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DRY CHEMICAL FIRE EXTINGUISHER COMPOSITION

Zbigniew J. Lobos, Monmouth Junction, N.J., assignor to Stop-Fire Inc., New Brunswick, N.J.

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This invention relates to fire extinguishing compositions and more particularly to a relatively dry free-flowing chemical powder which is useful in combatting all types of fires and such as known as class A, B and C and including metal fires.

Conventional fire extinguishing powders, such as sodium bicarbonate or the like carbonate base compositions are suitable for use in fighting burning oils, greases, and flammable liquids, and which are known as class B fires. The carbonate base dry powders are also useful for combatting electrical equipment fires which are known as class C fires. The dry carbonate base powders, however, are relatively ineffective for use in combatting ordinary wood and coal fires, and such as classified as class A fires. This is because the carbonate material does not stick to the hot surfaces of the burning material. As a consequence, re-ignition and back fires result.

For the same reason such dry powders are ineffective for extinguishing metal fires because of the violent and explosive reaction created between the burning metal and their decomposition products. There is accordingly an urgent need for a dry, chemical powder which is useful in combatting all classes of fires as well as metal fires. The present invention provides such a composition.

Some improvement has been obtained with the use of fire extinguishing powders composed of a finely divided mixture of a phosphate, e.g., monoammonium phosphate and an aldehyde type resin, such as urea formaldehyde or the like synthetic resin, with organic material, such as dried waste sulfite liquor and inorganic substances, e.g., silica or siliceous material. All or part of the phosphate acid salt may be replaced by boric acid or boric acid salts to provide a foam-forming fire extinguishing composition. The disadvantages encountered with the use of these known compositions, however, have been numerous. One disadvantage is that it is necessary to incorporate a relatively large amount (20 to 30% by weight of the composition) of organic material to provide for formation of the foam. The organic material, however, is combustible thus lowering the efficiency of the composition in combatting the fires, especially class B fires.

Attempts also have been made heretofore to provide improved fire extinguishing compositions, and various chemicals have been employed. Use has been made of boric acid and ammonium salts of sulfuric as well as phosphoric acid. These substances melt as relatively high temperatures, such as produced on burning wood, coal and metals, and form a thin layer or coating of the melted salts on the burning surfaces. Also solutions of these salts have been used to saturate wood, textiles, and the like, to render them fire resistant. Use of these high temperature melting substances in dry powder fire extinguishing compositions has been ineffective because the protective coating formed is too thin and fails to prevent the occurrence of back fires and re-flaming of the fire after being apparently put out.

It is a principal object of this invention to provide an improved fire extinguishing composition in the form of a dry chemical powder which contains monoammonium phosphate as the principal constituent. This phosphate is acidic and is admixed with a small quantity of solid powdered organic aliphatic acid having one or more carboxyl groups in the molecule or their ammonium or metallic

salts. The added organic acid or salt enhances the reaction of the composition whereby the ammonium phosphate quickly decomposes upon application of the composition on the fire.

The combination of dry, powdered ingredients decomposes rapidly and concurrently in the fire with evolution of gases, mostly carbon dioxide, and the formation of a foaming mass. The foamy mass, which is a mixture of melted monoammonium phosphate and bubbles of gases, sticks firmly to the burning surfaces of wood or other solid combustible material and the like as in class A fires. This sticky foam which adheres to the hot surface prevents re-igniting of the fire once put out.

The foam-producing composition of this invention has been found to be highly proficient for extinguishing class B fires, e.g., flammable liquids, electrical fires and metal fires. It is essential, however, to employ as the foaming agent the low molecular weight aliphatic carboxyl acids or their ammonium or metallic salts and which are solid up to 140° F., and decompose at temperatures above about 140° F. at ordinary atmospheric pressure. The aliphatic acids suitable for use have a relatively high boiling point above about 185° F. and which do not sublime but thermally decompose. Only the aliphatic acids or their salts are suitable which have a relatively small molecule but a large proportion of the carboxyl groups. For example, the higher aliphatic acids, such as the saturated or unsaturated fatty acids are not suitable because they merely increase the carbon content without increasing the formation of gases, which is essential to produce a sticky foamy mass in accordance with my improved fire extinguishing composition. The present invention thus distinguishes from prior composition wherein bitumens, waxes and high molecular weight aliphatic acids, alcohols and esters have been suggested as addition agents. Such high molecular weight compounds, however, are not suitable for my fire extinguishing composition. Examples of the aliphatic carboxylic acids and their salts found useful are as follows: maleic acid, citric acid, ammonium citrate, calcium citrate, tartaric acid, ammonium tartrate, sodium or potassium tartrate, fumaric acid, ammonium formate, malic acid, ammonium malate, and amino acetic acid (glycine).

The carboxylic acids and salts thereof which are poisonous are preferably not employed, as well as those which are too hydroscopic under high relative humidity conditions. For example, because of the poisonous characteristic properties of oxalic acid and maleic acid they are preferably not used. Citric acid and ammonium formate are somewhat hygroscopic under high relative humidity conditions so that it is best not to use these compounds where high humidity is prevalent. Oxalic acid and crotonic acid are not employed because they sublime or boil off at the burning temperatures of fires before decomposition takes place and are therefore not suitable.

The amount of the carboxylic acid or salt used in the fire extinguishing composition generally ranges from about 0.5 to 10% by weight of the fire extinguisher product. For the preferred composition, it is best to use between 1% and to 5% by weight of the aliphatic carboxylic acid or its salt.

While it has been proposed heretofore to use urea formaldehyde resins, carbohydrates, such as starch and sugar, and the proteinaceous materials, e.g., casein and glue, in fire extinguishing compositions to increase the carbon content of the foam formed, such substances are inflammable and very hygroscopic especially the urea formaldehyde resins. In accordance with the present invention, it has been discovered that unexpectedly superior results are obtained when employing the aforementioned aliphatic carboxylic acid compounds. Particularly useful are ammonium citrate, ammonium tartrate, sodium

and potassium tartrate, calcium citrate and amino acetic acid which compounds are not inflammable and are at least not hygroscopic at 90% of relative humidity. These are important requisite chemical characteristics of the compounds which enhance the fire extinguishing properties of the composition.

The dry particles of the composition are coated with silicone resin to make them free-flowing and resistant to caking.

It is a principal object of the present invention to provide a dry chemical fire extinguishing composition which is adapted for application to all classes of fires. The composition is free of cellulose and organic substances, the presence of which lowers the efficiency of the composition as a fire extinguisher.

Another object of the invention is to provide a fire extinguishing composition in the form of a dry powder which has the following properties—

(1) A fire extinguishing composition adapted to extinguish all classes of fires including metal fires.

(2) A fire extinguishing composition which contains only non-hygroscopic and not combustible fire extinguishing constituents, and

(3) It is resistant to moisture and can withstand an atmosphere of 90% relative humidity without deterioration.

(4) It is foam compatible and forms a spongy mass which clings tenaciously to the hot surface of the burning material thus smothering out the fire.

These and other objects and advantages of the invention will become apparent to those skilled in the art from the following description.

Typical mixtures which produce a free flowing fire extinguishing composition are given in the following examples, the parts being by weight—

Example I

	Parts by weight, percent
Monoammonium phosphate	91.85
Tricalcium phosphate precipitated	5.00
Silica (300 mesh particles)	0.45
Amino-acetic acid (glycine) (200 mesh particles)	2.00
Silicone (dimethyldiethoxysilane)	0.70

Example II

Monoammonium phosphate	79.35
Tricalcium phosphate (precipitated)	5.00
Barium sulphate (200 mesh particles)	12.00
Ammonium tartrate (200 mesh particles)	2.50
Silica (300 mesh particles)	0.45
Silicone (50–50 mixture of dimethyldiethoxysilane and allyltrichlorosilane)	0.70

Example III

Monoammonium phosphate	63.35
Tricalcium phosphate (precipitated)	5.00
Barium sulphate (200 mesh particles)	12.00
Ammonium sulphate (200 mesh particles)	16.00
Ammonium citrate (200 mesh particles)	2.50
Silica (300 mesh particles)	0.45
Silicone (Example I)	0.70

The ingredients of the compositions as set out in the foregoing examples are initially admixed, except for the silicone, for example using a conventional ribbon mixer for approximately 30 minutes. During the last 10 to 15 minutes of mixing, the silicone is added slowly and the whole mass continued mixing for another 30 to 45 minutes or longer, to produce a homogeneous mixture wherein each of the particles are coated with silicone resin. The mixture is then poured into drums or a suitable container and stored at room temperature (70° F.) for approximately 12 hours or overnight to permit polymerization of the silicone. The next day the dry, powder mixture is poured into the fire extinguishing container for distribution and use. The addition of the superfine silica substantially enhances the free flowing properties of the

dry mixture. The fire extinguishing composition of the invention is completely foam compatible, being free of long chain fatty acid salts, and permits the composition to be used together with mechanical foam such as may be discharged from other type fire extinguishers, and without danger of destroying such foams. The fire extinguishing composition of the invention thus complies with the regulations promulgated by the United States Coast Guard.

The preferred amount of monoammonium phosphate present has been found to range from 59% to 93% by weight based on the dry mixture. As a broad minimum and maximum range the content of monoammonium phosphate should be between 60% and 92% by weight of the composition.

The finished product, after polymerization of the silicone coating, has excellent free-flowing properties, is water repellent and highly resistant to caking. The dry, granular product can be passed through valve controlled nozzles without clogging and applied to fires as fluid stream-like mass of particles. A heavy blanket of the free-flowing powder composition effectively smothers and cools fires, quickly extinguishes them. Such silicone coated powders of the invention have been found to possess enhanced fire extinguishing properties over ordinary particles uncoated with silicone polymerizates.

The silicones useful in producing the free-flowing fire extinguishing powder, and which may be polymerized without heat and solvents are the silanes and the polysiloxanes which undergo further polymerization. Suitable silicones employed to coat the finely divided particles are preferably ones which may be polymerized to form a cross linked polysiloxane. It is desirable to use a trifunctional silicone which is capable of becoming cross-linked upon polymerization on the finely divided solid particles whereby the particles are rendered water repellent.

Among the polysiloxanes useful are the alkyl trihalosilanes, e.g., methyltrichlorosilane, amyltrichlorosilanes, octadecyltrichlorosilane, cyclohexyltrichlorosilane, allyltrichlorosilane, vinyltrichlorosilane, and aryltrihalosilanes including phenyltrichlorosilane and alkylalkoxysilanes, e.g., methyltriethoxysilane etc. and mixtures or blends thereof. Also copolymerized polysiloxanes by hydrolysis with difunctional silanes, such as dimethyldiethoxysilane, dimethyldichlorosilane and diphenyldihydrosilane.

The silicones are available commercially, and marketed by Dow Corning as DC–1107 and DC–1108. The General Company also supplies a silicone liquid Dri-Film 268 silicone fluid which is a blend of partially hydrolyzed methylhydrogen polysiloxanes. A silicone useful consists of a 50–50 mixture, by volume, of dimethyldiethoxysilane and phenyltrichlorosilane.

During use of the fire extinguishing composition when the same is applied to a fire, a thermal decomposition of the aliphatic carboxylic acid, amino carboxylic acid or their ammonium or metallic salts takes place to release carbon dioxide or both carbon dioxide and nitrogen. This results in producing with melted monoammonium phosphate an adherent foamy mass, which smothers out the fire. The fire extinguishing action of the combination of the phosphate and aliphatic carboxylic acid compounds is substantially greater than either one alone and thus a synergistic action results which makes the composition an efficient fire extinguisher for combatting all types or classes of fires.

As emphasized hereinbefore, it is essential in my invention to provide a free-flowing dry powdery chemical composition composed of monoammonium phosphate and solid organic aliphatic acidic reactant, which composition, when applied to a fire, forms a foamy, sticky mass which quickly smothers the fire. The foamy mass formed from melted monoammonium phosphate and released gases, mostly carbon dioxide, greatly increases the volume of the melt with resultant formation of a relatively thick

foamy coating which clings to the burning surfaces. To provide an efficacious fire extinguishing compoistion the minor amount of organic substances present are only those having a low molecular weight, and which produce a relatively small quantity of carbon but maximum amount of gases especially nitrogen and carbon dioxide.

While the invention has been described with particular reference to specific compositions, such as typified by the examples, it will be understood that other embodiments thereof may be made without departing from the spirit and scope of the invention and as defined in the appended claims.

What is claimed is:

1. A dry free-flowing chemical fire extinguishing composition in the form of a finely divided mixture consisting essentially of 59–93% of monoammonium phosphate, precipitated tricalcium phosphate 5%, finely divided silica 0.45%, amino acetic acid 0.5–10.0% dimethyldiethoxysilane, polymerized to form a coating on the particles of said mixture.

2. A dry free flowing chemical fire extinguishing composition in the form of a finely divided mixture of particles and consisting essentially of (A) 59–93% monoammonium phosphate, (B) 5% of tricalcium phosphate, (C) 0.5–10% of a compound selected from the group consisting of solid low molecular weight aliphatic carboxylic acids which are solid up to 140° F. and decompose at temperatures above approximately 140° F. at atmospheric pressure, and the ammonium, sodium, potassium, and calcium salts thereof, and (D) an ingredient that renders said composition free flowing, non-caking and water-repellent.

3. A composition according to claim **2**, in which (D) is a silicone resin that forms a coating on the particles, plus inert fillers that bring the composition to 100%.

4. A composition according to claim **2**, in which (D) is a filler selected from the group consisting of silica and barium sulfate, and a silicone resin that forms a coating on the particles.

5. A composition according to claim **2**, consisting essentially of (A) 59 to 93% of monoammoniom phosphate, (B) 5% of tricalcium phosphate, (C) 0.5 to 10% of a solid aliphatic carboxylic acid compound melting above 140° F. and decomposing below its sublimation temperature, and ammonium, sodium, potassium and calcium salts thereof, the balance being (D) ingredients that make said composition free flowing, non-caking and water-repellent and are selected from the group consisting of silica, barium sulfate, and a polymerized silicone resin that forms a coating on the particles.

6. The composition according to claim **5**, in which (C) is selected from the group consisting of citric acid, ammonium citrate, calcium citrate, tartaric acid, ammonium tartrate, sodium tartrate, potassium tartrate, fumaric acid, ammonium formate, malic acid, ammonium malate and amino-acetic acid.

7. A dry free-flowing chemical fire extinguishing composition in the form of a finely divided mixture of particles and consisting essentially of about 79.35% monoammonium phosphate, about 5% of tricalcium phosphate, about 12% of barium sulfate, about 2.50% of ammonium tartrate, about 0.45% of silica and about 0.70% of a mixture of approximately equal parts of dimethyldiethoxysilane and allyltrichlorosilane, polymerized to form a coating on the particles.

8. A dry free-flowing chemical fire extinguishing composition in the form of a finely divided mixture of particles and consisting essentially of about 63.35% monoammonium phosphate, about 5% of precipitated tricalcium phosphate, about 12% of finely divided barium sulfate, about 16% of finely divided ammonium sulfate, about 2.5% of finely divided ammonium citrate, about 0.45% of finely divided silica and about 0.70% of a silicone, polymerized to form a coating on the particles.

9. The method of making a dry free-flowing chemical fire extinguishing composition in the form of a finely divided mixture of particles and which comprises mixing 60 to 92% of monoammonium phosphate, 5% of tricalcium phosphate, 1 to 5% of an aliphatic carboxylic acid compound from the group consisting of citric acid, ammonium citrate, calcium citrate, tartaric acid, ammonium tartrate, sodium tartrate, potassium tartrate, fumaric acid, ammonium formate, malic acid, ammonium malate and amino-acetic acid, and a filler selected from the group consisting of barium sulfate and silica, and adding during the last stages of mixing of a monomeric silicone, and polymerizing said silicone to form a coating on the particles.

10. A method of combatting fires of burning combustible materials which comprises applying to said burning materials a solid dry chemical fire extinguishing composition in the form of finely divided particles and consisting essentially of (A) at least 59% of monoammonium phosphate, (B) up to 7% of tricalcium phosphate, (C) up to 10% of a solid aliphatic carboxylic acid compound of 1 to 6 carbon atoms melting above 140° F. and decomposing below its sublimation temperature selected from the group consisting of monocarboxylic acids, polycarboxylic acids, hydroxy substituted acids and amino substituted acids and ammonium, sodium, potassium and calcium salts thereof, and (D) ingredients that render said composition free-flowing, non-caking and water-repellent selected from the group consisting of inert inorganic fillers and silicone resins that form a coating on said particles.

11. A fire extinguishing composition as set forth in claim **2**, in which the solid aliphatic carboxylic acid compound is selected from the group consisting of ammonium citrate, ammonium tartrate, sodium tartrate, calcium citrate and citric acid.

12. A dry free-flowing chemical fire extinguishing composition in the form of a finely divided mixture, said mixture consisting of the following constituents in the approximate parts by weight given—monoammonium phosphate 90 parts, precipitated tricalcium phosphate 5 parts, glycine 2 parts, finely divided silica ½ part, and ¾ part of dimethyldiethoxysilane, polymerized to form a coating on the particles.

13. A dry free-flowing chemical fire extinguishing composition in the form of a finely divided mixture, said mixture consisting of the following constituents in the approximate parts by weight given—monoammonium phosphate 80 parts, precipitated tricalcium phosphate 5 parts, ammonium tartrate 2½ parts, finely divided fillers chosen from the group consisting of silica and barium sulfate 12½ parts, and ¾ part of a 50–50 mixture of dimethyldiethoxysilane and allyltrichlorosilane, polymerized to form a coating on the particles.

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JULIUS GREENWALD, *Primary Examiner.*

JOSEPH R. LIEBERMAN, *Examiner.*