions is well known. For some years the U.S. Forest Service and other state and federal conservation agencies have been using as fire fighting chemicals such salts as diammonium phosphate, ammonium sulfate, sodium calicum borate and sodium carbonate. These compounds, alone or in various mixtures, have been used as solids, or in various liquid or solution forms. Currently, the most advantageous way to use formulations of these chemicals for fighting forest fires is to drop them from aircraft. Both fixed-wing and helicopter aircraft are employed for air-dropping fire-fighting chemicals. The chemicals are generally air-dropped onto unburned forest ahead of a fire, to serve as fire retardants, preventing the fire's further spread.

Aqueous solutions of the chemicals noted above have been found to be extremely effective for aerial fire fighting. In practice, such solutions are made up at airports or air strips, pumped into tanks on aircraft, and dropped from the aircraft onto fires as conditions require. It has been found, however, that the aqueous solutions are extremely corrosive to many of the metals they encounter in use. In particular, they have been found to seriously corrode aluminum, copper and bronze, all metals used in aircraft construction. Corrosion damage to fire-fighting aircraft, caused by the solutions dropped, has become a serious economic and safety problem.

Salt solution splashed or drifted onto aluminum fuselage and control surfaces has been observed to etch holes in these surfaces. Solution which has splashed on copper or bronze bearings has seriously corroded the bearings, impairing their operation. Aluminum tanks and pipes in which the solutions are made and stored have become breached or corroded. As a consequence, a need has arisen for an effective aqueous fire retardant composition which is non-corrosive toward aluminum, copper, bronze and other structural metals, without losing its fire-fighting effectiveness.

OBJECTS

It is an object of this invention to provide an effective fire-retardant composition of low corrosivity toward metals. Another object of the invention is the provision of a low-cost relatively non-corrosive mixture of fire-retardant chemicals. Still another object is the provision of a fire-retardant composition containing a particular mixture of diammonium phosphate and ammonium sulfate. A method of fighting fires with such compositions is another object of the invention. Other objects of the

invention will be apparent from the following detailed description of the compositions thereof.

STATEMENT

These objects are accomplished by the first-retardant composition comprising an aqueous gel, said gel comprising essentially as the fire extinguishing ingredients a dissolved mixture of ammonium sulfate and diammonium phosphate wherein the weight ratio of said sulfate to said phosphate is from about 1:1 to about 5:1, and said aqueous gel has a pH between about 6.5 and about 7.5, and a viscosity of at least 1000 centipoises.

The fire retardant compositions of the invention may be prepared in any convenient way. For example, the ammonium sulfate and the diammonium phosphate may be conveniently premixed in the desired proportions, and the resulting mixture dissolved in water prior to use. Alternatively, the ammonium sulfate and diammonium phosphate may be separately dissolved in the water in the desired proportions.

The concentration of the inorganic mixture in the aqueous vehicle may vary over a wide range, depending, in part, on the economics involved. It is desirable to use aqueous systems containing at least one pound of total inorganic salts per gallon of water, and preferably greater than about a pound and a quarter per gallon. Upper limit of concentration will, of course, be the limit of solubility of the salts in the aqueous system.

The improved results achieved by the aqueous compositions of the invention stem from the particular ratio of the particular ammonium salts employed. It is, in fact, well known in the art to employ ammonium phosphate and ammonium sulfate either alone or in combination with one another and with other components in fire retardant formulations. In general, however, such formulations have been dry, as exemplified by such U.S. patents as the following:

Reiss, U.S. 2,881,138, issued Apr. 7, 1959
Steppe et al., U.S. 3,017,348, issued Jan. 16, 1962
Cawood, U.S. 3,063,940
Simes, U.S. 3,179,588

Such dry formulations, however, present little or no corrosion problem. Aqueous systems containing various ammonium salts in various ratios are taught by such U.S. patents as that to Schuler, U.S. 502,867, issued Aug. 8, 1893.

AMMONIUM SALTS

The reduced corrosivity of the compositions of the in-tion are achieved by aqueous gels comprising diammonium phosphate $(NH_4)_2HPO_4$ and ammonium sulfate

$$(NH_4)_2SO_4$$

in a particular weight ratio. That ratio lies from 1 part of the sulfate to 1 part of the phosphate, to 5 parts of the sulfate to 1 part of the phosphate. The aqueous gels of the invention having this ratio of ammonium sulfate to diammonium phosphate are characterized by a pH of between 6.5 and 7.5, and by substantially reduced corrosivity toward structural pump, tank and aircraft metals. Particularly, reduced corrosivity is exemplified by the aqueous gel wherein the sulfate to phosphate ratio lies from about three parts of ammonium sulfate to one part of diammonium phosphate, to that having a ratio of five parts of ammonium sulfate to one part of ammonium phosphate.

pH CONTROL

One important feature of the aqueous compositions of the invention is the range of hydrogen ion concentration therein. By maintaining the hydrogen ion concentration, herein identified conventionally by the pH notation, with-

in specified limits, the corrosivity of the ammonium salt formations is materially reduced.

Such reduction in corrosivity is achieved by maintaining the pH of the aqueous diammonium phosphate compositions of the invention between about 6.5 and about 7.5. This maintenance of pH is accomplished by including in the aqueous diammonium phosphate composition only a specified amount of ammonium sulfate. Such pH control is achieved by employing the ammonium sulfate in a weight ratio of from about 1:1, based on the diammonium phosphate, to about 5:1 on the same basis. The pH of representative aqueous compositions of diammonium phosphate and ammonium sulfate is shown in the following Table I. The compositions tabulated have a concentration of one pound of total ammonium salts per gallon of water, and also contain sufficient carboxymethyl cellulose to give a viscosity of 1000 cp., Rhodamine B dye, and both benzotriazole and sodium fluosilicate corrosion inhibitors.

TABLE I

Weight ratio, diammonium phosphate to ammonium sulfate:	pH
$(NH_4)_2SO_4$ alone	6.0
1:5	7.0
1:3	7.0
1:1	7.4
$(NH_4)_2HPO_4$ alone	7.7

VISCOSITY

In aerial firefighting, unthickened solutions of ammonium salts in water have been found to be relatively ineffective. When dropped from aircraft, such solutions tend to drain rapidly off foliage, to splash off intended targets, and to be quickly absorbed by soil. Accordingly, it is necessary to thicken the solution to a consistency such that it will adhere to targets and thus protect them.

It has been found that a viscosity of at least one thousand centipoises is required for the gels of the invention to achieve these desirable results. Such a viscosity is achieved by gelling the ammonium salt solutions of the invention with a water-miscible thickener or gelling agent. Exemplary of such thickeners are carboxymethyl cellulose, such polypectates as ammonium polypectate and sodium polypectate, algin, and such algin salts as sodium alginate, some clays such as bentonite and attapulgite, various gelatins, anhydrous silica, starch, and various soaps. Of these thickeners, carboxymethyl cellulose combines the desirable properties of relatively low cost with substantial thickening power, and is the preferred thickener. While the concentration of the thickener will depend both on its nature and on the nature of the system in which it is employed, the thickener employed in the formulations of the invention will be used at a concentration such that the resulting composition will have a viscosity of at least one thousand centipoises, and preferably from twelve hundred to eighteen hundred centipoises. In general, at least about 5% w. of the thickener gives sufficient viscosity to the gels.

The reduced corrosivity of the formulations of the invention toward aluminum is illustrated in the following Table II. In the table, penetration in mils/yr. of aluminum by various solutions containing one pound of ammonium salts per gallon of water is shown. Each solution was thickened with carboxymethyl cellulose to a viscosity of 1000 cp.

TABLE II

Metal	Time, hrs.	$(NH_4)_2HPO_4$	Wt. Ratio, $(NH_4)_2HPO_4/(NH_4)_2SO_4$ 1:1	1:3	1:5
Aluminum	0–24	1.96			
	24–48	2.16	0.0	0.5	0.8
	48–96		0.0	0.0	0.0
pH of solution		7.7	7.4	7.0	7.0

Substantially less attack on the aluminum was made by the compositions of the invention than by diammonium phosphate alone.

The compositions heretofore described display substantially reduced corrosivity toward copper, aluminum and other structural metals. However, by including benzotriazole in the compositions to at least about 0.1% w., based on the total ammonium salts, and preferably between about 0.1% w.–1.0% w. on the same basis, a surprising further reduction in corrosivity was achieved.

BENZOTRIAZOLE

In Table III are presented data showing the effect of adding small amounts of benzotriazole to the diammonium phosphate/ammonium sulfate compositions of the invention. Set forth in the table are the penetrations, in mils/yr. of the test metal, of various aqueous systems having a concentration of about 1 pound of total ammonium salts per gallon of water. Where benzotriazole was employed, it was used at a concentration of 0.21% w. or 0.42% w., based on the total salts. The test solutions contained sufficient carboxymethyl cellulose to give each a viscosity of 1000 cp. In the table, benzotriazole is abbreviated as bz. for compactness.

TABLE III

Metal	Time, hrs.	$(NH_4)_2HPO_4$ alone		Weight Ratio $(NH_4)_2HPO_4/(NH_4)_2SO_4$ 1:1			1:3			1:5		
		w/o bz.	0.42% w. bz.	w/o bz.	0.21% w. bz.	0.42% w. bz.	w/o bz.	0.21% w. bz.	0.42% w. bz.	w/o bz.	0.21% w. bz.	0.42% w. bz.
Copper	0–24	43.7	7.7	26.3		1.5	18.1	8.8	1.7			
	24–48	50.1	16.4	29.5		5.9	22.4	8.5	3.2	12.7	6.0	0.6
	72–96									19.8	7.9	1.0
pH of solution				7.7	7.7	7.7	7.4	7.4	7.4	7.0	7.0	7.0

The inclusion of the benzotriazole dramatically reduced the corrosion of the test metals.

SODIUM FLUOSILICATE

In use, the gel formulations of the invention become deposited not only on the copper and bronze elements of aircraft but also on the aluminum fuselage. It is therefore desirable that the formulations display reduced corrosivity to aluminum and its alloys. While the particular aqueous diammonium phosphate/ammonium sulfate gels of the invention are substantially less corrosive toward such metals than are other ammonium salt solutions, their corrosivity can be further reduced by inclusion of a stabilizing amount of sodium fluosilicate. Thus, it has been found that inclusion of between about 0.1% w. to about 1.0% w. of sodium fluosilicate, based on the ammonium salts, is effective to impart to the gels of the invention a reduced corrosivity toward aluminum and aluminum alloys.

To illustrate the corrosion-reducing properties imparted by the sodium fluosilicate to the ammonium sulfate/diammonium phosphate gel compositions of the invention, the following Table IV is presented. In the tests described therein, the test solutions had the following composition:

Diammonium phosphate/ ammonium sulfate	As specified.
Carboxymethyl cellulose	9.010% by weight, based on total weight.
Rhodamine B pigment	.05% by weight, based on total weight.
Sodium fluosilicate	.841% by weight, based on total weight.

The tests were performed at room temperature with partially immersed coupons of the metals specified. Corrosion attack on the coupons is set forth as penetration in mils per year.

TABLE IV.—CORROSION OF METAL

Metal and Total Duration of Test, Hrs.	Phosphate to Sulfate Ratio		
	1:1	1:3	1:5
Aluminum 6061:			
49	0.0	0.5	0.8
94	0.0	0.0	0.0
235	0.2	0.3	0.1
Copper:			
49	20.5	18.4	12.7
94	31.6	20.3	19.8
235	26.3	23.0	20.8
pH of Retardant Gel:			
0	7.55	7.05	6.98
94	7.38	7.08	6.88
235	7.50	7.20	7.00

Not only is sodium fluosilicate effective to reduce the corrosivity of the ammonium salt solution of the invention, but it also serves, surprisingly, to stabilize the system itself against biological degradation. The gelling agents of the invention are, to the extent that they are organic in nature, subject to bacterial attack. Upon bacterial infection of the system, the molecular weight of the gelling agent becomes reduced and the viscosity of the system decreases rapidly. Presence of the sodium fluosilicate serves to prevent such microbial degradation and thus preserve the viscosity of the gel during storage.

One advantage of the fire-retardant aqueous diammonium phosphate/ammonium sulfate compositions of the invention is their effectiveness as residual fertilizers. Not only do they serve to limit the spread of forest fires but, once washed off trees and branches onto the soil, they serve as readily-available sources of plant nutrient nitrogen, phosphorus and sulfur. The compositions thus have the advantage of stimulating regrowth of grass, bushes and trees in burned-over areas and thus assisting in reforestation. Such growth also stabilizes the soil in water sheds and retards the washing away of soil from burned-over areas.

MARKING AGENT

To assist aircraft pilots in following the dropping of their loads, it is desirable to include in the compositions of the invention a small amount of marker dye or pigment. The dye serves to show the location and extent of coverage of the fire-retardant composition on the target area. A wide variety of dyes are available for this purpose, in all colors and hues. Both fluorescent and non-fluorescent dyes may be used. Naturally, a dye or pigment should be selected whose color gives maximum contrast against the target grass or foliage; such colors as yellows, oranges, and reds are preferred to greens, blues and browns. The amount of dye or pigment employed will, of course, depend on the intensity of color any particular coloring agent imparts to the fire-retardant composition. A visible amount of the marking agent will be required; in general, at least about 0.001% w. of most dyes and pigments has been found to be sufficient, while use of more than about 1.0% w. appears unnecessary.

Representative dyes that may be employed as marking agents in the compositions of the invention are those dyes shown in the Colour Index of the Society of Dyers and Colourists. Typical dyes include

Rhodamine B (hydrochloride of diethyl m-amino-phenolphthalein) red, fluorescent

Azo Red A (sodium salt of 4-sulfo-α-naphthaleneazo-α-naphthol-3,6-disulfonic acid) red

Naphthol Orange (sodium salt of p-sulfobenzene-azo-α-chloro-m-phenylene-diamine-sulfonic acid) yellow

Naphthol Orange (sodium salt of p-sulfobenzene-azo-α-naphthol) orange-red

While coloring agents such as dyes or pigments may be either soluble or insoluble in the aqueous compositions of the invention, water-soluble dyes are preferred since they are more readily formulated with the compositions described, can be more uniformly distributed throughout the gel formulation, and do not settle out on storage.

FORMULATION AND USE

The compositions of the invention can be readily formulated with methods well known in the art. They may be loaded into aircraft tanks and dropped onto fires or fire-threatened areas with conventional equipment and by using conventional methods. They may be dropped from either fixed-wing or helicopter aircraft from any convenient height and in any desired amount.

The compositions of the invention are characterized by important advantages over the aqueous fire-fighting compositions of the art. Unlike borate compositions, which are toxic to some varieties of trees and plants, the ammonium salt compositions are actually beneficial to forest and rangeland. The compositions are substantially less corrosive to aircraft, storage tank and pumping equipment than the aqueous diammonium phosphate retardant compositions known to the art. Furthermore, they are economical, readily prepared from available chemical materials, and have been found to be highly effective in forest fire control.

To illustrate the nature of the formulations of the invention, the following typical compositions are set forth. It should be understood, however, that these examples are illustrative only and are not to be regarded as limitations to the appended claims since the basic teachings thereof may be varied at will as will be understood by one skilled in the art. In the examples, the proportions are expressed in parts by weight unless otherwise indicated.

FORMULATION I

[1:1 wt. ratio $(NH_4)_2HPO_4/(NH_4)_2SO_4$]

Dry Component	Percent w.	Pounds/Ton
Diammonium Phosphate	45.052	901.0
Ammonium Sulfate	45.052	901.0
Carboxymethyl Cellulose	9.010	180 0
Sodium Fluosilicate	0.841	17.0
Rhodamine B Dye	0.05	1.0
		2,000.0

This dry formulation was mixed with water to a concentration of one pound of ammonium salts per gallon of water. The resulting mixture was a red solution having a viscosity of about 1000 centipoises and a pH of about 7.4.

FORMULATION II

[1:3 wt. ratio $(NH_4)_2HPO_4/(NH_4)_2SO_4$]

Dry Component	Percent w.	Pounds/Ton
Diammonium Phosphate	22.525	450.5
Ammonium Sulfate	67.525	1,351 5
Ammonium Polypectate	9.010	180.0
Sodium Fluosilicate	0.425	8.5
Benzotriazole	0 425	8.5
Rhodamine B Dye	0.05	1.0
		2,000.0

This formulation, when made up into a solution having a concentration of 1 pound of ammonium salts per gallon of water, has properties comparable to those of Formulation I; save that its pH is about 7.0.

FORMULATION III

[1:5 wt. ratio $(NH_4)_2HPO_4/(NH_4)_2SO_4$]

Dry Components	Percent w.	Pounds/Ton
Diammonium Phosphate	15.017	300.0
Ammonium Sulfate	75.087	1,502.0
Carboxymethyl Cellulose	9.010	180 0
Sodium Fluosilicate	0.841	17.0
Rhodamine B Dye	0.05	1.0
		2,000 0

This formulation was mixed with water to a concentration of one pound of ammonium salts per gallon of water.

The resulting mixture was a red solution having a viscosity of about 1000 centipoises and a pH of about 7.0.

Where dimensions of viscosity of the formulations of the invention are given, the measurement thereof was made with a Brookfield Viscometer, using a No. 3 spindle @ 30 r.p.m., and applying a multiplication factor of 40 to the reading on the scale of 100.

When any of these formulations is dropped on grass or foliage in front of a forest fire, the formulation adheres to the grass or foliage without material drainage or run-off. The resulting protected area chars in the heat, but does not flame, and effectively prevents the further spread of the fire therethrough. Location and extent of the protected area is shown in red by the presence in the system of the dye.

I claim as my invention:

1. A fire-retardant composition consisting essentially of

(a) water,

(b) a water-miscible thickener, and

(c) dissolved diammonium phosphate and ammonium sulfate;

the weight ratio of said diammonium phosphate to said ammonium sulfate being from about 1:1 to about 1:5; and said fire-retardant composition having a viscosity of at least 1000 centipoises and a pH of between about 6.5 and about 7.5.

2. The fire retardant composition of claim **1** wherein the composition has from 0.1% w. to 1.0% w. of sodium fluosilicate.

3. The fire retardant composition of claim **1** wherein the composition has from 0.1% w. to 1.0% w. benzotriazole.

4. The fire retardant composition of claim **1** having at least 5% w. of carboxymethyl cellulose as said thickener; and wherein the weight ratio of diammonium phosphate to ammonium sulfate is from about 1:3 to about 1:5.

5. The fire-retardant composition of claim **4** wherein the composition has a concentration of diammonium phosphate plus ammonium sulfate of at least one pound per gallon of water; from 0.1% w. to 1.0% w. sodium fluosilicate, and from 0.1% w. to 1.0% w. benzotriazole.

6. The fire retardant composition of claim **4** wherein the composition has a visible amount of colored marking agent.

7. The method of fighting forest fires, comprising depositing from an aircraft onto an area adjacent a forest fire the composition of claim **1.**

8. The method of fighting forest fire, comprising the aerial deposition of the composition of claim **5** onto an area adjacent a forest fire.

9. The fire-retardant composition of claim **1** wherein the weight ratio of diammonium phosphate to ammonium sulfate is from about 1:3 to about 1:5.

10. The fire-retardant composition of claim **1** wherein said thickener is selected from the group consisting of carboxymethyl cellulose, ammonium polypectate, sodium polypectate, algin, sodium alginate, bentonite, attapulgite, gelatin, anhydrous silica, starch and soap.

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