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Applicant: **FIRE CONTROL TECHNOLOGIES,
INC.
274 Riverside Avenue
Westport Connecticut 06880(US)**

72

Inventor: **Tarpley, William B.
29 Gunning Lane
Downington Pennsylvania(US)**
Inventor: **Ruscitto, Gerald L.
24 Overhill Drive
South Coatesville Pennsylvania 19320(US)**

74

Representative: **Oliver, Roy Edward et al
POLLAK MERCER & TENCH High Holborn
House 52-54 High Holborn
London WC1V 6RY(GB)**

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Thixotropic fire suppressant composition containing carboxy polymer gelling agent.

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A non-aqueous fire-suppressing composition contains a non-polar thixotropically gelled liquid and a carboxy polymer gelling agent in an amount sufficient to gel the liquid in the presence of an ammonium salt. The composition may further contain a non-corrosive drying agent and/or a viscosity modifier functional at low temperatures.

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THIXOTROPIC FIRE SUPPRESSANT COMPOSITION CONTAINING CARBOXY POLYMER GELLING AGENT

Background Of The Invention

The present invention relates to a fire-suppressing composition containing an ammonium salt in powder form in a non-polar liquid which is thixotropically gelled by a carboxy polymer gelling agent.

Liquified gases have been used to disseminate fine powders including pesticides, medicinal products, cosmetic products, and fire extinguishing powders. To prevent the packing and clogging of these powders, gelling agents such as "CAB-O-SIL" (a trademark of Cabot Corporation) have been used. Gelled liquid fire-suppressing suspensions are taught in U.S. Patent Nos. 4,226,727 and 4,234,432.

The aforesaid patents disclose the use of the following gelling agents: pyrogenic silica, montmorillonite clay, oleophilic vinyl addition polymer, pyrogenic titanium dioxide, aluminum or magnesium salts of fatty acids, colloidal attapulgite clay, colloidal quaternized bentonite, sub-micron magnesium oxide and sub-micron potassium bicarbonate.

Ammonium salts are useful fire-suppressing agents in powdered form. It has been found that a suspension of such powders having improved stability results from the addition of a carboxy polymer in small amounts as a gellant.

Summary Of The Invention

A non-aqueous fire-suppressing composition is provided comprising a non-polar thixotropically gelled liquid, a carboxy polymer gelling agent in an amount effective to gel the liquid, and an ammonium salt. The composition may include as further additives either a viscosity modifier functional at low temperatures, a drying agent, or both.

The present invention also pertains to a method of extinguishing fires by applying the aforesaid composition.

Unless specified otherwise, all percentages stated herein are understood to be weight percents.

Detailed Description Of The Invention

A suspension of ammonium salts in powder form in a gelled non-polar liquid results from the present invention. A carboxy polymer gelling agent is used to form the suspensions, which are thixotropic and exhibit excellent stability.

The gelled liquid component of the present invention includes one or more fire-quenching liquids in combination with one or more fire-quenching liquified gases and/or one or more overpressurized gases. If a fire-quenching liquified gas (e.g. trifluorobromomethane) is used, the fire-quenching liquid may be omitted.

The gelled liquid component must be capable of filling the interparticulate spaces in the suspension under pressure, i.e., when the suspension is at rest. Preferably, it is capable of expanding upon release of pressure to a gaseous vapor or droplet cloud carrying the fire-extinguishing particles. Finally, the gelled liquid component must provide some measure of fire quenching capability.

Fire-quenching liquids useful in the gelled liquid component include, but are not limited to, the following: methylene bromide, methyl iodide, tetrafluorodibromoethane, trifluorotrichloroethane, fluorotrichloromethane, chloroform, bromoform, carbon tetrachloride, and the like.

Liquified gases which may be used according to the present invention include, but are not limited to, the following: trifluorobromomethane, difluorochlorobromo methane, perfluoropropane, perfluorocyclobutane, dichlorodifluoromethane, tetrafluoromethane, methyl bromide, trifluoromethane, trifluorochloromethane, hexafluoroethane, and the like. Several of these gases have been designated as Halon materials. "Halon" is the National Fire Protection Association designation for halogenated fire extinguishing materials. Halon products are available from Great Lakes Chemical Company, DuPont Company, and ICI Americas, Inc. Halon 1211 - (difluorochlorobromomethane), Halon 1301 (trifluorobromomethane), and mixtures thereof, are useful. A mixture comprising from about 50% to about 60% difluorochlorobromomethane and from about 40% to about 50% trifluorobromomethane is particularly useful at low temperatures.

Overpressurizing gases useful in the gelled liquid component include nitrogen, carbon dioxide, helium, argon, and the like.

The gelled liquid component comprises from about 70 to about 30 percent by weight of the composition according to the present invention.

The solids component, comprising from about 30 to 70 weight percent of the present composition contains one or more powdered ammonium salts and one or more carboxy polymer gelling agents. Nonlimiting examples of suitable powdered ammonium salts include mono-, di-, and triammonium phosphate, ammonium calcium phosphate, sodium ammonium phosphate, ammonium sulfate, ammo-

nium chloride and ammonium aluminum sulfate. Monoammonium phosphate (MAP) powder is particularly useful. ABC dry chemical fire-extinguishing powder, which is 90 to 95 percent MAP, is preferred.

Other fire-suppressing powders may be used in conjunction with one or more ammonium salts. Such powders include sodium bicarbonate, potassium bicarbonate, urea adducts of potassium bicarbonate such as are available from ICI under the trademark "MONAX", sodium chloride, potassium chloride, and the like. Where a non-fire-suppressing is selected as the powdered ammonium salt, an auxiliary fire-suppressing powder is necessary.

The gelling agent is a polymer containing carboxyl groups in the free acid form. Excluded from the present invention are polymeric materials wherein carboxyl groups are substantially in neutralized or salt form. We have found these agents to be adequate absent conversion to the free acid.

Included in the present invention are polymers which are functional derivatives of free polycarboxylic acids, e.g., polyacrylamides, wherein the functional groups have been substantially hydrolyzed to the free acid form. As an illustration, we have found that the 40% hydrolyzed polyacrylamide available from National Starch & Chemical Co. under the trademark "POLYHALL 40-J" will satisfactorily gel the nonpolar liquid component of the present composition, in the presence of an ammonium salt. Forty percent of the nitrile groups in this polyacrylamide are hydrolyzed to the corresponding acid function. On the other hand, "POLYHALL 33-J", wherein only 33% of the nitrile groups are hydrolyzed, forms a much weaker suspension. For polymers having groups which are functional derivatives of carboxyl, those skilled in the art will be able to readily determine by routine experimentation the extent to which such groups must be first converted to the free acid form for gellation of the nonpolar liquid to occur.

The carboxy polymer acids useful in the present invention include carboxy vinyl polymers, such as those available from B.F. Goodrich under the "CARBOPOL" trademark; polysaccharides having pendent free carboxyl groups such as alginic acid and guar derivatives; hydrolyzed or partially hydrolyzed polyacrylamides such as "POLYHALL 40-J" (40% hydrolyzed); synthetic resins containing free carboxyl groups, such as the ionic exchange resins which are copolymers of methacrylic acid and divinyl benzene available from Rohm & Haas Co., Philadelphia, Pa. under the trademark "AMBERLITE IPC-50". Other polymeric materials having free carboxyl groups, or having groups

functionally equivalent to carboxyl which are readily convertible to the free acid form, are known to those skilled in the art, and may be employed in the present invention.

We have found that many excellent thickening and/or suspending agents which lack the free carboxyl function do not gel non polar liquids in the presence of ammonium compound.

Without wishing to be bound by any theory or mechanism of action, we believe the suspending power exerted over non-polar liquids by the carboxy polymer gelling agents described is due to a synergistic interaction between the free carboxyl function and the ammonium compound. Where the gelling agent was mixed with difluorochlorobromomethane, or a blend of difluorochlorobromomethane and trifluorobromomethane in the absence of ammonium compound, no gel formed. The gelling agent was insoluble in the liquid, and floated to the surface.

The preferred gelling agents are carboxy vinyl polymers. "CARBOPOL" 934 and 941 are particularly suitable. "CARBOPOL" is offered by the manufacturer to thicken and suspend insolubles, and to stabilize emulsions, primarily in aqueous systems. Where "CARBOPOL" is to be used with less polar liquids, the manufacturers recommend the addition of an amount of long chain fatty amine as a gelling adjuvant. We have found that "CARBOPOL" is ineffective as a gelling agent for the liquified halogenated hydrocarbon gases which form the liquid component of the present composition, even in the presence of the recommended gelling adjuvants. What is surprising is that "CARBOPOL" will gel such non-polar liquids in the presence of an ammonium compound.

It has been discovered that if a carboxy polymer is added to the liquid component with an ammonium compound such as monoammonium phosphate (in the form of ABC powder), it gels the relatively non-polar fire-extinguishing liquids and liquified gases constituting the gelled liquid component, without the need for polar gelling adjuvants. The resulting suspension is thixotropic and displays excellent performance as a fire-extinguishing composition, even after extended storage. Satisfactory storage stability has been demonstrated using "CARBOPOL" up to 18 months. Powdered MAP did not pack or clog but remained in suspension forming a thixotropic composition which could be easily disseminated. MAP loadings of 40 to 66 weight percent have been possible with 0.5 to 4.0 weight percent "CARBOPOL".

A composition of the present invention was prepared according to Example 1, containing 45% solids and 55% of the liquified gases difluorochlorobromomethane and trifluorobromomethane.

Example 1

41.5% monoammonium phosphate

3.5% "CARBOPOL" 941

44.0% difluorochlorobromomethane

11.0% trifluorobromomethane

The above proportions of MAP, gellant, and liquified gas provided excellent fire extinction, as determined in a standard Underwriters Laboratory 2-B-rated fire test (5 square feet of burning heptane). The fire was extinguished in 3.5 seconds, using approximately 216 grams or 50 weight percent of extinguisher contents.

Performance declined as the weight percent solids in the composition was increased 45%. More extinguishant was needed to extinguish the same size fire, until a concentration of solids was reached that was so high that expulsion of the extinguisher contents by the action of the liquified gases was prevented. As the level of solids was decreased below 45% (and the proportion of liquified gas in the composition proportionately increased) the extinguisher began to act as a conventional Halon-type extinguisher, until it was unable to extinguish a 2-B-rated fire.

A typical composition using a further fire extinguishing powder (KHCO_3) in addition to an ammonium salt is as follows:

Example 2

10% monoammonium phosphate

30% KHCO_3

4% "CARBOPOL" 941

44.8% difluorochlorobromomethane

11.2% trifluorobromomethane

The following experiments were performed demonstrating the increased fire-extinguishing effectiveness of the present gelled concentrate composition in comparison with Halon or monoammonium phosphate, when used alone.

Example 3

Two hundred grams of monoammonium phosphate (ABC powder) in nitrogen pressurized to 100 p.s.i. was released on an Underwriters Laboratory 1-B-rated fire (2.5 square feet of burning heptane) - (with 30 seconds pre-burn). The fire was not extinguished, despite expulsion of 95 weight percent of the contents of the containing vessel onto the fire.

Example 4

In extinguishing hardware identical to that used in Example 3, 200 grams of a blend containing 80% difluorochlorobromomethane and 20% trifluorobromomethane, by weight, were released on an identical fire. The fire was not extinguished, despite expulsion of 95 weight percent of the contents of the containing vessel onto the fire.

Example 5

In extinguishing hardware identical to that used in Examples 3 and 4, 200 grams of the composition according to Example 1 were released on an identical fire. The fire was extinguished upon expulsion of 71 weight percent of the vessel contents.

The synergistic interaction between MAP and various carboxy polymer gelling agents was demonstrated according to the following procedure.

Example 6

1.8 grams "CARBOPOL" 941 were ground in a ball mill to a fine particle size and dry-milled with 50 grams of MAP. The mixture was added to 78 grams of difluorochlorobromomethane, shaken and allowed to stand overnight. A uniform gel suspension was observed the next day.

Other agents were tested according to the procedure of Example 6, except that 2x-3x the amount of gelling agent was necessary to induce an initial suspension. The results appear in Table 1 below. A minus sign (-) indicates the complete absence of a suspension wherein MAP settled into a large mass at the bottom of the vessel. The mass resisted resuspension upon shaking. A plus sign (+) indicates gellation, with some settling of MAP overnight which was easily resuspended with only one or two gentle shakes of the hand. A double plus sign (+ +) indicates the presence of a highly uniform gel structure with either no settling or very slight observable settling of MAP.

TABLE 1
Effect Of Varying Gelling Agent

<u>Run</u>	<u>Material</u>	<u>Amount</u> <u>(grams)</u>	<u>After</u> <u>24 hrs.</u>
1	Carboxy vinyl polymer ("CARBOPOL 941", B.F. Goodrich)	1.8	++
2	Alginic acid ("KELACID", Kelco)	5.5	+
3	Alginic acid ("KELACID", Kelco)	11.0	++
4	Polyvinyl alcohol ("ELVANOL" 85-82, DuPont)	5.5	-
5	Polyvinyl alcohol, borated ("ELAVANOL") 85-80 DuPont)	5.5	-
6	Polyvinyl alcohol, plus 1% boric acid dry mix ("ELVANOL" 85-82)	5.5	-
7	Hydroxyethyl cellulose ("NATROSOL", Hercules)	not recorded	-
8	Hydroxypropyl cellulose ("KLUCEL", Hercules)	not recorded	-
9	Polyvinylpyrrolidone (GAF)	1.8	-
10	Poly(methylvinyl ether/maleic anhydride) copolymer ("GANTREZ-AN", GAF)	11.0	-
11	Methacrylic acid/divinyl/benzene copolymer ("AMBERLITE IRC-50", Rohm & Haas)	11.0	+
12	Carboxymethyl cellulose - sodium salt (Hercules)	1.8	-

13	Carboxymethyl cellulose - sodium salt (Hercules)	5.5	-
14	Polyacrylamide, 40% hydrolyzed ("POLYHALL 40-J", National Starch)	5.5	+
15	Polyacrylamide, 33% hydrolyzed ("POLYHALL" 33-J", National Starch)	5.5	-
16	Amphoteric starch, ("CATO-15", National Starch)	5.5	-
17	Carboxymethylated guar gum ("JAGUAR CMG", Celanese)	5.5	-
18	Carboxymethylated guar gum (converted to free acid form)	5.5	++

"JAGUAR CMG", a carboxymethylated guar gum derivative available from the manufacturer as a sodium salt, was converted to the free acid form in a 70% aqueous solution of methanol, followed by a certification with glacial acetic acid and stirring. The solution was allowed to stand overnight, then was filtered and washed with pure methanol until all acetic acid was removed.

For Runs 7 and 8, the amount of gelling agent was not recorded, but it is believed to be between 5 and 11 grams.

"CATO-15", used in Run 16, an amphoteric starch available from National Starch Company, contains carboxylic acid groups, but these groups are neutralized by the presence of amine functions in the same molecule. Hence, no gellation occurred.

The effect of the identity of the ammonium compound upon gellation was investigated in Example 7-13 by following the procedure of Example 6 using 4 grams of "CARBOPOL 941", 60 grams of difluorochlorobromomethane and 36 grams of ammonium compound. The results are set forth in Table 2.

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TABLE 2

Effect Varying Ammonium Compound

<u>Example</u>	<u>Ammonium Compound</u>	<u>After 24 hrs.</u>
7	Monoammonium phosphate	++
8	Sodium ammonium phosphate	++
9	Ammonium sulfate	++
10	Ammonium chloride	++
11	Diammonium phosphate	++
12	Ammonium aluminum sulfate	++
13	Ammonium alginate	-

Although "CARBOPOL 941" did not succeed in forming an acceptable suspension of ammonium alginate in difluorochlorobromomethane (Example 13), it is believed that the negative result is due not to the absence of interaction between ammonium alginate and the carboxy vinyl gelling agent, but rather because of the hard, coarse nature of the sodium alginate powder, which was found very difficult to grind to the appropriate fine particle size necessary for suspension.

The ammonium salts used according to the present invention are hygroscopic. Monoammonium phosphate, in particular, readily absorbs moisture from the atmosphere, thereby adding water to the composition. The presence of water is undesirable for two reasons. First, water promotes the formation of HBr and HF. At elevated temperatures, Halon materials will break down and react with any free water present to readily form these acids. HF and HBr are highly corrosive, and attack the metal components of the delivery vessel. Second, liquified gases such as the Halon materials have a refrigerating effect. Any free water present in the composition readily freezes to form ice which clogs the delivery system. To protect against the formation of acid and ice, it is necessary that free water be kept from the composition.

Depending on the particular application, the composition therefore may include a drying agent in an amount sufficient to sequester any moisture in the system. Preferably, the drying agent is a non-corrosive material which will not harm the metal components of the delivery vessel. Suitable dry-

ing agents comprise metal salts and oxides. Molecular sieves may also be used for this purpose. Other drying agents are known to those skilled in the art. We have found that sodium sulfate, calcium sulfate, calcium chloride and calcium oxide are effective. Calcium oxide is preferred because of its secondary effect as a neutralizing agent in counteracting acids which may be generated through the breakdown of Halon materials.

Depending on the application, the fire-suppressing composition of the present invention may also include at least one viscosity modifier in an effective amount. Ideally, the viscosity modifier acts to prevent separation of the gel at temperatures as low as -40°F, and prevents excessive thinning of the composition at temperatures up to 120°F. Chlorides of sodium, magnesium, aluminum and potassium may be used. Other metal salts may be used.

The same salt may function as both drying agent and viscosity modifier.

The gelled liquid compositions according to the present invention may be prepared by first mixing the various solid components with an intensive mixer, then adding the liquid component, with continued mixing. Alternatively, the solids components may be added to the liquid component, with intensive mixing.

The following Examples 14-24 are set forth to illustrate the present invention wherein the gelled liquid component comprises a mixture of difluorochlorobromomethane and trifluorobromomethane. Amounts of ingredients are expressed in grams.

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TABLE 3

Example	MAP	"CARBOPOL"	CF ₂ ClBr	CF ₃ Br	Drying Agent		Viscosity Modifier	
					Na ₂ SO ₄	CaCl ₂ CaO	NaCl MgCl ₂	AlCl ₃
14	318.5	11.5	148.5	121.5	-	-	-	-
15	"	"	"	"	2.0	-	-	-
16	"	"	"	"	-	1.0	-	-
17	"	"	121.5	148.5	-	5.0	-	-
18	167	6	142.4	116.6	-	-	6.7	-
19	318.5	11.5	148.5	121.5	2.0	-	12.7	-
20	167	6	142.4	116.6	2.0	-	6.7	-
21	"	"	"	"	-	5.0	-	3.3
22	"	"	116.6	142.4	2.0	-	-	5.5
23	"	6	142.4	116.6	-	5.0	6.7	-
24	"	"	"	"	-	2.0	"	-

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

Claims

1. A non-aqueous fire-suppressing composition CHARACTERIZED by:

- (a) a non-polar thixotropically gelled liquid;
- (b) a carboxy polymer gelling agent in an amount effective to thixotropically gel the liquid; and
- (c) an ammonium salt.

2. A composition according to claim 1 CHARACTERIZED by an ammonium salt selected from the group consisting of monoammonium phosphate, diammonium phosphate, triammonium phosphate, ammonium calcium phosphate, sodium ammonium phosphate, ammonium sulfate, ammonium chloride and ammonium aluminum phosphate.

3. A composition according to claim 1 or 2 CHARACTERIZED by a carboxy polymer gelling agent selected from the group consisting of

(i) carboxy vinyl polymers, and

(ii) polysaccharides, polyacrylamides,

and synthetic resins having pendant free carboxyl groups or functional equivalents thereof which have been converted to the free acid to the extent necessary to induce gellation of the non-polar liquid.

4. A composition according to any of claims 1-3 CHARACTERIZED by about 70-30% gelled liquid, about 0.5-8.0% gelling agent, and about 30-70% ammonium salt.

5. A composition according to any of claims 1-4 CHARACTERIZED by a further additive selected from the group consisting of a drying agent and a viscosity modifier functional at low temperatures, and combinations thereof.

6. A composition according to any of claims 1-5 CHARACTERIZED by a fire-suppressing powder selected from the group consisting of sodium bicarbonate, potassium bicarbonate, urea adducts of potassium bicarbonate, sodium chloride and potassium chloride.

7. A composition according to any of claims 1-6 CHARACTERIZED by at least one fire-quenching liquid and at least one overpressurizing gas selected from the group consisting of nitrogen, carbon dioxide, helium, and argon.

8. A composition according to any of claims 1-6 CHARACTERIZED by as at least one fire-quenching liquified gas as the gelled liquid.

9. A composition according to claim 8 CHARACTERIZED by at least one fire-quenching liquid and at least one fire-quenching liquified gas as the gelled liquid.

10. A composition according to claim 7 or 9 CHARACTERIZED by a fire quenching liquid selected from the group consisting of methylene bromide, methyl iodide, tetrafluorodibromoethane, trifluorotrichloroethane, fluorotrichloromethane, chloroform, bromoform and carbon tetrachloride.

11. A composition according to claim 8 or 9 CHARACTERIZED by a fire-quenching liquified gas selected from the group consisting of trifluorobromomethane, difluorochlorobromomethane, perfluoropropane, perfluorocyclobutane, dichlorodifluoromethane, tetrafluoromethane, methyl bromide, trifluoromethane, trifluorochloromethane and hexafluoroethane.

12. A composition according to claim 11 CHARACTERIZED by a gelled liquid which is a blend of difluorochlorobromomethane and trifluorobromomethane.

13. A composition according to claim 12 CHARACTERIZED by a blend of about 50 to about 60 percent difluorochlorobromomethane and about 40 to about 50 percent trifluorobromomethane.

14. A composition according to claim 12 or 13 CHARACTERIZED by a carboxy vinyl polymer as the gelling agent.

15. A composition according to claim 14 CHARACTERIZED by 70-30% liquified gas which is a blend of about 50-60% difluorochlorobromomethane and about 40-50% trifluorobromomethane, about 0.5-8.0% carboxy vinyl polymer gelling agent, and about 35-50% monoammonium phosphate.

16. A method of fire suppression CHARACTERIZED by the application of a composition according to any of the preceding claims.



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, A	GB-A-2 006 620 (ENERGY AND MINERALS RESEARCH) * Page 1, lines 35-40; page 2, lines 32-37 and line 49 - page 3, line 37; example 11; claims 1, 4, 5, 11-15 *	1, 2, 4, 6, 8-11, 16	A 62 D 1/08 A 62 D 1/00
D, A	US-A-4 226 727 (W.B. TARPLEY, Jr. et al.) * Column 6, lines 20-31; column 7, line 56 - column 8, line 16; column 8, lines 42-53; examples 3, 7; claims *	1, 2, 4, 6, 8-13, 16	
A	US-A-3 345 289 (M. FREIFELD et al.) * Whole document *	1-3, 14, 16	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	US-A-3 634 234 (W.W. MORGENTHAUER) * Column 1, line 52 - column 2, line 19; column 2, lines 34-53; example 2; claims *	1-3, 16	A 62 D
A	US-A-3 229 769 (R.N. BASHAW) * Column 1, line 55 - column 2, line 7; claims *	1-3, 16	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-04-1986	Examiner FLETCHER A.S.
CATEGORY OF CITED DOCUMENTS			
X	particularly relevant if taken alone	T	theory or principle underlying the invention
Y	particularly relevant if combined with another document of the same category	E	earlier patent document, but published on, or after the filing date
A	technological background	D	document cited in the application
O	non-written disclosure	L	document cited for other reasons
P	intermediate document	&	member of the same patent family, corresponding document