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(54) Title: FIRE RETARDANT COMPOSITIONS WITH REDUCED ALUMINUM CORROSIVITY

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(57) Abstract: Corrosion-inhibited fire retardant compositions and methods of making and using the same are provided. The corrosion-inhibited fire retardant compositions are comprised of at least one fire retardant component, at least one biopolymer having a particle size diameter of less than about 100 microns, and a corrosion inhibiting system. The corrosion inhibiting system is comprised of at least one corrosion inhibiting compound selected from a group of compounds including azoles, insoluble ferric pyrophosphate. of at least one corrosion inhibiting compound selected from a group of compounds including azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acctate, ferrous ammonium sulfate, ferrous bromide, ferric seluconate, ferrous iodide, ferric acctate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous brumarate, ferrous oxide, ferric lactate, ferric resinate and any combination thereof. In a specific embodiment, the corrosion-inhibited fire retardant composition includes a xanthan biopolymer. thereof. In a specific embodiment, the corrosion-inhibited fire retardant composition includes a xanthan biopolymen.

FIRE RETARDANT COMPOSITIONS WITH REDUCED ALUMINUM CORROSIVITY

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Serial Number 09/723,567, filed November 28, 2000, which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

10 Not applicable.

FIELD OF THE INVENTION

The present invention relates to corrosion-inhibited fire retardant compositions. More specifically, the invention is directed to ammonium polyphosphate concentrates and other solutions containing suspended and/or soluble iron compounds and at least one biopolymer.

BACKGROUND

Aerial application of fire-retardant compositions to combat the spread of wildland fires is common. The composition of fire retardants concentrates designed for managing and controlling wildland fires are of two generally types,

20 those which, when mixed or diluted with water to end-use concentration, result in either a gum thickened solution, and those which do not contain a gum thickener and, consequently, result in water-like solutions, which are not rheologically modified. These water-like retardant solutions exhibit inferior drop characteristics. The former may be supplied as dry powders or as suspensions or slurries generally referred to as fluids. Those concentrates that result in water-like solutions when diluted with water may contain suspended components, as well, but are generally referred to as liquid concentrates. Fire retardant

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concentrates that are supplied as fluids or liquids are preferred by some because they can be simply and easily diluted to end-use strength with little mixing hardware and manpower.

Ammonium polyphosphate liquids have been used as aerially applied fire
retardants. These liquids have certain advantages in comparison to other firesuppressing compositions since they can be transported and stored prior to use in
the liquid form rather than being mixed from dry ingredients. However,
concentrated liquid fire retardants and solutions prepared therefrom are
extremely corrosive to aluminum and brass and mildly corrosive to other

materials of construction used in handling, storage and application equipment.
As used herein, all metals include alloys thereof. Accordingly, aluminum
includes aluminum 2024T3, 6061 and 7074, steel includes 1010 and 4130 steel
and brass includes yellow and naval brass. Since wildland fire retardants are
most frequently transported to the fire and applied aerially, it is imperative that
corrosive damage to the materials of construction of fixed-wing aircraft and
helicopters be minimized.

Accordingly, the United States Department of Agriculture ("USDA")

Forest Service has established, in "Specification 5100-304b (January 2000)

Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application" (hereinafter, "Forest Service Specifications"), hereby incorporated by reference in its entirety, maximum allowable corrosion rates for 2024T3 aluminum, 4130 steel, yellow brass and Az-31-B magnesium. For example, the corrosivity of forest fire retardants, in concentrate, to aluminum, steel and yellow brass must not exceed 5.0 milli-inches ("mils") per year as determined by the "Uniform

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Corrosion" test set forth in Section 4.3.5.1 of the aforementioned USDA, Forest Service Specifications. If the product is applied from fixed-tank equipped helicopters, the corrosivity of the fire retardants to magnesium must not exceed 5.0 mils per year. The Forest Service Specifications identify the maximum amount of corrosion acceptable when both the retardant concentrate and its diluted solutions are exposed to each metal indicated above at temperatures of 70° Fahrenheit ("F") and 120°F in both totally and partially immersed configurations. The maximum allowable corrosivity of aerially applied fire retardant diluted solutions to aluminum is 2.0 mils per year ("mpy"), and the maximum corrosivity to brass and steel is 5.0 mpy when partially immersed, and 2.0 mpy when tested in the partially immersed condition. In the partially immersed configuration, one-half of the coupon is within the solution and one-half is exposed to the vapors in the air space over the solution.

In an effort to address the corrosivity problems encountered with the use of fertilizer grade ammonium polyphosphates, sodium ferrocyanide was incorporated into the corrosive compositions. Sodium ferrocyanide has proven to be an effective corrosion inhibitor in fire retardant compositions containing ammonium polyphosphate fertilizer solutions. However, while sodium ferrocyanide is effective as a corrosion inhibitor, several disadvantages of its use make its incorporation in wildland fire retardant compositions undesirable. Specifically, the environmental and toxicological safety of ferro(i)cyanides is, at best, questionable. When exposed to acidic conditions and/or ultraviolet radiation from natural sunlight, the ferro(i)cyanide radical readily degrades releasing free iron and cyanide and/or hydrogen cyanide, which are toxic to humans, animals and aquatic life. Further, free iron emanating either from

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dccomposition of a portion of the ferro(i)cyanide radical, or introduced from other components or impurities within the composition, will subsequently react with remaining non-decomposed ferro(i)cyanide to form ferrous ferricyanide ("Turnbull's Blue") or ferric ferrocyanide ("Prussian Blue"), which emit a persistent blue-black or indigo-blue coloration, staining all that they contact. Consequently, neither ferricyanide nor ferrocyanide can be used in fire-retardants that are expected to fade and become non-visible over time, for example, in fugitive retardant compositions.

The magnitude of the above concerns is increased since wildland fire retardants are generally applied aerially in a less than completely controlled manner. Due to the presence of variables such as vegetative cover, smoke, or wind drift that impact the trajectory of the free-falling solution, aerially applied wildland fire retardant solutions may land on or near people, animals and in bodies of water, or on soil where it could enter the water supply.

In addition, the rheological properties of wildland fire retardant solutions during periods of extreme and relaxed shear, and its elasticity are recognized as important properties. The rheological properties of forest and brush land fire retardant solutions are important because they significantly affect the performance of the retardant during and following aerial discharge and subsequent distribution within the fuel ladder. The degree of dispersion, integrity of the retardant cloud, magnitude of wind-induced drift, as well as the continuity of coverage, retention on and penetration of the fuel complex are among those performance-related characteristics impacted. Fire retardant solutions, which exhibit increased viscosity and elastic properties, are more desired because they

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are less affected by the extreme forces encountered in aerial application, e.g. wind effects, gravity, and shear force due to forward momentum.

Historically, wildland fire retardant solutions, as prepared for application, have been of three general rheological types: (1) unthickened liquid fertilizer solutions with little effective viscosity and elasticity; (2) clay thickened aqueous ammonium sulfate solutions with high apparent viscosity, but little effective viscosity and no elasticity; and (3) high viscosity, pseudoplastic and elastic, gum thickened ammonium phosphate and/or sulfate solutions, which maintain an increased viscosity level and elastic character even when subjected to great amounts of shear.

Guar gums, natural polysaccharides that are extracted from the guar bean, have been used in aerially applied fire retardant to enhance the rheological properties of the retardant solutions. Guar gum thickeners function in an acceptable manner when the ammonium polyphosphate based fire retardant composition is diluted relatively soon after preparation. The rate of degradation of the guar gum thickener varies with the composition of the fertilizer grade ammonium polyphosphate and can be as short as a few hours to one week. However, when the concentrated retardant is stored for more than about one week, the rate of viscosity decreases to an unacceptable level. For example, experiments have shown that a fire retardant concentrate stored for one month prior to dilution shows little tendency to increase in viscosity for several hours and does not reach its expected viscosity level for perhaps a week. Since wildland fires occur on a non-predictable basis and a rapid response is required to treat them, this type of behavior is unacceptable.

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Conventional xanthan biopolymers thickeners having particle sizes in excess of about 100 microns have also been used to alter the rheological characteristics of aerially applied fire retardants. Conventional commercially available xanthan biopolymers include but are not limited to Kelzan® and Kelzan S® from CP Kelco, Wilmington, DE, and Xanthan AC® from Jungbunzlauer International AG, Basel, Switzerland. However, like guar gums, conventional xanthan biopolymer thickeners perform unacceptably in liquid ammonium polyphosphate compositions. Even when prepared freshly, ammonium polyphosphate fire retardant concentrates containing these conventional xanthan biopolymers have a decreased ability to increase the viscosity of the solution in a timely manner, upon subsequent dilution with water. As such, the use of conventional xanthan biopolymer thickeners to improve the rheological characteristics of ammonium polyphosphate based fire retardant compositions for aerially application is less desired.

Accordingly, there is a need to provide safe and acceptable wildland fire retardants for the suppression or management of wildland fires that are not corrosive to the equipment associated with the transportation, handling and application of the retardant, have favorable rheological and aerial application characteristics and are environmentally and toxicologically friendly, thereby avoiding the above disadvantages.

SUMMARY OF THE INVENTION

In overcoming the above disadvantages, it is an object of the invention to produce a wildland fire retardant composition that has a reduced-tendency to corrode various metals, favorable rheological and aerial application characteristics, and is not negatively affected by exposure to sunlight or acidic

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conditions, resulting in the release of toxic by-products that could be both environmentally and toxicologically hazardous.

It is a further object of the invention to provide a fire retardant composition that is compatible with the concept of a fugitive or fading color system, able to become invisible over time with exposure to natural sunlight.

The above and other objects are met by the present invention, which provides a corrosion-inhibited fire retardant composition including at least one fire retardant composition that includes at least one ammonium polyphosphate, at least one biopolymer having a particle diameter less than about 100 microns, 10 and a corrosion inhibiting system that includes at least one corrosion inhibiting compound selected from a group of compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate (mixture or blend of sodium citrate and insoluble ferric pyrophosphate), ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof; wherein the corrosion inhibiting system is present in a minor effective amount to substantially reduce the corrosiveness of the fire retardant composition.

In a second aspect, the present invention provides a method of preparing the above-described corrosion-inhibited fire retardant compositions of the invention that includes the steps of forming an intermediate concentrate composition suitable for transportation and storage that includes the above-

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described corrosion-inhibited fire retardant composition of the invention; wherein the corrosion inhibiting system is present in a minor amount effective to substantially reduce the corrosivity of the fire retardant composition of the invention and diluting the intermediate concentrate with water to form the corrosion-inhibited fire retardant compositions of the invention.

In yet a third aspect, the present invention provides a method of suppressing wildland fires that includes aerially applying to wildland vegetation, ahead of wildland fire, a fire suppressing composition that is comprised of water and the above-described corrosion-inhibited fire-retardant compositions of the invention.

In a fourth aspect, the present invention provides a method of inhibiting corrosion that includes providing a corrodible material and contacting it with an effective amount of the above-described corrosion inhibiting system of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Not applicable.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been discovered that a fire-retardant composition can be prepared that has a reduced tendency to corrode various metals, including aluminum, that is superior to known fire retardants in rheological aerial application characteristics and is toxicologically and environmentally safe. The corrosion-inhibited fire retardants of the invention include at least one fire retardant composition comprised of at least one ammonium polyphosphate and a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from a group of corrosion

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inhibiting compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, insoluble ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof. Generally, the corrosion inhibiting system is present in a minor amount effective to substantially reduce the corrosiveness of the fire retardant composition.

In one embodiment of the invention, a small amount of at least one biopolymer is added to the fire retardant compositions of the invention. When small amounts of biopolymers are added to the fire retardant compositions of the invention, further reduction in aluminum corrosivity is experienced. As shown in Tables 7a and 7b below, the corrosion-inhibited fire retardant compositions of the invention containing biopolymers pass the corrosion requirements in both concentrate and diluted solutions. Generally, the fire retardant compositions of the invention, in concentrate, comprise in the range of about .01% to about 5.0% biopolymer. However, as one skilled in the art will appreciate, compositions comprising biopolymer concentrations outside of this range are also effective. Further, biopolymers having particle diameters outside of the above range may be incorporated into the compositions of the invention without departing from the spirit and scope of the invention. For example, fire retardant compositions containing biopolymers having particle sizes greater than about 100 microns in

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combination with biopolymers having particle sizes less than about 100 microns would be obvious to one skilled in the art.

In one specific embodiment of the invention, the concentrated fire retardant composition comprises about 1.0% biopolymer. In another specific embodiment of the invention, the concentrated fire retardant composition comprises about 3.0% biopolymer.

The biopolymer may be any biopolymer having a particle size less than about 100 microns. Biopolymers suitable for use in the present invention include, but are not limited to rhamsan, xanthan and welan biopolymers having an average particle diameter less than about 100 microns. Conventional xanthan thickeners having average particle diameters in excess of about 100 microns perform unacceptably in contact with liquid ammonium polyphosphate compositions. However, the inventors have found that reducing the particle diameter of biopolymers improves the ability of the biopolymers to rapidly increase the viscosity of the fire retardant composition upon subsequent dilution with water and exhibit increased corrosion inhibition, generally.

For example, a xanthan gum, with a weight average particle diameter in the range of about 100 to about 180 microns performs unacceptably in the fire retardant composition of the present invention, while a chemically identical xanthan gum with an average particle diameter in the range of about 20 to about 70 microns performs acceptably.

In one embodiment, the corrosion-inhibited fire retardant compositions of the invention include at least one xanthan biopolymer having an average particle diameter less than about 100 microns. Unlike prior art fire retardant compositions comprising guar gum thickeners and conventional xanthan

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biopolymers having average particle diameters greater than about 100 microns, the rate of viscosity of the fire retardant compositions of the invention that include xanthan biopolymer show viscosity development that is unaffected by the length of time that the biopolymer is in contact with the ammonium polyphosphate fire retardant solution. Some xanthan biopolymers suitable for use in the present invention are found in Xanthan Gum-natural biopolymer for scientific water control, Fifth Edition, herein incorporated by reference in its entirety.

The corrosion-inhibited fire retardant compositions of the invention, specially adapted for aerial application to wildland fires, are prepared by forming an intermediate concentrate composition comprising the above-described fire retardant composition containing the above-described corrosion inhibiting system. The intermediate concentrate is then diluted with water to form the corrosion-inhibited fire retardant composition of the invention. Generally, the corrosion inhibiting system is present in the corrosion-inhibited fire retardant of the invention in a minor amount effective to substantially reduce the corrosiveness of the fire retardant composition.

In accordance with the present invention, the corrosion-inhibited fire retardants of the invention include a fire retardant comprised of at least one ammonium polyphosphate. Ammonium polyphosphate is also referred to as polyammonium phosphate and may include both ortho- and polyphosphate, other ammonium phosphates such as pyro- and metaphosphates, the alkali metal equivalents thereof, as well as a blend of phosphate polymers.

The ammonium polyphosphate solutions that are used as agricultural fertilizer and wildland (vegetative) fire retardants are manufactured by

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neutralizing aqueous solutions of wet-process phosphoric acid, generally containing about 68% to about 74% phosphorus pentoxide with anhydrous ammonia in such a manner that both high temperature and pressure are experienced. When prepared in this manner, a portion of the impure orthophosphoric acid polymerizes or condenses, resulting in the formation of pyrophosphate, short chain polyphosphates and, in most instances, small amounts of cyclic or metaphosphates. That portion of the acid that does not polymerize, of course, remains as orthophosphoric acid. Ammoniation of this mixture of phosphate species occurs within the reactor, as well, resulting in an aqueous solution containing ammonium ortho, pyro, tripoly, tetrapoly and some higher chain and cyclic phosphate species. These condensed phosphates generally exhibit increased water solubility as compared to orthophosphates and, consequently, more highly concentrated solutions can be prepared when they are present. The relative concentrations of the various species depends primarily on the temperature and pressure achieved within the reactor. Commercial solutions generally contain from about 34% to about 37% phosphorus pentoxide. Phosphorus pentoxide concentrations above about 37% approach water solubility limits resulting in solutions that are not stable, from which solids may precipitate during ambient temperature storage. Solutions of this type are generally referred to as either 10-34-0 or 11-37-0 liquid concentrates; the numerical designation refers to the percentage of their plant nutrient composition, i.e., ammoniacal nitrogen, phosphorus pentoxide and potassium oxide.

It should be noted that the condensed phosphates that are present in liquid concentrate solutions are subject to hydrolyses, which results in depolymerization. The rate of hydrolytic degradation increases with time,

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temperature, and the relative acidity of the solution. Therefore, ammonium polyphosphate concentrates and their solutions may vary in species composition as received, and as time progresses during their subsequent storage.

These liquid concentrates may additionally contain small amounts of diammonium sulfate and a host of metal and alkali-metal impurities. The quantity and quality of these impurities vary with the composition of the phosphate ore, the utilized process and the extent of purification that is conducted during manufacture of the wet-process phosphoric acid. Since these solutions are manufactured primarily as nutrients, the quality control parameters of greatest interest are the percentages of their contained nutrients - nitrogen and phosphorus - and the clarity, stability and color of the solution rather than purity per se.

The corrosion inhibiting system of the invention is comprised of at least one corrosion inhibiting compound selected from a group of corrosion inhibiting compounds consisting of azoles, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric lactate, ferric oleate, ferrous furnarate, ferrous oxalate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof. In one preferred embodiment, the corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound. The combination of such soluble and insoluble corrosion

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inhibiting iron containing compounds appears to provide the optimum combination of corrosion inhibition.

A minor amount of the corrosion inhibiting system of the invention effective to substantially reduce the corrosiveness of the fire retardant composition is included in the corrosion-inhibited fire retardant compositions of the invention. A minor effective amount of the corrosion inhibiting system is that amount, which substantially reduces the corrosivity of the fire retardant. As is understood by one of ordinary skill in the art, what constitutes a substantial reduction in corrosivity is largely dependent on the specific fire retardant used in the fire retardant composition of the invention, as well as the specific composition of the corrosion inhibiting system, and can be readily determined by one of skill in the art without undue experimentation.

In one embodiment, the corrosion inhibiting system of the invention is present in a minor amount effective in the corrosion-inhibited fire retardant composition, in concentrate, to obtain a retardant having at least one of a maximum corrosivity to aluminum of 5.0 mpy, yellow brass of 5.0 mpy, and steel of 5.0 mpy, as determined by the "Uniform Corrosion Test" set forth in Section 4.5.6.1.2 of "Specification 5100-304b (January 2000) Superseding Specification 5100-304a (February 1986)," entitled "Specification For Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the USDA.

In a specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about .01% to about 10.0% of the total corrosion-inhibited fire retardant. In another specific embodiment, the corrosion inhibiting system of the invention comprises in the range of about 0.3% to about 6.0% of the total corrosion-inhibited fire retardant. In yet another specific embodiment,

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the corrosion inhibiting system of the invention comprises in the range of about 0.6% to about 5.0% of the total corrosion-inhibited fire retardant.

Prior to use, and in one embodiment of the invention, the corrosion-inhibited compositions of the invention are blended with water to form dilute solutions containing the amount of phosphorus pentoxide required to achieve the maximum amount of vegetation coverage at an application rate sufficient to reduce the flammability of the vegetative fuels to the desired level. The water used in the composition of the invention may be tap water, or water from other convenient water sources. Generally, the compositions are diluted one part concentrate to in the range of about three to seven parts water. In a specific embodiment, the compositions of the invention are diluted one part concentrate to in the range of about four to six parts water. However, it should be noted that the compositions of the invention may be diluted outside of the above ranges, for example where improved retardant penetration is desired. In a specific embodiment, the fire retardant compositions of the invention comprise less than about 1.18% biopolymer in dilute solution.

In a specific embodiment, the compositions of the invention are blended with water to form dilute solutions containing the amount of phosphorus pentoxide required to meet USDA, Forest Service Specification fire-retardant effectiveness requirements. This concentration, which is determined via combustion-retarding effectiveness testing described in USDA, Forest Service Specification 5100-304b, "4.5.2. Combustion Retarding Effectiveness Test," will generally depend on the percentage of phosphorus pentoxide present in the concentrated composition, and the extent of its availability for retarding reactions. The corrosion-inhibited fire retardant composition of the invention is

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typically diluted to an amount effective to achieve maximum coverage of vegetation at an application rate sufficient to reduce the flammable fuels to a desired level. The minimum USDA, Forest Service Specifications, for combustion retarding effectiveness, as specified in Specification 5100-304b, is generally obtained when the corrosion-inhibited fire retardant concentrate of the invention is diluted with about 1 to about 8 volumes of water.

To suppress wildland fires, the corrosion-inhibited fire retardant compositions of the invention are diluted with water and applied on threatened vegetation, ahead of approaching wildland fire. Ammonia from both the ammonium phosphate and the ammonium sulfate are liberated at temperatures below the ignition temperature of the fuel. The phosphoric and sulfuric acids are both initially effective fire retarding acids. The phosphoric acid will remain present and effective with the vegetative fuel until temperatures exceed 600°C. However, the boiling point of sulfuric acid is much lower, and the amount present will decrease as the fuel temperature increases. Thus, at least a portion of the sulfuric acid is lost prior to the ignition temperature of the fuel. The resultant mineral acids subsequently react with the cellulosic components of vegetative fuels on which they are applied. Their thermal decomposition is thereby altered in such a manner that they will no longer serve as fuel. These reactions are described in U.S. Pat. No. 4,839,065 to Vandersall, which is hereby incorporated by reference in its entirety.

The fire retardant compositions of the invention may also contain suspending agents. Suspending agents effectively reduce the rate of separation and settling during long term storage. Thus, as one skilled in the art would appreciate, the amount of suspending agent depends upon its relative

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effectiveness per unit applied, the desired length of storage and the additional additives incorporated into the compositions of the invention. As used herein, suspending agents useful in the compositions of the invention include colloidal clays, for example, attapulgus, fuller's earth, sepiolite, montmorillonite, and kaolin clays. As used herein, attapulgus clay includes, but is not limited to attapulgite and polygorskite. As used herein, kaolin clay includes, but is not limited to Kaolinite, [Al₂Si₂O₇-2(H₂O)] and [Al₂O₃-2SiO₂-2(H₂O)].

As will be apparent to those skilled in the art, the corrosion-inhibited fire retardant of the invention may contain or be mixed with other functional components or additives such as suspending agents, coloring agents, surfactants, stabilizers, opacifying agents, other corrosion inhibitors, any combination thereof, or with other functional components.

For example, and in one embodiment of the invention, the corrosion-inhibited fire retardant composition of the invention includes at least one highly colored pigment. The colored pigment is incorporated to assist in the visual identification of treated and untreated vegetation. Suitable highly colored pigments include iron oxide, which produces many colors like brown and red, titanium dioxide pigments, which produce a white color, or an ultra-violet sensitive dye dispersed in biodegradable plastic. However, for certain uses, like along roadsides or in parks, it may be desirable to exclude any colorant from the mixture. Accordingly, as one skilled in the art would appreciate, the amount of colorant or pigment incorporated into the compositions of the invention depends on the degree of the dilution and visibility contemplated by the user. Visibility is usually obtained with red iron oxide when it is present in the diluted solution in the range of about 0.15% to about 0.4%, depending on the colorant characteristics

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and on the vegetative and topographical characteristics of that on which it will be applied. The amount incorporated in the concentrate will, of course, vary with the dilution rate required to provide adequate fire retarding effectiveness.

In another embodiment, the present invention includes at least one of red iron oxide or brown iron oxide, or a combination thereof. In yet another embodiment, the present invention includes a fugitive coloring agent, whose color fades upon exposure to the elements. In a further embodiment, the present invention includes opacifying pigments, which are generally not highly colored, but have the ability to cover and hide that on which it is deposited so that the highly colored pigment becomes more visible.

Surfactants may also be added to increase visibility, through the generation of a foam, and to improve penetration of the retardant solution into porous fuels. Accordingly, as one skilled in the art would appreciate, the amount and type of surfactant incorporated into the compositions of the invention depends on the degree of the dilution and visibility contemplated by the user.

Thickeners, for example, hydroxypropyl guar, may also optionally be added to the compositions of the invention. The existence of such gums in the compositions of the invention is not necessary for anti-corrosive or improved rheological characteristics to be realized. If employed, the quantity of other gums in the compositions of the invention will vary depending in part on the nature and concentration of the fire-retardant salts present, the presence of impurities, and the presence of other components. Accordingly, and in one embodiment of the invention, the compositions of the invention contain thickeners, for example, hydroxypropyl guar, or other non-ether derivative guar thickeners. In other

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embodiments of the invention, the compositions do not contain thickeners, for example, hydroxypropyl guar.

It has been discovered that azoles are effective corrosion inhibitors for brass. In one embodiment of the invention, the compositions of the invention comprise at least one azole. As used herein, an azole is any of a group of chemical compounds with a five-membered ring containing one or more nitrogen atoms. Azoles suitable for use in the corrosion-inhibited fire retardants of the invention include, but are not limited to tolytriazole, henzotriazole, mercaptobenzothiazole, dimercaptothiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof. The amount of azole or other corrosion inhibitor is dependent upon the corrodible metal for which corrosion resistance is desired, the level of resistance desired, and the specific concentration of the fire retardant composition employed, including corrosion inhibiting compounds contained therein.

However, in one embodiment of the invention, the corrosion-inhibited fire retardant concentrates include at least one azole, present in a minor amount effective to obtain a corrosivity of yellow brass to a maximum of 5.0 mpy, as determined by the "Uniform Corrosion Test" set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-304a (February 1986)," entitled "Specification For Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the USDA. In a specific embodiment of the invention, the fire retardant concentrates of the invention comprise in the range of about .01% to about 1.0% tolytriazole. In yet another

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specific embodiment, the compositions of the invention include in the range of about 0.2% to about 0.6% tolytriazole. In yet another specific embodiment, the compositions of the invention include in the range of about 0.3% to about 0.5% tolytriazole.

A method of inhibiting corrosion using the above-described corrosion inhibiting system of the invention is also provided. According to the method of the invention, a corrodible material is provided and contacted with an effective amount of the corrosion inhibiting system of the invention to substantially reduce the corrosiveness of the fire retardant.

In one embodiment of the invention the corrodible material is also contacted with at least one above-described suspending agents. In another embodiment, the method of inhibiting corrosion further includes the step of contacting the corrodible material with at least one above-described biopolymer having a particle size less than about 100 microns. Accordingly, the method includes providing a corrodible material and contacting the corrodible material and at least one above-described biopolymer having a particle size less than about 100 microns and an effective amount of the corrosion inhibited system of the invention.

Any corrodible material may be used according to the method of inhibiting corrosion of the invention. In one embodiment, the corrodible material is selected from a group of corrodible materials consisting of steel, brass, aluminum, and any alloy thereof.

Prior to use, and in one embodiment of the invention, the corrosion inhibiting system and biopolymer, if present, are blended with water prior to or

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during contact with the corrodible material. The water used in the composition of the invention may be tap water or water from other convenient water sources.

In one embodiment, the corrosion inhibiting system of the invention includes at least one additive selected from a group of additives including suspending agents, coloring agents, surfactants, opacifying pigments, stabilizers, corrosion inhibitors and any combination thereof.

While the corrosion-inhibited fire retardant compositions of the invention reduce aluminum corrosivity in the absence of biopolymers, biopolymers are not significantly effective for reducing corrosion to aluminum in the absence of the corrosion inhibiting system of the invention. However, it has been discovered that the corrosion-inhibited fire retardant composition of the invention containing biopolymers shows improved rheological characteristics in the absence of the corrosion-inhibiting system of the invention. Specifically, increased viscosity is shown in dilute solutions comprising the above-described corrosioninhibited fire retardant composition, in the absence of the corrosion inhibiting system of the invention. Accordingly, in one embodiment, fire retardant composition of the invention comprises at least one above-described fire retardant composition comprised of at least one ammonium polyphosphate and at least one above-described biopolymer having a particle diameter of less than about 100 microns. This embodiment, which does not include the above-described corrosion inhibiting system of the invention, will hereinafter be referred to as the viscosity-increased fire retardant compositions of the invention.

While suspending agents may be utilized in all of the fire retardant compositions of the invention, the use of suspending agents is not necessary for improved rheological characteristics to be realized in both the concentrated and

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dilute fire retardant compositions, or for the corrosion inhibiting characteristics of the corrosion-inhibited fire retardant compositions of the invention to be realized.

The viscosity-increased fire retardant compositions of the invention generally comprise in the range of about .01% to about 5.0% biopolymer, in concentrate composition. However, as one skilled in the art will appreciate, compositions comprising biopolymer concentrations outside of this range are also effective in increasing the viscosity of fire retardant compositions. In one specific embodiment of the invention, the viscosity-increased fire retardant composition of the invention, in concentrate, comprises about 1.0% biopolymer. In another specific embodiment of the invention, the fire retardant composition, in concentrate, comprises about 3.0% biopolymer.

In one specific embodiment, the viscosity-increased fire retardant compositions of the invention include at least one above-described xanthan biopolymer. In a specific embodiment, the fire retardant compositions of the invention include at least one fire retardant composition comprised of at least one ammonium polyphosphate, in the range of about .01% to about 5.0% at least one xanthan biopolymer having a particle size less than about 100 microns, and at least one above-described additive or functional component.

The viscosity-increased fire retardant compositions of the invention are prepared in the same manner as the above-described corrosion-inhibited fire retardant composition of the invention. Accordingly, and in one embodiment of the invention, the viscosity-increased fire retardant compositions of the invention are prepared by forming an intermediate concentrate composition comprising the above-described fire retardant composition containing at least one ammonium

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polyphosphate and at least one above-described biopolymer having a particle size less than about 100 microns, and diluting the intermediate concentrate with water to form the viscosity-increased fire retardant composition of the invention. In one embodiment the compositions comprise less than about 1.18%

5 biopolymer.

In a specific embodiment, the fire retardant compositions of the invention are prepared by forming an intermediate concentrate composition comprised of at least one above-described fire retardant and at least one xanthan biopolymer having an average particle diameter less than about 100 microns, wherein the fire retardant compositions comprise in the range of about .01% to about 5.0% xanthan biopolymer, and diluting the intermediate concentrate with water to form the increased-viscosity fire retardant composition of the invention.

A method of suppressing wildland fires using the viscosity-increased fire retardant compositions of the invention is also provided. The method includes the steps of aerially applying to wildland vegetation a fire suppressing composition comprising water and the above-described viscosity-increased fire retardant composition. In a specific embodiment, the method includes aerially applying to wildland vegetation a fire suppressing composition comprising water, at least one ammonium polyphosphate composition, less than about 1.18% of at least one xanthan biopolymer having a particle size less than about 100 microns and at least one above-described additive.

All references and patents cited herein are hereby incorporated by reference in their entireties for their relevant teachings. Accordingly, any reference cited herein and not specifically incorporated by reference is,

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nevertheless, incorporated by reference in its entirety as if part of the present specification.

The following examples illustrate specific embodiments of the invention without limiting the scope of the invention in any way. In each example,

samples of ammonium polyphosphate fire retardant concentrates were mechanically admixed with iron containing compounds, biopolymer, additives, and in some cases, with an azole, as indicated in each table. Any mechanical mixing technique that is well known in the art may be used in the present invention. The concentrated fire retardant solutions are diluted with water, as indicated. The "Requirements" row illustrates the level of aluminum 2024-T3 corrosion allowed by the USDA, Forest Service Specifications 5100-304b, i.e., the maximum allowable corrosivity for product acceptance for use in wildland fire retardant compositions. The resulting samples were tested for corrosivity in accordance with USDA, Forest Service Specifications 5100-304b.

15 EXAMPLE 1-THE ALUMINUM CORROSIVITY OF NEAT AMMONIUM POLYPHOSPHATE SOLUTION

Table 1 illustrates the corrosion characteristics of neat, unadulterated fertilizer grade 10-34-0 and 11-37-0 ammonium polyphosphate liquid concentrates obtained from three different sources. All of the samples are either 10-34-0 or 11-37-0, as received, with no additions. The corrosivity of the samples were expressed in mils of metal loss on exposed metal surface extrapolated from 90 to 365 days (mpy) and ascertained using the aforementioned USDA, Forest Service Specifications for determining corrosivity. Both the concentrated retardant and its diluted solutions were tested at each temperature and condition indicated.

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The diluted solutions were prepared by admixing four to five volumes of water with one volume of the concentrated solution. Thus, the diluted solutions were in the range of between about 15% to about 20% by volume of the concentrate.

In accordance with the Forest Service Specifications for corrosion testing of fire retardants, a one-inch wide, four-inches long, one-eighth inch thick coupon of the aluminum was obtained from a standard source. The coupon is cleaned, dried and weighed according to standard USDA, Forest Service Specifications and suspended in a one quart, straight sided jar filled either 50% (partially) or 100% 10 (totally) full using a piece of nylon string. When suspended in a partially full jar, the coupon was 50% (two inches) immersed in the test solution with the other 50% extending up from the solution into the air space above it. When the jar was full with approximately 800 ml of the solution, the metal coupon was totally immersed in the solution. The jars were then closed with a screw cap and two or three identical corrosion jars (cells) of each partially and totally immersed coupons were stored at 70°F and 120°F for ninety days. At the end of the ninety day storage period, the jars were opened and the coupons were removed and cleaned according to the USDA, Forest Service Specifications. The coupon was then re-weighed after it dried and its weight loss was determined by comparing its initial and final weights. The calculated weight loss and density of the metal coupon were used to extrapolate to mils (0.001 inches) of aluminum that would be lost during a one-year period at the test condition, assuming that the weight loss was experienced uniformly across the coupon surface. The corrosion rate of both the partially and totally immersed coupons were calculated using the total

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surface area of the coupon. The samples at each condition were then averaged and reported as the corrosion rate. The results are shown in Table 1.

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m (1900) (mpy) 1 120°] 1 20°] 1 24.9 1 24.9 1 11.4 1 11.4 1 11.6 1 11.	indicated configuration (mov)	Diluted Solution	70°F 70°F 120°F	total	≤2.0 ≤2.0 ≤2.0	8.4 6.5 24.9	15.2 8.4 10.1 5.6	5.8	5.8 6.3 11.4 7.8	11.0	10.8	7,4	12.3 6.4 21.8 13.3	12.0 7.0 39.0 14.8	21.1	22.8	11.0 6.4	33.7	12.7	12.8 7.5 35.8 19.3	11.2 6.5 42.7 21.8	13.3	29.2	17.7 10.4 10.5 7.0	13.8	12.7		7.4	4.5 5.8-17.7 6.3- 5.8-42.9 5.6-21.8
	Hiomes	Solutio	170∘1	part	<2.€	6.5	8.4	_	6.3			L	6.4	7.0		L		_	_	7.5	6.5			10.4			7.2	7.4	
Nove Partial	insted cor	Diluted	70°F	total	≤2.0	8.4	15.2		5.8				12.3	12.0			11.0		12.7	12.8	11.2			17.7	13.8	12.7	13.1	12.2	5.8-17.
Cated configurat Dilluted Solutic TO°F 70°F 70°I S.2.0 \$2.0 \$2.0 8.4 6.5 15.2 8.4 6.3 15.2 6.4 12.0 7.0 11.0 11.0 11.2 6.5 11.2 6.5 11.2 6.5 11.2 6.5 11.2 6.5 11.2 6.5 11.2 6.5 11.2 6.5 11.2 7.7 11.2 6.5 11.2 7.7 11.2 6.5	d in the ind	200	120°F	partial	≤5.0	77.8	78.5		67.4				88.6	85.3						96.5	86.7			94.5			74.8	83.3	67.4-94.5
d in the indicated configurat 120°F 120°F Partial total total partial total	Table 1	man marrie (at	120°F	total	≥5.0	134.3	106.6	146.0	140.7	129.4	170.0	168.5	165.0	161.4	130.0	126.2	109.4	149.4	155.6	201.0	159.0	151.5	136.3	144.8	115.8	176.9	172.6	147.7	106.6-201.0
Table 1 Table 1 120°F	n Corrosia	centrate	70°F	partial	≥5.0	4.3	9.9		4.1				5.3	5.5						0.9	7.1			6.3			5.5	5.6	4.1-7.1
Table 1 Corrosivity when tested in the indicated configurate centrate Toforf 120°F 70°F 70°F 70°F 70°I 70°I 70°I 70°I 70°I 70°I 70°I 70°I	Aluminin	Neat Con	70°F	total	<5.0	8.7	12.4		8.1				10.2	10.9			4.3		9.5	12.7	13.1			12.0	6.6	15.2	10.9	9.01	4.3-15.2
Table Tabl			Ammonium	Polyphosphate Samples	Requirements	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	Sample 14	Sample 15	Sample 16	Sample 17	Sample 18	Sample 19	Sample 20	Sample 2.1	Sample 22	Average	Range (Lo-Hi)

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The corrosivity of the ammonium polyphosphate solutions to aluminum 2024T-3 was relatively low when the temperature was maintained at about 70°F. However, none of the samples of the neat ammonium polyphosphate solutions met the Forest Service Specifications for corrosivity of fire retardants. In addition, the results showed that increasing the solution temperature to 120°F dramatically increased the corrosion of the aluminum coupon by the neat ammonium polyphosphate samples, i.e., in excess of an order of magnitude.

EXAMPLE 2-THE ALUMINUM CORROSIVITY OF AMMONIUM POLYPHOSPHATE SOLUTION CONTAINING 1.2% IRON OXIDE (Fe $_2$ O $_5$) & 1.4% ATTAPULGUS CLAY

The corrosion characteristics of neat fertilizer grade ammonium polyphosphate solutions containing additional amounts (<3%) of a mixture of an iron oxide colorant and attapulgus clay is illustrated in Table 2. Each sample was prepared by admixing neat concentrated ammonium polyphosphate obtained from several sources with 1.4% attapulgus clay, and either 1.2% red iron oxide or 1.2% brown iron oxide, as indicated. In addition, 0.3% tolytriazole was also admixed into Samples 11, 15, 16, 18 and 19 and 0.5% tolytriazole was admixed into sample 20. Aliquots from these concentrate samples were then diluted by admixing 1.0 volume of concentrate with 4.25 volumes of tap water. The concentrates and their solutions were then tested for corrosivity and diluted in accordance with Forest Service Specifications. The results are shown in Table 2.

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Table 2

		Corrosion	Rate (milli-	Corrosion Rate (milli-inches per year	(ear)				
		Neat Concentrate	centrate			Diluted Solution	olution		
Ammonium Polimbombate Camples	Type of Iron	70°F	70°F	120°F	120°F	70°F	70ºF	120°F	120°F
Lory price princes	Calde	totai	parcial	TOTAL	partial	total	partial	tota.	partial
Corrosion of neat 10-34-0 Average from Table1	none	10.6	2.6	147.7	83.3	12.2	7.4	22.0	12.6
Requirements		≥5.0	≥5.0	≤5.0	\$5.0	≤2.0	≤2.0	22.0	<2.0
Sample 1	Bn Iron oxide ⁽¹⁾			1.4				4.4	
Sample 2	Bn Iron oxide(1)			0.7				3.7	
Sample 3	Bn Iron oxide(1)			1.4				2.3	
Sample 4	Bn Iron oxide(1)			6.4				10.1	
Sample 5	Rd Iron oxide ⁽²⁾	4.6	3.6	7.3	5.0	6.7	4.4	4.0	3.6
Sample 6	Rd Iron oxide ⁽²⁾	3.5	1.9	6.7	0.6	4.3	3.9	2.5	3.3
Sample 7	Rd Iron oxide ⁽²⁾			2.3				4.5	
Sample 8	Rd Iron oxide ⁽²⁾	3.5	3.8	1.7	1.6	2.8	4.3	3.5	3.6
Sample 9	Rd Iron oxide ⁽²⁾			3.0				3.1	
Sample 10	Rd Iron oxide ⁽²⁾			15.3				11.7	
Sample 11	Rd Iron oxide ⁽²⁾			32.1				7.1	
Sample 12	Rd Iron oxide ⁽²⁾			8.3				3.8	
Sample 13	Rd Iron oxide ⁽³⁾			26.3				3.9	
Sample 14	Rd Iron oxide ⁽²⁾			19.7				3.8	
Sample 15	Rd Iron oxide ^[3]			4.3				0.8	
Sample 16	Rd Iron oxide ⁽²⁾			6.7				5.3	
Sample 17	Rd Iron oxide ⁽²⁾			2.3				4.2	
Sample 18	Rd Iron oxide ⁽²⁾	1.4		8.0		2.7		2.0	
Sample 19	Rd Iron oxide ⁽²⁾	5.0	3.5	8.5	13.7	5.7	4.2	5.4	4.1
Sample 20	Rd Iron oxide ^[2]	4.4	2.4	11.2	2.8	4.1	4.0	2.3	2.8
Sample 21	Rd Iron oxide ⁽²⁾			2.0				1.9	
Sample 22	Rd Iron oxide ⁽²⁾			7.8				11.1	
Average		3.7	3.0	8.3	6.4	4.4	4.2	4.6	3.5
Range	ge 1.4-5.0 1.9-3.8 0.7-32.1	1.4-5.0	1.9-3.8	0.7-32.1	1.6-13.7	2.7-5.7	3.9-4.3	2.5-11.7	2.8-4.1

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The results indicated that the addition of small amounts of iron oxide and clay reduced the corrosion of totally immersed aluminum in a 70°F solution by 50% to 65%. In addition, the impact of the mixture on high temperature corrosion was even more dramatic than at low temperature. When the corrosion cell was stored at 120°F, the rate of aluminum corrosion decreased by about 75% to 90%. At both temperatures the corrosion rate on partially immersed coupons was greater than 50% of the totally immersed values, which indicated that significant interface or vapor/air phase corrosion occurs when the mixture is present in the solution. This differs from the corrosivity of the neat ammonium polyphosphate solutions of Table 1. However, the addition of 1.2% insoluble iron oxide and a suspending clay to the ammonium polyphosphate samples did not reduce the aluminum 2024-T3 corrosion rate of the concentrates or its solutions to within the limits required by the USDA, Forest Service Specifications.

EXAMPLE 3-THE ALUMINUM CORROSIVITY OF AMMONIUM
POLYPHOSPHATE SOLUTIONS CONTAINING A MIXTURE OF SOLUBLE
AND INSOLUBLE IRON COMPOUNDS

The data in Tables 3a and 3b illustrate the relative effectiveness of a number of corrosion inhibitor systems containing water soluble and water insoluble sources of iron, and mixtures thereof, in several sources and types of ammonium polyphosphate concentrates and their diluted solutions. The samples were prepared by admixing either 10-34-0 or 11-37-0 type ammonium polyphosphate solutions from various sources with varying concentrations of insoluble red iron oxide or brown iron oxide additives and attapulgus clay additives and varying the concentrations of other iron containing additives, as indicated. The solutions were subjected to high shear mixing in order to activate or hydrate the clay.

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Each concentrate and its diluted solution was tested for aluminum corrosivity in accordance with the Forest Service Specification protocols. The results are shown in Tables 3a and 3b.

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OREG	ORROSION (mpy)														
	Anmonium	Insolu	Insoluble Iron	Other Iron	Other Iron Containing Additive			Neat Cor	Neat Concentrate			Littered Solution	Solution		
	Polyphosphate	Oxide	Added			Fe. Content		70°F	70°F	120°F	120°F	J-02/	70°F	120°F	120°F
	Samples	*	Type	88	Additive	% insol.	% sol.	Total	pertial	total	Partial	total	partial	total	partial
	SAMPLE 1 (from Table 1)	0.0	Моше	0.0	None	0.00	0.00	1.6	5.2	140.6	79.5	10.8	6.9	16	5.6
		1.2	Iron oxide	0.0	Nonc	0,00	0.00	8.7	3	8.3	6.4	4.4	4.2	9.4	3.5
_		9.0	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.42	0.35			7.4				0.5	
		9.0	Br. Iron oxide	5.0	Sol. Ferric pyrophosphate	0.42	0.58			0.6				9.6	
		1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			2.2				1.0	
~		1.3	Br. Iron oxide	3.0	Sol. Ferric pyrophosphete	0.84	0.35			2.2				1.0	
		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			5.7				1.3	
_		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.9				2.5	
		1.2	Red Iron oxide	3.0	Sal. Ferric pyrophosphate	0.84	0.35			10.8				1.6	
٥		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			10.3				1.5	
_		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphete*	0.84	0.35			18.1				9.1	
22		1.2	Red Iron oxide		Sol. Ferric pyrophosphate*	0.84	0.35	3.1	3.1	6.1	3.9	4.4	3.6	1.6	3.4
25		9.0	Br. Iron oxide		Sol. Ferric citrate*	0.42	0.13			118.7				1.4	
4		9.0	Br. fron axide		Sol. Ferric citrate	0.42	0.66			5.5				9.6	
15		9.0	Br. Iron exide		Sol. Ferric citrate*	0.42	99.0			6.7				9.0	
36		1.3	Br. Iron oxide		Sul. Perric citrate*	0,84	0.40			6.0	L			0.5	
7		1.2	Br. Iron oxide		Sol. Ferric citrate*	0.84	0.40			15.3				3.3	
8		1.3	Red Iron oxide	1.8	Sol. Ferric citrate*	0.84	0.40			46.5				2.2	
2		1.2	Br. Iron oxide		Sol. Ferric citrate*	0.84	0.66			1.0				0.7	
8		1.2	Br. Iron oxide	٦	Sol. Ferric citrate	0.84	99.0			4.5				0.7	
7		1:5	Br. Iron oxide		Sol. Ferric citrate	0.84	0.66			3.9				9.0	
22		1.2	Br. Iron oxide	1	Sol. Perric citrate	0.84	0.66			1.0				0.7	
23		9.0	Br. Iron oxide	5.0	Sol. Ferric MI74 citrate	0.42	0.88			7.9				8.0	
7		1.2	Red fron oxide	1.8	Sol. Ferric NF4 citrate	0,84	0.32			53.9				3.4	
52		7.7	Red Iron oxide	3.0	Sol. Ferrons sulfate• 7H20	0.84	0.60			1.0				3.4	
26		1:5	Red Iron oxide	1.2/3.0	Insol./sol. Ferric pyrophosphate	1.13	0.35			7.5				1.3	
27	!			1.2/3.0	Insol./sol. Ferric pyrophosphate	0.29	0.35			2.0				1.2	
				1.2/3.0	Insol./sol. Ferric pyrophosphate	0.29	0.35			2.3				0.7	
23				3.0/3.0	Insol./sol. Ferric pyrophosphate	0.72	D.35			5.8				1.0	
30				1.2/3.0	insol ferric pyro/sol. Fe	0.29	99.0			2.1				1.2	
31	İ			1.2/3.0	Insol ferric ortho/sol Ferric	0.37	0.35			3.1				1.5	
1	These connection	me ronto	These connestitions contain 0.3-0.5% relatriazele for brass corresion inhibition	for brase co	rosion inhibition										

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Г	Ammonium Incolubi	Incolu	Incoluble from	Otherin	Other Inn Containing Addition			Nost C.	Mast Concentrate	9		Dilinted	Diluted Solution		
Γ	Polyphosphate	Oxide Added	Added		on Containing Dantage	Fe. Content	H	70°F	70°F	120°F	120°₽	70°F	70°F	120°F	120°F
Γ	Samples	%	Type	(%)	Additive	% insol.	% sol.	-	partial	total	partial	total	partial	total	partial
32	SAMPLE I			1.2/3.0	Insol ferric ortho/sol Ferric pyro	0.37	0.35			2.2				1.0	
33				1.2/3.0	Insol/sol. Ferric ortho	0.37	0.41			1.9				2.2	
34				1.2/3.0	Insol/sol. Ferric ortho	0.37	0.41			1.9				1.5	
35				1.2/4.0	Insol, Fc(III) orthophosphatc/sol Fc(III) NF4 citrose	0.37	0.70		-	2.3				1.4	
36		L		1.2/4.0	Insol. Fe(III)	0.37	0.70			1.8				1.2	
					orthophosphate/sol Fe(III) NH4 citrate										
37				1.2/8.0	Insol. Fe oxalate 2F120/sol. Ferric pyrophosphate	0.37	0.35			17.0				6.1	
38				1.2/3.0	Insol. Fe oxalate/sol. Fe sulfate	0.37	09.0			37.4				5.8	
39	SAMPLE 2	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	1.2	6.0	10.1	5.2	3.7	3.7	1.4	T.7
40		1.2	Br. Iron oxide	3.0	Sol. Ferric citrate	0.84	99.0			0.2				9.4	
41	SAMPLE 3	9.0	Br. Iron oxide	5.0	Sol. Ferric citrate	0.42	1.10			6.2				0.5	
42		1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.45	2.8	2.7	110.1	70.2	11.0	6.7	9.7	3.5
43		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			33.2				9'.2	
44	SAMPLE 4	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	8.7		76.5		6.4		8.0	
45	SAMPLE 5 ⁽²⁾	1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	2.3		2.8		2.8		1.1	
46		1.2	Red Iron oxide	4.0	Sol. Ferric pyrophosphate	0.84	0.46	1.8		2.8		2.6		1.8	
48		2.4	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	1.68	0.35	1.4		2.1		2.7		1.2	
49		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			4.0				2.1	
50		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35	1.6	1.0	2.4	1.7	2.0	3.2	1	2.0
51		1.2	Red fron oxide	3.0/3.0	insol/sol. Ferric	1.56	0.56	9.0		5.4		1.6		6.0	
Ī					pyrophosphate										
52	SAMPLE 6(3)	1.2	Br. Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.85	2.1	1.7	113.0	52.7	11.8	6.2	8.1	4.5
53		1.2	Red Iron oxide	3.0	Sol. Ferric pyrophosphate	0.84	0.35			21.0				9.6	
ũ	CANATA TO TAIL														

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For comparative purposes, line 1 illustrates the average corrosion characteristics of neat concentrate and dilute solutions from Sample 1, taken from Table 1, and line 2 illustrates the corrosion of the concentrate and diluted solutions when 1.2% iron oxide and 1.4% attapulgus clay, with the exception of the formulations on line 9 which contained 0.7% attapulgus clay and the formulation on line 11, which contained 2.8% attapulgus clay, was mixed with the neat concentrate solution, see Table 2. Samples 1-4 were 10-34-0 type ammonium polyphosphate samples obtained from various sources. Samples 5-7 were 11-37-0 type ammonium polyphosphate samples obtained from various sources.

The data in Tables 1 and 2 illustrate that corrosive attack of aluminum was most severe when exposed to the fire retardant concentrate and its solutions at clevated (120°F/49°C) temperature in the totally immersed configuration.

Consequently, the evaluation of corrosion inhibiting systems stressed testing under these conditions. Periodic testing at other conditions was conducted.

Lines 3 through 6 illustrate the corrosion inhibiting effectiveness of combinations of insoluble brown iron oxide and soluble ferric pyrophosphate. The results indicated that the USDA, Forest Service Specifications for corrosivity of fire retardants were met when 1.2% of the brown iron oxide was used in conjunction with 3.0% of the soluble ferric pyrophosphate. In addition, the results indicated that lower amounts of the insoluble iron oxide resulted in unacceptable corrosion in the concentrated retardant solution.

Lines 7 through 12 illustrate the effectiveness of corrosion inhibiting systems similar to those described in the preceding paragraph, except red iron oxide is substituted for brown iron oxide. The results indicate that the red iron

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oxide is effective in reducing the aluminum corrosion of the concentrated and diluted ammonium polyphosphate although perhaps not quite as effective as the brown iron oxide.

Lines 13-22 illustrate the corrosion inhibiting effectiveness of mixtures of insoluble iron oxide and soluble ferric citrate. The results indicated that ferric citrate was an equally effective substitute for soluble ferric pyrophosphate. In addition, the results indicate that a mixture of brown iron oxide and 3.0% soluble ferric citrate was capable of reducing the corrosivity of the ammonium polyphosphate samples to within acceptable levels for compliance with Forest Service Specifications for corrosivity of fire retardants.

Lines 23 and 24 illustrate the use of ferric ammonium citrate as a substitute for ferric citrate. The results indicated that the soluble ferric compounds were as effective as ammonium citrate in reducing corrosion of aluminum by ammonium polyphosphate solutions.

Lines 27 through 38 illustrate the effectiveness of systems in which only uncolored, soluble and insoluble iron containing compounds are used rather than the relatively highly colored persistent iron oxides. This is important where true fugitive retardants are desired, whereby the color gradually fades when exposed to natural sunlight and disappears so as not to permanently stain that on which it is applied.

Lines 26 through 38 illustrate the effectiveness of mixtures of soluble and insoluble ferric pyrophosphate. Acceptable aluminum corrosion properties were obtained when 3.0% of the former and 1.2% of the latter were used as the corrosion inhibiting system in an ammonium polyphosphate solution. The

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results also indicate that an increased level of insoluble ferric pyrophosphate did not further reduce the corrosivity of the concentrate.

Lines 27 though 38 illustrate the aluminum corrosion inhibiting effectiveness of mixtures of the various soluble and insoluble iron compounds.

Lines 37 and 38 revealed that, although effective, the tested ferrous salts were less

effective at equivalent iron addition rates as compared to the ferric compounds.

Lines 39 through 44 illustrate the aluminum corrosion inhibiting effectiveness of various soluble and insoluble iron compounds when used in conjunction with 10-34-0 ammonium polyphosphate concentrates obtained from alternative sources. These data indicate that the amount and ratio of corrosion inhibitor necessary to reduce corrosivity to an acceptable level will need to be optimized dependent on the source and characteristics thereof.

Lines 45 through 54 illustrate the aluminum corrosion inhibiting effectiveness of the subject compounds when used in various sources of 11-37-0 type ammonium polyphosphate concentrate and their diluted solutions.

EXAMPLE 4-CORROSION CHARACTERISTICS OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING WATER SOLUBLE IRON COMPOUNDS

Example 4 illustrates the effectiveness of water-soluble ferric

pyrophosphate, ferric citrate and ferrous sulfate as aluminum corrosion inhibitors in ammonium polyphosphate solutions. In each sample, the indicated soluble iron compounds and 1.4% attapulgus clay were admixed with neat ammonium polyphosphate. Aliquots were subsequently drawn from the concentrate and diluted with the prescribed amount of water. The aluminum corrosivity of both the concentrated fire retardants and their diluted solutions was determined in

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accordance with the aforementioned Forest Service Specifications. The results of this testing is shown in Table 4.

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Table 4

Dilute Solution	5.8-39.0	1.5	1.6	1.2	1.3	2.5	2.4	1.1	3.1
Concentrate	106.6-170.0	150.6	42.5	75.4	69.3	113.1	124.1	17.0	27.9
Total Fe (%)	0	20.0	0.35	0.35	0.35	0.53	99.0	99.0	09.0
Additive	None	Soluble ferric pyrophosphate	Soluble ferric pyrophosphate	Soluble ferric pyrophosphate	Soluble ferric pyrophosphate	Soluble ferric citrate	Soluble ferric citrate	Soluble ferric citrate	Ferrous sulfate•7H2O
(%)	0	9.0	3.0	3.0	3.0	2.4	3.0	3.0	3.0
Polyphosphate Samples	Average Sample from Table 1	1	2	3	4	5	9	7	8
	phate Total Fe Concentrate (%) Additive (%)	(%) Additive (%) Additive (%) 0 106.6-170.0	Concentrate Concentrate	tc (%) Additive Total Pe Concentrate 0 None 0 106.6-170.0 0.6 Soluble ferric pyrophosphate 0.07 150.6 3.0 Soluble ferric pyrophosphate 0.35 42.5	tc (%) Additive Total Fe Concentrate 0 None 0 106.6-170.0 0.6 Soluble ferric pyrophosphate 0.07 150.6 3.0 Soluble ferric pyrophosphate 0.35 42.5 3.0 Soluble ferric pyrophosphate 0.35 75.4	tc (%) Additive Total Fe Concentrate 0 None 0 106.6-170.0 0.6 Soluble ferric pyrophosphate 0.07 150.6 3.0 Soluble ferric pyrophosphate 0.35 42.5 3.0 Soluble ferric pyrophosphate 0.35 75.4 3.0 Soluble ferric pyrophosphate 0.35 69.3	tc (%) Additive Total Fe Concentrate 0 None 0 106.6-170.0 0.6 Soluble ferric pyrophosphate 0.07 150.6 3.0 Soluble ferric pyrophosphate 0.35 42.5 3.0 Soluble ferric pyrophosphate 0.35 75.4 3.0 Soluble ferric pyrophosphate 0.35 69.3 2.4 Soluble ferric citrate 0.53 113.1	(%) Additive Total Fe Concentrate 0 None 0 106.6-170.0 0.6 Soluble ferric pyrophosphate 0.07 150.6 3.0 Soluble ferric pyrophosphate 0.35 42.5 3.0 Soluble ferric pyrophosphate 0.35 75.4 3.0 Soluble ferric citrate 0.35 69.3 2.4 Soluble ferric citrate 0.53 113.1 3.0 Soluble ferric citrate 0.56 124.1	tc (%) Additive Total Fe Concentrate 0 None 0 106.6-170.0 0.6 Soluble ferric pyrophosphate 0.07 150.6 3.0 Soluble ferric pyrophosphate 0.35 42.5 3.0 Soluble ferric pyrophosphate 0.35 75.4 3.0 Soluble ferric citrate 0.53 113.1 3.0 Soluble ferric citrate 0.53 113.1 3.0 Soluble ferric citrate 0.66 124.1 3.0 Soluble ferric citrate 0.66 124.1

(1) Aluminum 2024T3 coupons tested in the manner described in USDA, Forest Service specification 5100-304b. Values obtained when the corrosion cell was maintained at 120°F (50°C) for 90 days with the coupon totally immersed therein. The data is expressed in milli-inches per year.

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The results indicate that both soluble ferric and ferrous iron containing salts show utility as aluminum corrosion inhibitors in ammonium polyphosphate solutions. Relatively small concentrations (0.35%) of soluble iron derived from a soluble ferric pyrophosphate decreased the corrosion rate of totally immersed aluminum exposed to 120°F solutions of the diluted fire retardant to within the USDA Forest Service Specification requirements. The data illustrate that soluble iron containing compounds are most effective in controlling the corrosivity of diluted solutions. Since the corrosivity of both the concentrate and its diluted solutions is of importance, mixtures of water soluble and water insoluble iron compounds generally provide superior performance.

EXAMPLE 5-CORROSION CHARACTERISTICS OF AMMONIUM POLYPHOSPHATE SOLUTIONS CONTAINING OTHER WATER INSOLUBLE IRON COMPOUNDS

Table 5 illustrates the effectiveness of water insoluble ferric orthophosphate, insoluble ferric pyrophosphate and ferrous oxalate as aluminum corrosion inhibitors in ammonium polyphosphate concentrates and their diluted solutions. 1.4% attapulgus clay was mixed with the concentrated ammonium polyphosphate, with the exception of Samples 6 and 7 which contained 0.7% and 2.8% attapulgus clay, respectively. Samples 13, 18 and 24 contained, also, an insoluble iron oxide as a solution colorant. The resultant fire retardant concentrates and their diluted solutions were evaluated in terms of aluminum corrosivity in accordance with the USDA Forest Service Specification requirements. The results of the testing are shown in Table 5.

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Table 5

	Ammonium	Iron (Iron Oxide Addition	Other It	Other Insal. Fe Additive	Total Fe.	Neat C	Neat Concentrate			Dilute	Diluted Solution		
	Polyphosphate					Content	70°5	70°F	120°F	120°F	₹.07	70°F	120°F	120°F
	Samples	%	Туре	8	Additive	(%)	Total	partial	total	Partia 1	total	partial	total	partial
П							Corros	ion Rate (1	Corrosion Rate (milli-inches per year	per year)				
_]	Neat 10-34-04	0.0	None	0.0	None	0.00	9.1	5.2	140.6	79.5	10.8	6.9	16.0	9.4
	Sample i	0.0	None	1.2	Pertic pyrophosphate	0.29			2.9				1.7	
	Sample 2	0.0	None	2.4	Pertic pyrophosphate	0.58			5.6				3.7	
Ļ	Sample 3	0.0	None	3.0	Pertic pyrophosphate	0.72			3.5				1.1	
[ٍ ا	Sample 4	0.0	Nane	3.0	Fertic ругораоврате	0.72			6.5				2.2	
Ĺ	Sample 5	0.0	None	9.0	Ferric pyrophosphate	0.72			2.1				1.4	L
	Sample 6	0.0	None	3.0	Ferric pyrophosphate	0.72			3.6				2.1	
_	Sample 7	0.0	None	3.0	Ferric pyrophosphate	0.72		L	1.0				1.7	
	Sample 8	0.0	None	2.4	Ferric pyrophosphate	0.58			10.7				1.0	
10	Sample 9	0.0	None	3.0	Ferric pyrophosphate	0.72			5,5				6,3	
]	Sample 10	0.0	None	3.0	Ferric pyrophosphate	0.72	2.4	L	6.2		3.1		7.	
12	Sample 11	0.0	None	3.0	Ferric pyrophosphate	0.72			3,4				1.3	L
-	Sample 12	0.0	None	3.0	Ferric pyrophosphate	0.72			3.2				2.2	
14	Sample 13th	1.2	Red Iron oxide	0:0	None	0.84	3.7	3.0	8.3	6.4	4.4	4.2	4.6	3.5
15	Sample 14	1.2	Red Iron oxide	3.0	Perric pyrophosphate	1.56	2.0	1.3	4.8	3.0	1.5	3.1	9.0	2.0
16	Sample 15	1.2	Red Iron oxide	3.0	Ferric pyrophosphate	1.56	1.6		6.2		1.6		1.0	
14	Sample 16	1.2	Red Iron oxide	3.0	Penic pyrophosphate	1.56	2.5		0.7		2.5		0.6	
8	Sample 17	1.2	Red Iron oxíde	3.0	Регііс ругорію врівате	1.56	1.9	1.2	0.5	0.2	1.1	2.4	8.0	1.9
61	Sample 18	1.2	Red Iron oxide	3.0	Ferric pyrophusphate	1.56	2.1		2.7		1.1		9.0	
20	Sample 19	0.0	None	1.2	Ferric orthophosphate	0.16			105.3	L			1.7	
::	Sample 20	0.0	None	1.8	Ferric orthophosphate	0.55		L	108.6				3.8	L
22	Sample 21	0.0	None	2.4	Ferric orthophosphate	0.73			9.3				4.1	
23	Sample 22	0.0	None	3.0	Ferric orthophosphate	0.92			2.3				4.2	L
4.7	Sample 23	1.2	Brown Iron oxide	3.0	Ferric orthophosphate	1.25			1.5				1.0	
25	Sample 24	0.0	None	1.2	Ferrous oxalate	0.37			0.06				2.7	L

Average values from Table 1.

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The corrosion inhibiting effectiveness of insoluble ferric pyrophosphate was shown by a comparison of the compositions containing only this component, lines 2-13, with line 1. The effectiveness was also shown by comparison with 1.2% red iron oxide, line 14. These comparisons illustrate the effectiveness of insoluble ferric pyrophosphate as an aluminum corrosion inhibitor for concentrated ammonium polyphosphate and its solutions. It was shown to be superior to red iron oxide when compared on an equal ferric iron level.

Accordingly, the insoluble ferric pyrophosphate would be preferred in many applications since it is not highly colored like the conventional iron oxides, which result in highly visible and persistent discoloration of that on which it is applied. Consequently, inhibitor systems containing these components would be suitable for use in fugitive colored fire retardant formulations.

Lines 15-19 illustrate the further reduction in aluminum corrosion, which was obtained by combining iron oxide and ferric pyrophosphate in the same corrosion inhibiting system. The results indicated that several of these formulations met the USDA, Forest Service Specifications for corrosivity of aluminum in both the concentrate and dilute forms.

The data contained in lines 20 and 23 illustrate the effectiveness of insoluble ferric orthophosphate in inhibiting the corrosion of aluminum exposed to ammonium polyphosphate solutions. The results indicated that the pyrophosphate moiety may be somewhat superior to orthophosphate for inhibiting the corrosion of aluminum.

The data contained in line 24 indicates that increasing the ferric iron content of the corrosion inhibiting system by using mixtures of ferric

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orthophosphate and iron oxide was also an effective way of meeting the USDA, Forest Service Specifications for corrosivity of aluminum.

The data contained in line 25 illustrates the aluminum corrosion inhibiting effectiveness of small amounts of ferrous (FeII) iron when incorporated in ammonium polyphosphate concentrates and their diluted solutions.

EXAMPLE 6-EFFECTIVENESS OF AZOLES AS CORROSION INHIBITORS IN AMMONIUM POLYPHOSPHATE FIRE RETARDANT COMPOSITIONS

Example 6 illustrates the effectiveness of azoles as yellow brass corrosion inhibitors in concentrated ammonium polyphosphate based fire retardant formulations and in their diluted solutions. Each sample was prepared by mixing 1.4% attapulgus clay, 1.2% red iron oxide and the indicated azole corrosion inhibitor with the neat, concentrated ammonium polyphosphate. Subsequently, the concentrates were diluted with water in the manner described herein. The samples were then tested in accordance with USDA Forest Service Specification requirements.

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THE IMPACT OF AZOLES ON THE CORROSION OF YELLOW BRASS EXPOSED TO CONCENTRATED AMMONIUM POLYPHOSPHATE AND ITS DILUTED SOLUTIONS.*

Table 6

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The results indicated that azoles, including both tolytriazoles and salts thereof, are effective corrosion inhibitors for yellow brass in ammonium polyphosphate concentrates and solutions. These data and others included in previous Examples illustrate the advantages of using azoles in conjunction with the iron containing inhibitors of this invention to reduce both aluminum and brass corrosivity of the fire retardant compositions to within desirable limits. EXAMPLE 7-THE IMPACT OF XANTHAN BIOPOLYMER ON 11-37-0 BASED

LIQUID CONCENTRATE RETARDANT FORMULATIONS

Table 7 illustrates the impact of xanthan (Keltrol BT®) on the viscosity and aluminum corrosion of ammonium polyphosphate fire retardant concentrates and their dilute solutions containing water soluble and water insoluble sources of iron, xanthan biopolymer having a particle size less than about 100 microns, additives and mixtures thereof, as indicated. The samples 15 were prepared by admixing 11-37-0 type ammonium polyphosphate solutions with various concentrations of attapulgus clay, tolytriazole, iron oxide, xanthan gum, insoluble ferric pyrophosphate and soluble ferric pyrophosphate or sodium citrate, as indicated. The solutions were subjected to high shear mixing in order to activate or hydrate the clay, where necessary. Dilution was accomplished by admixing five volumes of water with one volume of the concentrated 11-37-0 or compositions based thereon. All references to xanthan in Tables 7a and 7b refer to a commercial grade of xanthan, Keltrol BT®, which has an average particle diameter less than about 100 microns.

Each concentrate and diluted solution was tested for aluminum corrosivity in accordance with the Forest Service Specification protocols and the viscosity of

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each concentrate and diluted solution was tested by methods of testing viscosity that are well-known in the art. The results are shown in Tables 7a and 7b.

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No. Curronisms (see Section 100.0) Polyphosphate (100.0) y. Curronism (100.0) y. Curronism (100.0) orphiate (100.0) orphiate (100.0) iii (100.0)	8 8 99.0 99.0 11.0 11.0 100.0	C C 5 1.44 1.44 1.25 1.25 1.25 1.25 1.25 1.25 1.25 1.25	D E E 94.1 14.0 14.1 1.2 1.2 1.2 1.0 3.0 100.0 1	<u> </u>	P G G G G G G G G G G G G G G G G G G G	H H 90.1 1.4 0.3 1.2 1.2 1.2 1.0 3.0 3.0 0 100.0	1.4 1.4 0.3 0.3 0.3 1.2 4.3 4.3 1.7 1.00.0	50.1 1.4 0.3	Ж 97.5	L 94.5
han gim hint (inol) hint (sol) 100.0 100.0								90.1	97.5	94.5
100.0 100.								1.4	97.5	94.5
him genn Phate (msc) Phate (col) 100.0 66								0.3	ĺ	
than genn phate finel] phate feol) 100.0								0.3	_	
han gum Phate (sol) 100.0 100.0								-	0.3	0.3
than geam. Pulate (soil) 100.0 150.0 55	 							7.5	1.2	1.2
Plate (fine)] plate [60] 100.0								1.0	0,1	1.0
100.0 100.0				+++++	H + H + H			4.3		3.0
100.0										
100.0	1 1				-			1.7		
58 58				++				100.0	100.0	100.0
88 88	100			+	+					
63 63				H	Н					
63				L	Н					
89			191 22			L	238	226	18	95
			-	F		L	338	378	78	86
288	ľ		477 497	-	F	396	200	408	52	905
L	_			F	-	_	1020	1510	99	88
	_			_	┞	_				
m Corrosion (mpy)					L					
<55.0 6.7		1.1	2.6 0.6	6.0	L	0.7	9.0	8.0	7.2	2.0
3.6		9.0		H	4 0.5		9.0	9.0	3.9	1.2
<5.0 110.4	_		4.7 0.9	L	9.1	1.7	-	1.1	48.4	1.5
120P <5.0 70.5 6	68.9 (2	2.4	3.0 0.8	0.5	5.0.5	9.0	0.7	8.0	24.7	1.2
		_				L				
Dilute Solution (5:1 mix ratio)	_				L					
Viscosity (cps)*										
5		8	163 8	177	7 8	187		192	165	173
14 days	_		- 251	15	8 9	185			22.9	169
9	20	8	147 8	155		175		160	148	160
90 days 6		0	118 8	H	3 8		10	107	73	103
Almoston				-						
	_		1	-	-	-				
13.6	-	_	0.8	-	-	0.7	2.7	0.7	1.2	0.6
27.0 7.8	-	-		1.6	2.0	1.6	2.0	1.5	2.7	4.4
<2.0 3.2	-	_	0.7			9.0	0.9	0.7	8.0	8.0
<2.0 5.4	4.4	3.4	2.1 2.3	1.5	5 2.4		2.0	1.3	67	2.5

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			Table 7b	7b				
Formulation No.	Corrosion							
Components (wt.%)	Reqm'ts	M	z	0	д	ď	M	s
Ammonium Polyphasphate (conc.)		0.70	94.1	1.19	88.1	1.88	95.5	92.5
attapulgus clay			1.4	1.4	1.4	1.4		
tolytriazole			0.9	0.3	0.3	0.3	0.3	0.3
Tron nxide			1.2	1.2	1.2	1.2	1.2	1.2
Keltrol BT-yanthan gum		3.0	3.0	3.0	3.0	3.0	3.0	3.0
Ferric pyrophosphate (insol)				3.0	3.0	4.3		3.0
Ferric pyrophosphate (sol)					3.0			
Sodium citrate						1.7		
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0
Concentrate								
Viscosity (cps)*								
Initial		78	270	278	337	311	83	108
14 days		7.1	216	248	298	310	88	103
30 days		81	228	280	457	264	88	125
90 days		85	275	016	1010	2007	80	163
Aluminum Corrosion (mpy)								
70T	≤5.0	5.6	2.5	0.7	0.7	2.0	6.3	1.4
70P	_ 5.0	3.3	1.6	9.0	0.5	9.0	3.7	1.1
120T	5.0	95.9	1.1	0.7	9.0	0.7	25.4	1.2
120P	5.0	58.9	1.3	0.5	0.4	9.0	12.4	6.0
Dilute Solution (5:1 mix ratio)								
Viscosity (cps)*								
Initial		1010	0601	1050	1090	1050	1050	1090
14 days		096	1040	1030	1110	1010	1010	1050
30 days		266	1040	1010	1090	966	1010	1040
90 days		960	066	1000	1050	1040	960	1000
			i					
Aluminum Corrosion (mpy)								
70T	<2.0	9.5	1.5	0.8	0.8	6.0	1.4	0.7
70P	<2.0	6.1	2.5	1.6	1.7	1.7	2.3	1.4
120T	0.0	2.5	9.0	0.7	2.0	8.0	1.2	9.0
120P	22.0	3.2	1.3	1.2	6.0	1.1	1.8	1.3
	•							

* Samples stored at 90°F with steel coupon suspended therein. Sample homogenized prior to measuring viscosity

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The results indicate that in the absence of an iron containing corrosion inhibitor, the addition of 1.0% xanthan biopolymer has no significant effect on the corrosivity of either concentrated neat ammonium polyphosphate or its diluted solution. With reference to samples A and C, the results indicate that the addition of attapulgus clay, tolytriazole, and pigment grade iron oxide results in a dramatic reduction in the aluminum corrosivity of concentrated 11-37-0 and its diluted solutions.

With reference to samples C and D, the addition of 1.0% xanthan to 11-37-0 compositions containing attapulgus clay, tolytriazole and iron oxide further reduces the aluminum corrosivity of both the concentrated and diluted solutions. As indicated, the aluminum corrosivity of the concentrated solution is reduced to within the corrosion requirements of the specifications, but its diluted solutions, while reduced somewhat, are still marginally unacceptable.

With reference to samples E, G and I, the addition of 3.0% insoluble ferric pyrophosphate, 3.0% each of soluble and insoluble ferric pyrophosphate or a mixture of 4.3% insoluble ferric pyrophosphate, and 1.7% sodium citrate reduce the aluminum corrosivity of both the concentrated and diluted 11-37-0 solutions containing attapulgus clay and iron oxide to about the same degree as 1.0% xanthan.

With reference to samples F, H and J, the addition of 1.0% xanthan to the compositions of samples E, G and I, reduces the aluminum corrosivity of the resultant concentrate and diluted solutions to within the Forest Service Specifications in all testing conditions and situations.

The results also indicate that neat 11-37-0 ammonium polyphosphate concentrate, sample A, exhibits a viscosity of about 65 cps, while its diluted

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solution has a viscosity of 5-10 cps. The addition of 1.0% xanthan biopolymer to the concentrated 11-37-0 ammonium polyphosphate solution had no significant effect on viscosity. However, upon dilution the viscosity of the resultant solution was increased initially. The viscosity of the solution gradually decreased so that it was insignificantly different than the neat solution after a relatively short period of time.

Samples M through S illustrate the impact of increasing the concentration of xanthan biopolymer from 1.0% to 3.0% in the liquid fire retardant concentrate. The data indicate that the addition of 1.0% biopolymer to an iron containing ammonium polyphosphate composition results in a further reduction in aluminum corrosivity. However, increased concentrations of xanthan biopolymer do not appear to be more effective. Additional xanthan biopolymer does appear, however, to increase the viscosity of the dilute solution to within Forest Service Specifications.

15 With reference to sample M, the results indicate that 3.0% xanthan biopolymer may have a slight impact on both the viscosity and aluminum corrosivity of concentrated 11-37-0 ammonium polyphosphate compositions.

The diluted concentrate exhibits a stable viscosity in the range of 1000 cps, however, its aluminum corrosivity is only slightly reduced.

Samples K and R further indicate that the biopolymer has no significant impact on the viscosity of the concentrated product, but does reduce the aluminum corrosivity thereof by 50% when tested at elevated temperatures. With reference to samples L and S, the results indicate that Forest Service aluminum corrosion requirements can be met in formulations that do not include a suspending agent, such as attapulgus clay.

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With reference to samples H and P, the addition of soluble ferric pyrophosphate to formulations containing insoluble ferric polyphosphate and xanthan biopolymers does not further improve aluminum corrosivity.

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EXAMPLE 8-THE IMPACT OF XANTHAN BIOPOLYMERS WITH VARYING PARTICLE SIZING ON THE VISCOSITY OF LIQUID CONCENTRATE FIRE RETARDANTS

Table 8 illustrates the impact of xanthan biopolymers having various particle sizes on the rheological properties of ammonium polyphosphate fire retardant concentrates. The samples were prepared by admixing 3.0% of the xanthan biopolymers of various weight average particle size diameters, as indicated in Table 8, with concentrated ammonium polyphosphate type fire retardants. Dilution was accomplished by admixing five volumes of water with one volume of the concentrated fire retardant.

The viscosity of each dilute solution was tested by methods of testing viscosity that are well-known in the art. The rapid viscosity increase upon dilution (Diluted Viscosity – 10 minutes) was tested. The stable viscosity upon dilution (Diluted Viscosity – 30 days) was tested. The rapid viscosity increase of the solution after one-year (After 1 Year ((cps)) was tested. The stable viscosity of the solution after one-year (After 1 Year ((cps)) was tested. The results are shown below in Table 8.

TABLE 8 – PROPERTIES OF LIQUID CONCENTRATE FIRE RETARDANTS

THICKENED WITH XANTHAN BIOPOLYMER WITH VARYING PARTICLE
SIZING

		Diluted V	iscosity	Hydration Rate**	After 1 Ye	ar ()cps)
Xanthan Biopolymer	WT. Ave. Dia	10 Minutes	30 Days		10 Minutes	30 Days
Rhodigel SM®	31	1433	1447	99	-40	-40
Jungbunzlauer ST®	38	1493	1543	98	+10	-53
Keltrol BT®	70	1147	1197	96	+126	· +6
ADM 40 mesh	98	1070	1690	63	+337	+30
ADM dispersible	~105	250	1537	16	+897	+80
Kelzan® (uncoated)	110	433	547	79	NA	NA
Kelzan S [®] (coated)	150	120	463	26		-

^{** 10} minute viscosity as a % of maximum viscosity achieved.

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The results indicate that liquid concentrate fire retardant compositions comprising biopolymers having weight average particle diameters in the range of about 31 to about 70 microns exhibit ideal rheological properties. However, fire retardant concentrates comprised of biopolymers having particle diameters larger than about 100 microns do not exhibit desirable rheological properties.

EXAMPLE 9-THE IMPACT OF PARTICLE SIZING OF THE VISCOSITY OF BIOPOLYMERS IN LIQUID CONCENTRATE FIRE RETARDANTS

Table 9 illustrates the particle sizing and performance of several xanthantype biopolymers in comparison with standard hydroxypropyl guar gum in liquid
fire retardant concentrates. The samples were prepared by admixing 3.0%
xanthan type biopolymers or guar gum, as indicated below in Table 9, with
concentrated ammonium polyphosphate type fire retardants. Dilution was
accomplished by admixing about five volumes of water with one volume of each
dilute fire retardant composition.

The viscosity of each sample ammonium polyphosphate solution was tested by the methods described in Example 8. The results are shown in Table 9 below.

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TABLE 9 – IMPACT OF PARTICLE SIZING ON THE PERFORMANCE OF XANTHAN BIOPOLYMERS IN LIQUID CONCENTRATE SOLUTIONS

	Jungbunzlauer	e co	0.0	0.0	2.2	15.6	35.8	50.1	49.9	38				1493	1543		1503	
ADM	Dienereible	A O	15.1	36.2	75.7	84.2	6.88	61.6	8.1	~105				250	1537		1147	
[A]	40 mach	9 6	17.4	37.7	68.9	76.3	81.5	85.8	14.3	86	ļ			1070	1690		1407	
	2		_	0.0	2.2	5.5	14.7	28.7	71.8	31				1433	1447		1393	
	Kelzan S®	22.0	41.2	58.3	79.1	83.4	86.3	9.88	11.4	150				120	463		310*	100
	Kelzan	0.0	19.3	42.9	77.2	83.2	6.98	6.68	10.1	110				433	NA		NA	
	Kelmi RT®	00	0.6	18.9	56.1	65.1	71.1	76.5	23.6	70				1147	1197		1283	0000
	Guar Gum	To the same of the								>100				1597	63		~10	
	Sieve Opening	250	177	125	63	53	44	38	<38	meter (μ) age)		Diluted Solution Viscosity (cps)	intrate	ites		One-Year Old Concentrate	ites	
	Sieve	09	80	120	230	270	325	400	×400	Particle Diameter (µ) (weight average)	,	Diluted Solu	Fresh Concentrate	10 minutes	30 days	One-Year O	10 minutes	30 3
										 53								

* diluted 30 days after preparation of the concentrate

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The results indicate that fire retardant concentrates comprising xanthantype biopolymers in the range of about 31 to 70 microns exhibit ideal rheological
properties. However, fire retardant concentrates comprised of biopolymers having
particle diameters larger than about 100 microns do not exhibit desirable
rheological properties. Fire retardant concentrates comprising guar gum having a
particle size diameter greater than about 100 microns also fail to exhibit desirable
rheological properties. Specifically, ammonium polyphosphate based fire
retardant concentrates containing guar gum appear to have highly unstable
rheological characteristics, which make the use of guar gum undesirable in some
embodiments of the invention. Accordingly, in one embodiment of the invention
the compositions of the invention do not include guar gum.

EXAMPLE 10-THE IMPACT OF PARTICLE SIZING AND BIOPOLYMER TYPE ON THE VISCOSITY OF BIOPOLYMERS IN AMMONIUM POLYPHOSPHATE SOLUTIONS

Table 10 illustrates the particle sizing and performance of xanthan-type biopolymers with welan and rhamsan biopolymers in ammonium polyphosphate type liquid fire retardants. The samples were prepared by admixing about 91.1% concentrated liquid ammonium polyphosphate solution, 1.2% attapulgus clay, 0.3% tolytriazole, 3.0% insoluble ferric pyrophosphate and 3.0% of the biopolymer indicated in Tables 10a and 10b. The biopolymers used included Kelzan®, Kelzan S®, Keltrol BT®, Kelcorete®, and a rhamsan biopolymer, all of which are commercially available from CP Kelco, Wilmington, DE. Kelzan® is an uncoated, conventional xanthan biopolymer, while Kelzan S® is a conventional xanthan biopolymer with an applied surface coating. Keltrol BT® is a xanthan biopolymer having a particle size diameter less than about 100 microns. Kelcocrete is a welan type biopolymer.

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The viscosity of each concentrate were measured by methods described in Example 8. Then, each sample was diluted with water at a mix ratio of 5 volumes of water per volume of concentrate. The 10-minute and 18-hour viscosity of the diluted sample was measured and the samples were stored in a laboratory at a temperature of about 70°F-74°F for varying periods of time, rediluted and viscosity measured. The viscosity of each sample was measured at 10 minutes, 1 hour, 24 hours, 7 days, 15 days, 21 days and 28 days after dilution. The results are shown in Tables 10a and 10b below.

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Table 10a IMPACT OF PARTICLE SIZING AND BIOPOLYMER TYPE ON THE VISCOSITY OF AMMONIUM POLYPHOSPHATE TYPE FIRE RETARDANTS

Biopo	Biopolymer	Kelzan®	Kelzan S®	Keltrol BT®	Kelcocrete®	rhamsan
Concentra (C	Concentrate Viscosity (CPS)	196	198	189	195	199
Initial Dil	Initial Dilution (CPS)					
	10 min.	433	140	1100	630	570
	18. hrs.	430	170	1060	1100	790
24 hrs. aft	24 hrs. after Dilution					
Time after	10 min.	563	173	1093	543	500
preparation	18 hrs.	557	203	1093	1027	800
7 Days aft	7 Days after Dilution					
	10 min.	550	86	1040	576	507
	60 min.	555	150	1057	700	620
	24 hrs.	590	187	1057	1043	840

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Table 10b IMPACT OF PARTICLE SIZING AND BIOPOLYMER TYPE ON THE VISCOSITY OF AMMONIUM POLYPHOSPHATE TYPE FIRE RETARDANTS

Biopolymer	mer	Kelzan®	Kelzan S [®]	Keltrol BT®	Kelcocrete®	rhamsan
Concentrate Viscosity (CPS)	iscosity	196	198	189	195	199
Days afte	15 Days after Dilution					
1	10 min.	490	160	1047	440	467
Ŷ	60 min.	503	177	1077	617	550
2	24 hrs.	540	217	1103	1010	823
Days afte	21 Days after Dilution					
1	10 min.	710	243	1083	410	550
9	60 min.	747	247	1107	570	663
7	24 hrs.	687	397	1043	937	837
Days after	28 Days after Dilution					
1	10 min.	547	200	1043	937	837
9	60 min.	563	237	1063	650	710
2	24 hrs.	613	260	1057	1047	903

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The results indicate that welan and rhamsan type biopolymers thicken more slowly than xanthan type biopolymers but are effective at increasing the viscosity of ammonium polyphosphate type fire retardant solutions. Xanthan type biopolymers having a particle size diameter of less than about 100 microns, however, rapidly increase the viscosity of ammonium polyphosphate type fire retardants upon dilution. Conventional biopolymers, e.g. xanthan type biopolymers having particle size diameters greater than about 100 microns, fail to develop the viscosity of the fire retardants in a timely manner. Accordingly, both coated and uncoated conventional biopolymers are unsuitable for use in thickening ammonium polyphosphate type fire retardants. In addition, the long-term data, i.e. measured viscosity 7, 15, 21 and 28 days after preparation of the concentrated sample, indicate that there is no particular change in the performance of the various biopolymers during storage in ammonium polyphosphate based fire retardants.

EXAMPLE 11- IMPACT OF USE LEVELS OF BIOPOLYMERS AND IRON ADDITIVES ON THE VISCOSITY OF AMMONIUM POLYPHOSPHATE SOLUTIONS

The optimal use levels of mixtures of biopolymer and insoluble ferric pyrophosphate when used to reduce the aluminum corrosion level of liquid ammonium polyphosphate type fire retardants and their dilute solutions was analyzed. Formulations were prepared by using ammonium polyphosphate type fire retardants with attapulgus clay, tolytriazole, and in some cases, iron oxide. Biopolymers having average particle size diameters of less than 100 microns and insoluble ferric pyrophosphate were also added, where indicated. Each formulation was prepared by adding the dry components separately to the fire retardants and mixing them using a high shear mixer at approximately 1000 rpm

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over about a 2 hour period. The high shear was used to hydrate the clay and disperse the insoluble components. Dilute solutions were prepared by admixing 1 part concentrate with 5 parts tap water. The concentrate formulations and their dilute solutions were tested in accordance with all four of the test conditions prescribed by the U.S. Forest Service Specifications, described herein. The results are shown below in Tables 11a, 11b and 11c.

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15.0 8228 96.25 1.40 0.30 95.50 1.40 0.30 15 33 50 53 3.00 1.00 100.00 1.00 150 193 273 1010 0.75 3.00 100.00 160 198 285 1310 94.55 1.40 0.30 23 85 85 23 85 85 15.3 95.55 1.40 0.30 145 256 438 1360 365 390 1010 2 8 8 2 0.50 3.00 100.00 94.80 1.40 0.30 0.50 2.00 100.00 95.80 1.40 0.30 1.00 3.00 193 421 430 1850 4.8 2.6 112.4 69.4 100.00 14.5 Dilute solution (5:1 mtx ratio)
Refractive index
Viscosity (cps)*
Influid
14 days
30 days Formulation Components (wt. Ammonium Polyphosphate
Amtenigus day
Tolyteirasole
Iron Oxide (Red)
Renc Oxide (Red)
Redroi BT
Redroi BT
Ferric Pyrophosphate (Insol.)

'Samples stored at 90°F with steel coupon suspended therein. Samples homogenized prior to measuring viscosity

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					Lable	Table LID								
Companson of 0.5, 0.75, and 1.0% Keltrol BT	0% Kelt	rol BT									Γ			
Formulation Components (wt. %)	C	£	I	Т	z	Q	G	1	×	0	В	ш	н	M
Ammonium Polyphosphate	96.80	96.55	96.30	96.50	96.25	95.80	95.55	95.30	95.50	95.25	93.1	94.80	94.55	94.30
Attapulgus clay	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.4	1.40	1.40	1.40
Tolyltriazole	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.3	0.30	0.30	0.30
Iron Oxide (Red)		,	,							,	1.2	,	,	
Iron Oxide (Brown)	_		,	0.30	08.0	,	,		0.30	0.30				
Keltrol BT	0.50	0.75	1.00	0.50	0.75	0.50	0.75	1.00	0.50	0.75	1.00	0.50	0.75	1.00
Ferric Pyrophosphate (Insol.)	1.00	1.00	1.00	1.00	1.00	2.00	2.00	2.00	2.00	2.00	3.00	3.00	3.00	3.00
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.001	100.0	100.0	100.0	100.0
Concentrate														
Viscosity (cps)*														
Initial	148	150	150	168	161	161	145	166	156	173	193	157	160	167
14 days	363	365	193	210	175	173	256	208	168	220	421	218	198	187
30 days	390	990	273	305	308	205	433	325	418	345	430	230	285	373
90 days	1940	1010	1010	006	1000	750	1360	860	1430	1050	1850	1150	1310	1390
늴														
70T ≤5.0	9.6	3.8	9.6	2.9	2.7	6.0	1.0	.3	1.2	0.1	4.0	9.0	9.0	6.0
	1.7	2.0	1.9	1.6	1.4	9.0	8.0	6.0	0.7	0.7	9.0	9.0	0.5	0.7
120T ≤5.0	18.9	15.2	9.11	7.1	5.3	1.2	Ξ	1.5	1.2	6.0	0.7	1.0	6.0	1:1
120P ≤5.0	43.9	16.2	46.4	3.7	2.8	8.0	6.0	6.0	0.7	6.0	6.0	9.0	9.0	8.0
Dilute solution (5:1 mix ratio)														
Refractive Index	14.6	15.4	15.0	15.0	15.0	15.0	15.4	15.6	14.9	15.0	14.5	15.4	15.3	15.4
Viscosity (cps)*						_								Γ
Initial	20	105	153	23	100	20	86	172	25	103	146	23	100	159
14 days	30	82	138	20	16	43	8/	155	45	- 26	130	40	85	143
30 days	31	8	125	33	7.8	37	80	145	61	62	132	33	\$4	126
90 days	18	23	28	15	2.8	13	43	20	15	53	96	19	23	9
												_		
70T <2.0	1.3	1.4	1.2	1.2	1.5	1.0	1.1	8.0	1.3	1.0	0.7	1.0	0.8	9.0
	3.9	3.5	3.6	3.2	3.3	3.1	3.3	5.9	3.1	2.8	1.9	9.0	2.9	2.4
ŀ	6.0	8.0	0.7	1.2	0.7	9.0	0.7	0.5	1.3	0.5	8.0	9.0	0.4	0.7
120P ≤2.0	1.7	02) 	2.4	1.9	2.1	2.3	2.5	1.7	2.6	2.0	1.5	2.2	1.6	1.2
*Samples stored at 90°F with steel coupon suspended therein. Samples homogenized prior to measuring viscosity.	at 90°F	with ste	odnoo je	n susper	ded the	rein. Sa	mples h	mogen	zed prio	r to mea	Suring v	iscosity		

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Formulation Components (wt. %)		-	Companion of 1.0, 2.0, 6.0% inschance refric Pyrophosphate	hatc								_		
	υ	Α	ш	Ļ	×	ĮĽ,	ď	Ξ	Z	0	м	-	_	×
nmonium Polyphosphate	96.80	95.80	94.80	96.50	95.50	96.55	95.55	94.55	96.25	95.25	93.1	96.30	95,30	94.30
Attapulgus clay	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.4	1.40	1.40	1.40
Tolyltriazole	0.30	0.30	0.30	0.30	0.30	0.80	0.30	0.30	0.30	0.30	0.3	0.30	0.30	0.30
fron Oxide (Red)	,		,		,		,	,		,	1.2		,	
ron Oxide (Brown)				0.30	0.30		,	,	0.30	0.30	,	,	,	
Keltrol BT	0.50	0.50	0.50	0.50	0.50	0.75	0.75	0.75	0.75	0.75	1.00	1.00	1.00	1.00
Ferric Pyrophosphate (Insol.)	-	2.00	3.00	1.00	2.00	1.00	2.00	3.00	1.00	2.00	3.00	1.00	2.00	3.00
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.001	100.0	100.0
Concentrate														
Viscosity (cps)*														
Unitial	148	161	157	168	156	150	145	160	161	173	193	150	166	167
14 days	363	173	218	210	168	365	256	198	175	220	421	193	208	187
30 days	390	205	230	305	418	390	433	285	308	345	430	273	325	373
90 days	1940	750	1150	900	1430	1010	1360	1310	1000	1050	1850	1010	860	1390
Aluminum Corrosion (mpy)														
	3.6	6.0	9.0	2.9	1.2	3.8	1.0	9.0	2.7	0.1	0.4	3.6	1.3	6.0
70P <5.0	1.7	9.0	0.5	1.6	0.7	2.0	8.0	0.5	1.4	0.7	0.5	1.9	6.0	0.7
	18.9	1.2	1.0	7.1	1.2	15.2	1.1	6.0	5.3	6.0	0.7	11.9	1.5	Ξ
120P <5.0	43.9	8.0	9.0	3.7	0.7	16.2	6.0	9.0	2.8	0.5	0.5	46.4	6.0	9.0
Dilute solution (5:1 mfx ratio)														
Refractive Index	14.6	15.0	15.4	15.0	14.9	15.4	15.4	15.3	15.0	15.0	14.5	15.0	15.6	15.4
Viscosity (cps)*														
Initial	20	20	53	23	- 25	105	86	100	109	103	146	153	172	159
14 days	30	£	40	20	45	85	78	82	91	- 26	130	138	155	143
30 days	31	37	33	33	61	90	80	25	73	62	132	125	145	126
90 days	18	13	19	15	15	23	43	23	23	29	90	28	7.0	40
3														
1	1.3	1.0	1.0	1.2	1.3	1.4	1.1	8.0	1.5	1.0	2.0	1.2	8.0	8.0
	3.9	3.1	9.0	3.2	3.1	3.5	3.3	2.9	3.3	2.8	1.9	9.6	5.9	2.4
- 1	6.0	9.0	0.0	1.2	1.3	8.0	0.7	9.4	0.7	0.5	0.8	0.7	0.5	0.7
120P ≤2.0	1.7	2.3	2.2	6.1	5.6	8:7	2.5	1.6	2.1	2.0	1.5	2.4	1.7	1.2

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The results indicate that the incorporation of some iron oxide within fire retardant concentrates and solutions of the present inventions is necessary to meet U.S. Forest Service Specification requirements. Fire retardant concentrates that include 1.2% iron oxide, 3% ferric pyrophosphate and 1% biopolymer, and their diluted solutions meet the U.S. Forest Service Specification requirements. The viscosity of the fire retardant concentrates containing 1% biopolymer gradually increased from about 150 to 200 cps immediately after manufacture to 1000 to 2000 cps. After three months of storage at 90°F, and upon dilution, the solution viscosity was in the range of 100 to 200 cps.

In view of the above, it is seen that the various objects and features of the invention are achieved and other advantages and results are obtained. Variations and modification may be made to the various steps and compositions of the invention without departing from the scope of the invention.

With reference to the use of the word(s) "comprise" or "comprises" or "comprising" in the foregoing description and/or in the following claims, unless the context requires otherwise, those words are used on the basis and clear understanding that they are to be interpreted inclusively, rather than exclusively, and that each of those words is to be so interpreted in construing the foregoing description and/or the following claims.

The claims defining the invention are as follows:

1. A corrosion-inhibited fire retardant composition comprising:

at least one fire retardant comprised of at least one ammonium polyphosphate;

at least one biopolymer having a particle size diameter less than about 100 microns; and

a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from the group consisting of at least one azole, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof;

wherein said corrosion inhibiting system is present in a minor amount effective to substantially reduce corrosiveness of said fire retardant composition.

- 2. The composition of claim I wherein said corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound.
- 3. The composition of claim 1 or 2 further comprising at least one additive selected from the group consisting of suspending agents, coloring agents, surfactants, stabilizers, corrosion inhibitors, opacifying pigments and any combination thereof.
- 4. The composition of claim 3 wherein said coloring agent is selected from the group of coloring agents consisting of fugitive coloring agents, opacifying pigments, and highly colored coloring agents.

- 5. The composition of claim 3 wherein said suspending agent is selected from the group of suspending agents consisting of attapulgus, sepiolite, fuller's earth, montmorillonite, and kaolin clay.
- 6. The composition of any one of claims 1 to 5 wherein said azole is selected from the group consisting of tolytriazole, benzotriazole, mercaptobenzothiazole, dimercaptothiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof.
- 7. The composition of any one of claims 1 to 5 wherein said corrosion inhibiting compound is at least one azole and said azole is present in said corrosion-inhibited fire retardant composition, in concentrate, in a minor amount effective to obtain a maximum corrosivity of yellow brass to a maximum of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 8. The composition of any one of claims 1 to 5 wherein said corrosion inhibiting system is present in a minor amount effective in said corrosion-inhibited fire retardant composition, in concentrate, to obtain at least one of a maximum corrosivity to aluminum of 5.0 mils per year, yellow brass of 5.0 mils per year, and steel of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 9. The composition of any one of claims 1 to 6 wherein said corrosion inhibiting system comprises in the range of about .01% to about 10% of said corrosion-inhibited fire retardant composition.

- The composition of any one of claims 1 to 6 wherein said corrosion inhibiting system comprises in the range of about .30% to about 6.0% of said corrosion-inhibited fire retardant composition.
- 11. The composition of any one of claims 1 to 6 wherein said corrosion inhibiting system comprises in the range of about 0.6% to about 5.0% of said corrosion-inhibited fire retardant composition.
- 12. The composition of any one of claims 1 to 11 comprising in the range of about .01% to about 5.0% said biopolymer.
- 13. The composition of any one of claims 1 to 11 comprising in the range of about 1.0% said biopolymer.
- 14. The composition of any one of claims 1 to 13 wherein said biopolymer is at least one biopolymer selected from the group of biopolymers consisting of rhamsan, xanthan and welan biopolymers.
- 15. The composition of claim 14 wherein said biopolymer is at least one xanthan biopolymer.
- 16. The composition of claim 15 wherein said xanthan biopolymer comprises about 1% of said corrosion-inhibited fire retardant composition.
- 17. The composition of any one of claims 1 to 16 further comprising at least one guar biopolymer.
- The composition of any one of claims 1 to 17 comprising in the range of about 2% to about 3% ferric pyrophosphate.
- The composition of claim 18 comprising in the range of about 2% to about 3% 19. ferric pyrophosphate and about 1% xanthan biopolymer.

- 20. The composition of claim 18 comprising in the range of about 1% to about 2% iron oxide, about 2% to about 3% ferric pyrophosphate, about 1% xanthan biopolymer, about 1% to about 2% attapulgus clay, and about .01% to about 1% tolytriazole.
- 21. The composition of any one of claims 1 to 20 further comprising water.
- A corrosion-inhibited fire retardant composition comprising:
 at least one fire retardant comprised of at least one ammonium polyphosphate;

attapulgus clay;

at least one xanthan biopolymer having a particle size less than about 100 microns;

at least one additive selected from the group consisting of suspending agents, coloring agents, surfactants, stabilizers, corrosion inhibitors, opacifying pigments and any combination thereof; and

a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from the group consisting of at least one azole, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof;

wherein said corrosion inhibiting system is present in a minor amount effective to reduce corrosiveness of said ammonium polyphosphate to a maximum corrosivity to aluminum of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground

Application," issued by the United States Department of Agriculture, Forest Service; and

wherein said biopolymer comprises in the range of about 0.01% to about 5.0% of said fire retardant composition.

- 23. A method of preparing a corrosion-inhibited fire retardant composition, adapted for aerial application to wildland fires, the method comprising the steps of:
 - forming an intermediate concentrate composition comprising:
 - a fire retardant composition comprised of at least one ammonium polyphosphate;
 - a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from the group of corrosion inhibiting compounds consisting of at least one azole, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof; and
 - (iii) at least one biopolymer having a particle size less than about 100 microns;

wherein said corrosion inhibiting system is present in a minor amount effective to substantially reduce corrosiveness of said fire retardant composition; and

- diluting said intermediate concentrate with water to form said corrosion-inhibited fire retardant composition.
- 24. The method of claim 23 wherein said corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound.

- 25. The method of claim 23 or 24 wherein said intermediate concentrate composition further comprises at least one additive selected from the group consisting of suspending agents, coloring agents, surfactants, stabilizers, corrosion inhibitors, opacifying pigments and any combination thereof.
- 26. The method of claim 25 wherein said coloring agent is selected from the group consisting of fugitive coloring agents, opacifying pigments, and highly colored coloring agents.
- 27. The method of claim 25 wherein said suspending agent selected from the group consisting of attapulgus clay, sepiolite, fuller's earth, montmorillonite, and kaolin clay.
- 28. The method of any one of claims 23 to 27 wherein said azole is selected from the group consisting of tolytriazole, benzotriazole, mercaptobenzothiazole, dimercaptomthiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof.
- 29. The method of any one of claims 23 to 28 wherein said corrosion inhibiting system comprises at least one azole and said azole is present in said corrosion-inhibited fire retardant composition, in concentrate, in a minor amount effective to obtain a maximum corrosivity to yellow brass of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 30. The method of any one of claims 23 to 28 wherein said corrosion inhibiting system is present in a minor amount effective to reduce the corrosiveness of said fire retardant composition, in concentrate, to at least one of a maximum corrosivity to aluminum of 5.0 mils per year, brass of 5.0 mils per year and steel of 5.0 mils per

year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.

- 31. The method of any one of claims 23 to 28 wherein said intermediate concentrate composition is diluted such that a maximum corrosivity of aluminum is 2.0 mils per year and the maximum corrosivity of brass and steel is 2.0 mils per year when tested in the totally immersed condition and 5.0 mils per year when tested in the partially immersed condition, as specified and determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 32. The method of any one of claims 23 to 28 wherein said fire retardant composition comprises in the range of about .01% to about 5.0% said biopolymer.
- 33. The method of any one of claims 23 to 28 wherein said fire retardant composition comprises in the range of about 1.0% said biopolymer.
- 34. The method of any one of claims 23 to 33 wherein said biopolymer is at least one biopolymer selected from the group consisting of a xanthan rhamsan and welan biopolymers.
- 35. The method of claim 34 wherein said biopolymer is a xanthan biopolymer.
- 36. The method of claim 35 wherein said xanthan biopolymer comprises about 1% of said corrosion-inhibited fire retardant composition.
- 37. The method of any one of claims 23 to 36 wherein said fire retardant composition further comprises at least one guar biopolymer.

- 38. The method of any one of claims 23 to 37 wherein said intermediate concentrate comprises in the range of about 2% to about 3% ferric pyrophosphate.
- 39. The method of claim 38 wherein said intermediate concentrate comprises in the range of about 2% to about 3% ferric pyrophosphate and about 1% xanthan biopolymer.
- 40. The method of claim 38 wherein said intermediate concentrate comprises in the range of about 1% to about 2% iron oxide, about 2% to about 3% ferric pyrophosphate, about 1% xanthan biopolymer, about 2% attapulgus clay, and about .01% to about 1% tolytriazole.
- 41. A method of preparing a corrosion-inhibited fire retardant composition, adapted for aerial application to wildland fires, the method comprising the steps of:
 - (a) forming an intermediate concentrate composition comprising:
 - at least one fire retardant comprised of at least one ammonium polyphosphate;
 - (ii) attapulgus clay;
 - (iii) a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from the group consisting of at least one azole, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, insoluble ferrous oxalate, soluble ferric citrate, soluble ferrous sulfate, insoluble ferric ammonium citrate, insoluble ferric orthophosphate, soluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof; and

(iv) at least one xanthan biopolymer having a particle size of less than about 100 microns;

wherein said corrosion inhibiting system is present in a minor amount effective to reduce the corrosiveness of said fire retardant composition, in concentrate, to aluminum of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service; and wherein said fire retardant composition comprises in the range of about .01% to about 5.0% said xanthan biopolymer prior to dilution; and

- (b) diluting said intermediate concentrate with water to form said corrosion-inhibited fire retardant composition such that a maximum corrosivity of aluminum is 2.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 42. A method of suppressing wildland fires comprising aerially applying to wildland vegetation a fire suppressing composition, wherein the fire suppressing composition comprises:

water; and

a corrosion-inhibited fire retardant composition comprising:

at least one fire retardant composition comprised of at least one ammonium polyphosphate;

at least one biopolymer having a particle size of less than about 100 microns; and

a corrosion inhibiting system comprising at least one corrosion inhibiting compound selected from the group consisting of at least one azole, insoluble ferric pyrophosphate, soluble ferric pyrophosphate,

ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate, and any combination thereof;

wherein said corrosion inhibiting system is present in a minor amount effective to substantially reduce the corrosiveness of said fire retardant composition.

- 43. The method of claim 42 wherein said corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound.
- 44. The method of claim 42 or 43 further comprising at least one additive selected from the group consisting of suspending agents, coloring agents, surfactants, stabilizers, corrosion inhibitors, opacifying pigments, and any combination thereof.
- 45. The method of claim 44 wherein said coloring agent is selected from the group consisting of fugitive coloring agents, opacifying pigments and highly colored colorants.
- 46. The method of claim 44 wherein said suspending agent is selected from the group consisting of attapulgus clay, sepiolite, fuller's earth, montmorillonite, and kaolin clay.
- 47. The method of any one of claims 42 to 46 wherein said azole is selected from the group consisting of tolytriazole, benzotriazole, mercaptobenzothiazole, dimercaptomthiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof.

- 48. The method of any one of claims 42 to 47 wherein said corrosion inhibitor is at least one azole and said azole is present in said corrosion-inhibited fire retardant composition, in concentrate, in a minor amount effective to obtain a corrosivity to yellow brass of a maximum of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 49. The method of any one of claims 42 to 47 wherein said corrosion inhibiting system is present in a minor amount effective to reduce the corrosiveness of said fire retardant composition, in concentrate, to at least one of a maximum corrosivity to aluminum of 5.0 mils per year, brass of 5.0 mils per year, and steel of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.
- 50. The method of any one of claims 42 to 47 wherein said corrosion inhibiting system comprises in the range of about .01% to about 10.0% of said corrosion-inhibited fire retardant composition.
- 51. The method of any one of claims 42 to 47 wherein said corrosion inhibiting system comprises in the range of about .30% to about 6.0% of said corrosion-inhibited fire retardant composition.
- 52. The method of any one of claims 42 to 47 wherein said corrosion inhibiting system comprises in the range of about .60% to about 5.0% of said corrosion-inhibited fire retardant composition.

- 53. The method of any one of claims 42 to 52 wherein said corrosion-inhibited fire retardant composition comprises in the range of about .01% to about 5.0% said biopolymer.
- 54. The method of any one of claims 42 to 52 wherein said corrosion-inhibited fire retardant composition comprises in the range of about 1.0% said biopolymer.
- 55. The method of any one of claims 42 to 54 wherein said biopolymer is selected from the group consisting of xanthan, rhamsan and welan biopolymers.
- The method of claim 55 wherein said biopolymer is a xanthan biopolymer. 56.
- 57. The method of claim 56 wherein said xanthan biopolymer comprises about 1% said corrosion-inhibited fire retardant composition.
- 58. The method of any one of claims 42 to 57 wherein said corrosion-inhibited fire retardant composition further comprises at least one guar biopolymer.
- 59. The method of any one of claims 42 to 58 wherein said fire suppressing composition comprises in the range of about 2% to about 3% ferric pyrophosphate.
- The method of claim 59 wherein said fire suppressing composition comprises 60. in the range of about 2% to about 3% ferric pyrophosphate and about 1% biopolymer.
- 61. The method of claim 59 wherein said fire suppressing composition comprises in the range of about 1% to about 2% iron oxide, about 2% to about 3% ferric pyrophosphate, about 1% xanthan biopolymer, about 2% attapulgus clay, and about .01% to about 1% tolytriazole.
- A method of suppressing wildland fires comprising aerially applying to wildland vegetation a fire suppressing composition, wherein the fire suppressing composition comprises:

water; and

a corrosion-inhibited polyphosphate composition comprising:

at least one ammonium polyphosphate;

attapulgus clay;

in the range of about .01% to about 5.0% at least one xanthan gum having a particle size less than 100 microns;

at least one additive selected from the group of consisting of coloring agents, surfactants, stabilizers, corrosion inhibitors, and any combination thereof; and

a corrosion inhibiting system comprised of at least one corrosion inhibiting compound selected from the group consisting of insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate and any combination thereof;

wherein said corrosion inhibiting system is present in a minor amount effective to reduce corrosiveness to said ammonium polyphosphate, in concentrate, to a maximum corrosivity to aluminum of 5.0 mils per year, as determined by the "Uniform Corrosion" test set forth in Section 4.5.6.1 of "Specification 5100-304b (January 2000) Superseding Specification 5100-00304a (February 1986)," entitled "Specification for Long Term Retardant, Wildland Fire, Aircraft or Ground Application," issued by the United States Department of Agriculture, Forest Service.

63. A method of reducing the corrosivity of a fire retardant to a corrodible material, wherein the fire retardant comprises at least one ammonium polyphosphate and the corrodible material is selected from the group consisting of steel, brass, aluminum, and any alloy thereof, the method comprising including in the fire retardant an effective amount of a corrosion inhibiting system comprised of at least

one corrosion inhibiting compound selected from the group consisting of at least one azole, insoluble ferric pyrophosphate, soluble ferric pyrophosphate, ferrous oxalate, ferric citrate, ferrous sulfate, ferric ammonium citrate, soluble ferric orthophosphate, insoluble ferric orthophosphate, ferric ammonium oxalate, ferric ammonium sulfate, ferric bromide, ferric sodium oxalate, ferric stearate, ferric sulfate, ferrous acetate, ferrous ammonium sulfate, ferrous bromide, ferrous gluconate, ferrous iodide, ferric acetate, ferric fluoroborate, ferric hydroxide, ferric oleate, ferrous fumarate, ferrous oxide, ferric lactate, ferric resinate and any combination thereof.

- 64. The method of claim 63 wherein said corrosion inhibiting system is comprised of at least one soluble corrosion inhibiting compound and at least one insoluble corrosion inhibiting compound.
- 65. The method of claim 63 or 64 wherein said fire retardant further comprises at least one additive selected from the group consisting of suspending agents, coloring agents, opacifying pigments, surfactants, stabilizers, corrosion inhibitors, and any combination thereof.
- 66. The method of claim 65 wherein said suspending agent is selected from the group consisting of attapulgus clay, Fuller's earth, montmorillonite, sepiolite and kaolin clay.
- 67. The method of any one of claims 63 to 66 wherein said at least one azole is selected from the group consisting of tolytriazole, benzotriazole, mercaptobenzothiazole, dimercaptomthiadiazole, 1,2 benzisothiazoline-3-1, 2-benzimidazolone, 4,5,6,7-tetrahydrobenzotriazole, tolylimidazole, 2-(5-ethyl-2-pyridyl) benzimidazole, phthalimide, any alkali metal salts thereof and combinations thereof.
- 68. The method of any one of claims 63 to 67 wherein said fire retardant further comprises at least one biopolymer having a particle size less than about 100 microns.

- 69. The method of claim 68 wherein said biopolymer is at a concentration that is in the range of about .01% to about 5.0% of said fire retardant.
- 70. The method of claim 69 wherein the concentration of the biopolymer is about 1.0% of said fire retardant.
- 71. The method of any one of claims 68 to 70 wherein said biopolymer is selected from the group consisting of xanthan, rhamsan and welan biopolymers.
- 72. The method of claim 71 wherein said biopolymer is a xanthan biopolymer.
- 73. The method of claim 72 wherein said xanthan biopolymer is at a concentration that is about 1% of said fire retardant.
- 74. The method of any one of claims 68 to 73 wherein the fire retardant does not comprise guar gum.
- 75. The method of any one of claims 63 to 74 wherein said fire retardant comprises in the range of about 2% to about 3% ferric pyrophosphate.
- 76. The method of claim 75 wherein said fire retardant comprises in the range of about 2% to about 3% ferric pyrophosphate and further comprises about 1% xanthan biopolymer.
- 77. The method of claim 75 wherein said fire retardant comprises about 1% to about 2% iron oxide, about 2% to about 3% ferric pyrophosphate, and about .01% to about 1% tolytriazole, and further comprises about 1% xanthan biopolymer, and about 1% to about 2% attapulgus clay.
- 78. The method of any one of claims 63 to 77 wherein said fire retardant further comprises water.

79. A method of reducing the corrosivity of a fire retardant to a corrodible material, wherein the fire retardant comprises at least one ammonium polyphosphate and the corrodible material is selected from the group consisting of steel, brass, aluminum, and any alloy thereof, the method comprising adding to the fire retardant an amount in the range of about .01% to about 5.0% of at least one xanthan gum having a particle size less than 100 microns and an effective amount of a corrosion inhibiting system comprised of ferric pyrophosphate.

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