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(57) **Abrégé/Abstract:**

This invention relates to fire retardant compositions and methods of preparing fire retardant compositions consisting of water and a fire retardant, the fire retardant being a salt of thiosulfuric acid which decomposes at flame temperature in an amount effective to retard wildland fires. In the preferred embodiment, the salt of thiosulfuric acid is ammonium thiosulfate. The fire retardant composition may also include desired components such as corrosion inhibitors, suspending agents, coloring agents, antimicrobials, and stabilizers.



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(21) International Application Number: PCT/US98/11271 (22) International Filing Date: 2 June 1998 (02.06.98) (30) Priority Data: 08/931,907 3 June 1997 (03.06.97) US (71) Applicant (for all designated States except US): CHEMONICS FIRE-TROL, INC. [US/US]; 734 E. Southern Pacific Drive, Phoenix, AZ 85034 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): CROUCH, Robert, L. [US/US]; 1607 W. Frier Drive, Phoenix, AZ 85021 (US). (74) Agents: DRUMMOND, William, H. et al.; Drummond & Duckworth, Suite 500, 4590 MacArthur Boulevard, Newport Beach, CA 92660 (US).		(81) Designated States: AU, CA, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FIRE RETARDANTS AND METHODS OF MANUFACTURE AND USE THEREOF (57) Abstract This invention relates to fire retardant compositions and methods of preparing fire retardant compositions consisting of water and a fire retardant, the fire retardant being a salt of thiosulfuric acid which decomposes at flame temperature in an amount effective to retard wildland fires. In the preferred embodiment, the salt of thiosulfuric acid is ammonium thiosulfate. The fire retardant composition may also include desired components such as corrosion inhibitors, suspending agents, coloring agents, antimicrobials, and stabilizers.		

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FIRE RETARDANTS AND METHODS
OF MANUFACTURE AND USE THEREOF

This invention relates to chemical fire retardant compositions.

In another respect, the invention pertains to methods of manufacture of such
5 compositions.

In still another respect, the invention concerns methods of using such
compositions for extinguishing and/or retarding the spread of wildfires.

In a further aspect, the invention relates to chemical concentrates adapted for
dilution with water to produce long term fire retardant.

10 In still other respects, the invention concerns compositions and methods of
production in which various components such as corrosion inhibitors, rheological
modifying agents, suspending agents, antimicrobials, stabilizers and coloring agents
are maintained in suspension in the concentrate liquid and, upon dilution, produces
the fire retardant composition.

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Controlling and extinguishing wildland fires with chemical compositions generally involves applying a liquid or foam fire retardant or suppressant composition from a helicopter, fixed-wing aircraft or ground vehicle to timber or other wildland foliage to either form a chemical fire break in front of an oncoming fire, or applying the chemical compositions directly to the burning foliage itself to extinguish the fire.

Chemical compositions employed as fire retardants in such fire control methods ordinarily comprise aqueous mixtures containing between about 5% and about 20% by weight of a fire retardant salt. The remainder of the composition comprises, a liquid carrier, and optionally, various functional additives which improve specific characteristics of the composition. These functional additives may include, e.g., rheological modifying agents (to improve the aerial drop and coverage characteristics), corrosion inhibitors (to reduce the corrosivity of the compositions to metal components of storage and application equipment), coloring agents (to allow identification of treated areas), stabilizing agents (to prevent separation of the various components of the composition during storage and transport), antimicrobial agents (to prevent microbial decomposition of certain components), etc.

Generally, the fire retardant component of the fire retardant composition is a salt that produces a mineral acid when heated. Common retardant salts are monoammonium orthophosphate, diammonium orthophosphate, monoammonium

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pyrophosphate, diammonium pyrophosphate, triammonium pyrophosphate, tetrammonium pyrophosphate, ammonium polyphosphate, substituted ammonium polyphosphate, amide polyphosphate, melamine polyphosphate, ammonium-alkali metal mixed salts of orthophosphate, ammonium-alkali metal mixed salts of
5 pyrophosphate, ammonium-alkali metal mixed salts of polyphosphate, ammonium-alkaline earth metal mixed salts of orthophosphate, ammonium-alkaline earth metal mixed salts of pyrophosphate, ammonium-alkaline earth metal mixed salts of polyphosphate, ammonium sulfate and blends thereof. These and other fire retardant salts and compositions containing them are discussed in U.S. Patent Nos.
10 3,196,108 (Nelson); 3,730,890 (Nelson); 3,960,735 (Lacey); 4,168,239 (Mertz); 4,176,071 (Crouch); 3,634,234 (Morgenthaler); 3,257,316 (Langguth); 4,822,524 (Strickland); 4,447,336 (Vandersall); and 4,839,065 (Vandersall).

When such fire retardants are used to extinguish or retard the spread of a wildland fire, the retardant and the wildland foliage coated by the retardant are
15 heated by flames. It is believed that as the typical retardant salt is heated, ammonia is released, leaving the mineral acid corresponding to the anion portion of the salt on the wildland foliage. Thus, typical fire retardants are salts that release phosphoric acid or sulfuric acid below the ignition temperature of the cellulose of the wildland foliage.

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Fire retardant salts of the prior art are corrosive to the metal parts of storage, mixing and application equipment. For example, ammonium phosphates, ammonium polyphosphates and related fire retardant salts are highly corrosive to aluminum, a principal structural component of aircraft vehicles used to aially
5 apply such retardants. Other known fire retardant salts such as ammonium sulfate are corrosive to certain metallic parts such as the steel and brass parts of storage and handling equipment for mixing and loading the fire retardant compositions aboard application vehicles. Accordingly, fire retardant mixtures typically include a corrosion inhibitor. Commonly used corrosion inhibitors include 2,5
10 dimercaptiothiadiazole (DMTD), sodium hexacyanoferrate (II), sodium silicofluoride, sodium dichromate, chromic acid and sodium thiosulfate. Some of these corrosion inhibitors are toxic. Some may impart undesirable color to the fire retardants and, in any event, the use of relatively large amounts of corrosion inhibitors is expensive and may complicate the manufacture of fire retardants. For
15 these and other reasons, it would be desirable to provide improved fire retardants, that include fire retardants which are less corrosive, such that much smaller amounts of corrosion inhibitors can be used, leading to less complicated manufacture, less undesirable color, less expense and lessened chance of environmental damage.

I have now discovered that certain salts of thiosulfuric acid which
20 decompose at flame temperature are effective to suppress wildland fires. Further, salts of thiosulfuric acid are less corrosive to certain metallic parts of storage and application equipment than the ammonium polyphosphate based liquid concentrate

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fire retardants of the prior art. This discovery enables one to provide powder concentrate and liquid concentrate fire retardant compositions without the addition of undesirable corrosion inhibitors, or in the alternative, enables one to employ smaller amounts of corrosion inhibitors. In particular, the use of sodium
5 hexacyanoferrate (II) which is currently used in connection with liquid concentrate fire retardants based on ammonium polyphosphate, but which imparts an undesirable deep blue color to fire retardant compositions, can be avoided.

Briefly, in accordance with my invention, I provide a powder, which with dilution with water, forms a liquid concentrate for producing a fire retardant
10 composition. Furthermore, dilution with additional water produces the fire retardant composition itself. The powder includes the salt of thiosulfuric acid which decomposes at flame temperature in an amount effective to suppress wildland fires. More particularly, the preferred salt of thiosulfuric acid that I have discovered which decomposes at flame temperature is ammonium thiosulfate. The powder
15 concentrate may also include corrosion inhibitors, rheological modifying agents, stabilizing agents, coloring agents and antimicrobial agents.

In accordance another embodiment of my invention, I provide the liquid concentrate for the preparation of fire retardant compositions especially adapted for ground and aerial application. The concentrate consists essentially of water and a
20 salt of thiosulfuric acid, but may also include corrosion inhibitors, rheological modifying agents, stabilizing agents, coloring agents and antimicrobial agents.

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Ammonium thiosulfate is presently available in liquid form under the trade names "Thio-Sul®" and "ATS" by the company Tessenderlo Kerley, Inc. and consists of approximately 55 - 60% ammonium thiosulfate and 40 - 45% water.

5 In accordance with a further embodiment of my invention, I provide a process for preparing a fire retardant composition especially adapted for aerial application, the process comprising the steps of forming a concentrate which consists essentially of ammonium thiosulfate and water, and thereafter mixing the concentrate with additional water in an amount to produce a fire retardant composition containing sufficient ammonium thiosulfate to suppress wildland fires.

10 In preparing the concentrate, the ammonium thiosulfate may be mixed with other desired components such as corrosion inhibitors, suspending agents, stabilizers, antimicrobials, rheological modifying agents and coloring agents. The mixing of the components of the concentrate may be accomplished with low shear mixers. However, if attapulgite clay is used as a suspending agent, as disclosed in
15 U.S. Patent No. 3,196,108 (Nelson), the mixing of the components of the concentrate is preferably accomplished by high shear action such as may be afforded by a Waring Blender or by impellers of high speed recirculating pumps or by bladed high speed discs.

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Examples of corrosion inhibitors which may be effectively employed in the practice of my invention are ortho-phosphate salts, aromatic triazole compounds and salts thereof, sodium benzoate, benzoic acid, cinnamic acid, sorbic acid, 2-mercaptobenzothiazole (MBT), and salts thereof, 2,5 - dimercaptothiadiazone (DMTD), sodium hexafluorosilicate, sodium molybdate and diammonium ortho-phosphate (DAP). It is believed that the preferred corrosion inhibitors are sodium benzoate, benzotriazole, sodium molybdate, tolyltriazole, 2,5-dimercaptothiadiazone and MBT.

The preferred antimicrobial agents are believed to be methyl paraben and propyl paraben.

Rheological modifying agents may also be effectively employed in the fire retardant compositions and concentrates of my invention. Rheological modifying agents are components which alter the flow properties, including altering the viscosity, surface tension, yield stress, and elasticity, of the fire retardant or concentrate. Rheological modifying agents include thickeners and flow conditioners. Some typical thickeners and flow conditioners are discussed in U.S. Patent No. 3,634,234 (Morgenthaler), U.S. Patent No. 4,447,336 (Vandersall), U.S. Patent No. 4,447,337 (Adl et al.), U.S. Patent No. 4,983,326 (Vandersall), U.S. Patent No. 4,822,524 (Strickland) and U.S. Patent No. 4,176,071 (Crouch). It is believed that the preferred rheological modifying agents of the present invention are guar gum, derivatized guar gum and foam.

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Liquid guar gum may be employed in the fire retardant of the present invention. It consists of powdered guar gum or derivatized guar gum suspended and dispersed in a non-aqueous liquid carrier. A typical example of this material can be purchased from Rantec Corporation under their designation LT75.

5 Typically, the fire retardant liquid concentrate is diluted with water to the desired final effective mix ratio and then about 1.0 to about 2.25 percent by weight of the liquid guar gum is added to achieve a desirable viscosity ranging from 500 to 1500 centipoise. The addition of the liquid guar gum may be accomplished by a Moyno gas pump sold by the company Robbins & Meyers. The final viscosity can be
10 selected and will depend on the vegetation to which the mixture is applied, the type of delivery vehicle, the conditions of delivery (drop height, forward speed) and local wind conditions.

After forming the liquid concentrate which consists of ammonium thiosulfate, water and any desired components such as corrosion inhibitors,
15 suspending agents, coloring agents, antimicrobial, and stabilizers, the concentrate can be stored for extended periods without appreciable separation of the components. Since all of the components of the final fire retardant composition, except additional water for dilution, are present in the concentrate, transportation of the materials from the manufacturing facility to the application equipment loading
20 site is facilitated. The concentrate may then be stored at the loading site until

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needed and then finally diluted as desired with water to produce the final fire retardant composition just before the composition is loaded into the equipment for application at the fire site.

5 The amount of water of dilution employed to convert the powder or liquid concentrate to the final fire retardant composition will vary widely depending upon the exact composition of the concentrate and the desired retardant effectiveness of the final composition. The desired effectiveness will, in turn, depend on the type of vegetation to which the composition is ultimately to be applied, wind conditions, etc. Any number of techniques may be used to dilute the concentrate for use as a
10 fire control retardant. For example, the concentrate may be diluted in a holding tank. Alternately, the concentrate and water may be introduced from separate feed lines into a common conduit wherein the mixing takes place. The resulting fire retardant solution may be discharged directly from the mixing conduit into the delivery tank of the delivery vehicle.

15 The following examples illustrate the practice of the invention, but are not intended as limitations on the scope thereof. In each example, the indicated components of the fire retardant formulation are mechanically mixed by any of several mixing techniques well known in the art to provide the indicated final compositions.

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EXAMPLE 1

This example illustrates a liquid concentrate of the present invention which is to be diluted approximately 2:1 (water:concentrate) or more by volume to produce a wildland fire retardant composition. Liquid guar gum concentrate may be added as
5 needed for enhanced rheological properties. Further, liquid color agents may be added to enhance conspicuity.

	<u>COMPONENT</u>	<u>WT%</u>
	Ammonium thiosulfate	9.999 - 50.00
	Water	40.00 - 45.00
10	Corrosion inhibitor(s)	<u>0.001 - 5.00</u>
		100.00

EXAMPLE 2

This example illustrates a liquid concentrate of the present invention which is to be diluted approximately 2:1 (water:concentrate) or more by volume to produce a
15 wildland fire retardant composition. The need for corrosion inhibitors, stabilizers, colorant, antimicrobial agents, etc. is determined by the end use conditions. Liquid guar gum may be added as needed for enhanced rheological properties.

	<u>COMPONENT</u>	<u>WT%</u>
	Ammonium thiosulfate	59.999 - 36.00
20	Water	40.00 - 45.00
	Corrosion inhibitor(s)	0.001 - 5.00
	Suspending agent(s)	0.000 - 5.00
	Stabilizer(s)	0.000 - 5.00
	Antimicrobial(s)	0.000 - 2.00
25	Colorant(s)	<u>0.000 - 2.00</u>
		100.00

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EXAMPLE 3

This example illustrates a liquid concentrate of the present invention to be diluted approximately 2:1 (water-concentrate) or more by volume to produce a wildland fire retardant composition. Liquid coloring agents, either fugitive pigment or red iron oxide, may be added to enhance conspicuity. The need for corrosion inhibitors, stabilizers, antimicrobial agents, etc. is determined by the end use conditions. Liquid guar gum concentrate may be added as needed for enhanced rheological properties.

	<u>COMPONENT</u>	<u>WT%</u>
10	Ammonium thiosulfate	59.999 - 38.00
	Water	40.00 - 45.00
	Corrosion inhibitor(s)	0.001 - 5.00
	Suspending agent(s)	0.000 - 5.00
	Stabilizer(s)	0.000 - 5.00
15	Antimicrobial(s)	<u>0.000 - 2.00</u>
		100.00

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EXAMPLE 4

This example illustrates a wildland fire retardant liquid concentrate composition of the present invention, including ammonium thiosulfate in an amount effective to retard wildland fires optimized with other chemical retardants such as diammonium orth-phosphate (DAP) and monoammonium ortho-phosphate (MAP) and diammonium sulfate (AS). This composition would be diluted approximately 1 part concentrate plus 6 parts water. The dilute retardant product thus formed has a retardant effectiveness of approximately 0.60 as measured according to USDA Forest Service Specification 5100-304a (1986).

10	<u>COMPONENT</u>	<u>WT%</u>
	Ammonium Thiosulfate (55-60 % wt in water)	48.7575
	Diammonium Sulfate	31.8566
	Diammonium Phosphate	14.6683
15	Colorant(s)	1.8451
	Attapulgate Clay	1.6300
	Benzotriazole	0.0974
	2,3-dimercaptothiadiazole	0.4663
	Sodium Molybdate	0.3886
20	Tolyltriazole	<u>0.2902</u>
		100.00000

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EXAMPLE 5

This example illustrates a liquid concentrate of the present invention which is to be diluted approximately 2:1 (water:concentrate) or more by volume to produce a wildland fire retardant composition.

5	<u>INGREDIENTS</u>	<u>% IN CONC</u>
	Ammonium Thiosulfate	96.79296
	(55-60% wt in water)	
	Red Iron Oxide Colorant	0.83522
	Attapulgate Clay	1.72400
10	Benzotriazole	0.04448
	2-3 Dimercaptothiadiazole	0.42589
	Sodium Molybdate	0.17745
	Tolyltriazole	<u>0.26989</u>
		100.00000

15 EXAMPLE 6

This example illustrates a liquid concentrate of the present invention which is to be diluted approximately 2:1 (water:concentrate) or more by volume to produce a wildland fire retardant composition. Liquid guar gum concentrate may be added in variable amounts to the diluted mixture as needed for enhanced rheological properties. Liquid color concentrate, either fugitive pigment or red iron oxide, may also be added in variable amounts to the diluted mixture to enhance conspicuity.

	<u>COMPONENT</u>	<u>WT%</u>
	Ammonium thiosulfate	58.92
	Water	39.28
25	Benzotriazole	0.400
	2-mercaptothiadiazole	0.400
	Sodium benzoate	<u>1.000</u>
		100.000

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EXAMPLE 7

This example illustrates a wildland fire retardant liquid concentrate composition of the present invention, including ammonium thiosulfate, optimized by including additional chemical retardants such as diammonium sulfate (AS). This
5 composition would be diluted approximately 1 part concentrate plus 5.5 parts water. The dilute retardant product thus formed has a retardant effectiveness of approximately 0.60 as measured according to USDA Forest Service Specification 5100-304a (1986).

	<u>INGREDIENTS</u>	<u>% IN CONC</u>
10	Ammonium Thiosulfate (55-60% wt in water)	45.06369
	Diammonium Sulfate	50.19148
	Colorant(s)	1.70126
	Attapulgate Clay	1.72400
15	Benzotriazole	0.09061
	2,3-dimercaptothiadiazole	0.86750
	Sodium Molybdate	0.36146
	Tolyltriazole	<u>0.26989</u>
		100.00000

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EXAMPLE 8

This example illustrates a liquid concentrate of the present invention to be diluted approximately 2:1 (water:concentrate) or more by volume to form a fire retardant composition. Liquid color concentrate, either fugitive pigment or red iron oxide, may be added to the diluted mixture in a variable amount to enhance conspicuity.

	<u>COMPONENT</u>	<u>WT%</u>
	Ammonium thiosulfate	58.92
	Water	39.28
10	Sodium benzoate	1.000
	Benzotriazole	0.400
	2-mercaptobenzothiazole	<u>0.400</u>
		100.000

EXAMPLE 9

This example illustrates a liquid concentrate of the present invention to be diluted approximately 2:1 (water:concentrate) or more by volume to form a wildland fire retardant composition. Liquid guar gum concentrate may be added as needed for enhanced rheological properties.

	<u>COMPONENT</u>	<u>WT%</u>
20	Ammonium thiosulfate	56.04
	Water	37.36
	Sodium benzoate	1.000
	Benzotriazole	0.400
	2-mercaptobenzothiazole	0.400
25	Attapulgate Clay	4.000
	Fading Pigment	0.500
	Titanium dioxide	<u>0.300</u>
		100.000

CLAIMS

1. A liquid composition for suppressing wildland fires comprising:

- a) water;
- b) a salt of thiosulfuric acid which is effective to retard wildland fires, said salt of thiosulfuric acid in an amount of at least about 5% by weight of the composition wherein said composition is substantially free of water-based acrylic resin.

2. A liquid concentrate that is adapted to be diluted with water to form a composition for retarding wildland fires, the liquid concentrate comprising:

- a) water;
- b) an amount of at least about 5% by weight of the composition of a fire retardant in said concentrate consisting of a salt of thiosulfuric acid wherein said composition is substantially free of water-based acrylic resin.

3. A powder that is adapted to be diluted with water to form a composition for retarding wildland fires wherein said composition is substantially free of water-based acrylic resin, the powder comprising:

- a) a powder comprising a salt of thiosulfuric acid in an amount sufficient to provide at least about 5% by weight of the fire retarding composition; and

b) a corrosion inhibitor.

4. A powder that is adapted to be diluted with water to form a composition for retarding wildland fires wherein said composition is substantially free of water-based acrylic resin, the powder comprising:

a) a powder comprising a salt of thiosulfuric acid in an amount sufficient to provide at least about 5% by weight of the fire retarding composition; and

b) a stabilizer.

5. A powder that is adapted to be diluted with water to form a composition for retarding wildland fire, wherein said composition is substantially free of water-based acrylic resin, the powder comprising:

a) a powder comprising a salt of thiosulfuric acid in an amount sufficient to provide at least about 5% by weight of the retarding composition; and

b) a coloring agent.

6. The method for preparing fire-retardant compositions adapted for aerial application, which method comprises the steps of:

forming an intermediate concentrate composition suitable for transportation and storage, said concentrate composition comprising water and a salt of thiosulfuric acid; and,

diluting said concentrate with additional water to form the fire retardant composition wherein said salt of

thiosulfuric acid is present in the fire retardant composition in an amount of 5% by weight after said diluting and wherein said composition is substantially free of water-based acrylic resin.

7. In a fire suppressant composition, specially adapted for aerial application to suppress wildland fires, comprising

a liquid carrier,

a fire retardant component, in an amount of at least about 5% by weight of said composition,

at least one functional additive component, selected from the group consisting of corrosion inhibitors, rheological modifying agents, suspending agents, antimicrobial agents, stabilizers and coloring agents,

the improvements in said composition in which,

(a) said fire retardant component comprises ammonium thiosulfate in an amount of at least about 1.5% by weight of said composition, and

(b) said fire suppressant composition is substantially free of nitrates, nitrites or zinc compounds.

8. The method for preparing a fire suppressant composition, specially adapted for aerial application to suppress wildland fires, comprising the steps of:

(a) forming an intermediate concentrate composition, suitable for transportation and storage, said concentrate composition comprising water and ammonium thiosulfate; and

- (b) diluting said concentrate with additional water to form said fire suppressant composition containing at least about 1.5% by weight of ammonium thiosulfate.

9. The method of suppressing wildland fires, comprising the step of aeri ally applying to wildland foliage a fire suppressing composition comprising

water;

ammonium thiosulfate in an amount of at least about 1.5% by weight of said composition; and

at least one functional additive component, selected from the group consisting of corrosion inhibitors, rheological modifying agents, suspending agents, antimicrobial agents, stabilizers and coloring agents.