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2,901,428

FIRE EXTINGUISHING METHOD

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The present invention relates to improved fire extinguishing compositions, and more particularly to fire extinguishing compositions containing finely divided resins obtained by condensation of aldehydes with amino compounds capable of condensation with aldehydes and to a method of extinguishing fires with such composition.

Fire extinguishing compositions which, besides water, contain foam forming materials, such as saponin or proteinaceous compounds, have been known for a long time. When such fire extinguishing compositions are applied to a fire, they form a layer of foam over the burning material which smothers the flame. Furthermore, fire extinguishing compositions are known which, in addition to water, contain crust forming materials, such as water glass, graphite, heavy spar (barite) or silicones. In use of such fire extinguishing compositions, it was found that in many instances the foam formed is soon destroyed or that the crust flakes off, so that only a poor or transient extinguishing effect is obtained. A number of powdered dry fire extinguishing compositions are also known, which usually contain a substance, such as sodium bicarbonate, which liberates carbon dioxide upon heating, which extinguishes the flame by limiting access of air thereto. This type of fire extinguishing composition, however, has the disadvantage that it does not adhere sufficiently to the burning material and consequently cannot give any long lasting protection.

In fighting fires, three general classes of fires are encountered which Underwriters' Laboratories, Inc., of Chicago, Illinois, designate as follows:

Class A fires of material such as paper, wood, textiles, rubbish and the like.

Class B fires of rapidly burning material, such as gasoline, oil or greases.

Class C fires which are electrical equipment fires.

The different natures of such classes of fires are such that up to the present time there has been no single fire extinguisher which has been listed by the Underwriters' Laboratories as suitable for all three classes of fires. Dry chemical fire extinguishers are generally approved for class B and C fires and the Underwriters' Laboratories indicate that they are not effective on deep seated fires in ordinary class A combustibles, but may have some value on incipient surface fires in such materials. The common soda-acid fire extinguishers, on the other hand, are approved for class A fires, but are not suitable for class B and C fires.

Furthermore, in the fire fighting art, there is considerable difference between extinguishing a fire in combustible material in which a fire extinguisher must be applied to the material in which combustion has already commenced and in providing combustible material with fire retardant coatings or impregnations to protect such materials from fires from an external source. In one instance, the material is already burning whereas in the other instance it is merely a question of protecting material which is not burning from the heat of a fire which might occur in the vicinity of the protected material.

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In accordance with the invention, it was unexpectedly found that many of the drawbacks of prior fire extinguishing compositions could be avoided, and an excellent fire extinguishing action could be obtained, with fire extinguishing compositions, particularly those of the dry powder type, containing foam forming substances, such as phosphoric acid and/or boric acid, or their salts or addition products, and finely divided condensation products of aldehydes, both saturated and unsaturated, with reactive amino compounds, that is those containing at least one —NH_2 group, such as, for example, urea, thiourea, guanidine, dicyandiamide and melamine. Preferably, the amino component is urea or its derivatives, such as mentioned above, and the aldehyde component is formaldehyde or acrolein, or mixtures thereof. Of course, instead of formaldehyde, materials, such as paraformaldehyde and hexamethylenetetramine, which yield formaldehyde, can be employed.

Resins suitable for the compositions in question are described in many publications, e.g., in the U.S.A. Patent 2,452,054, in the German Patents 730,357, 802,846, 803,854, 833,707, 897,408 and in the French Patents 748,854, 799,269, 43,211 and 49,184.

The fire extinguishing compositions according to the invention, when applied to burning materials, form a very adherent, tough stable carbon containing foam which prevents access of air to the burning material, and consequently extinguishes the flame and prevents the material from burning further. The foam produced also has an excellent insulating effect and consequently hinders rekindling of the combustible material. The foam probably is produced in that, under the influence of the heat of the fire, the condensation product is transformed into a viscous liquid which is transformed into a foam by the gases generated by the phosphoric or boric acid compounds. At the same time, the condensation product decomposes at least partially to produce a material rich in carbon and to produce gases which assist in the production of the foam.

The inorganic foam forming substances, such as phosphoric acid and boric acid compounds, of the fire extinguishing compositions, according to the invention, can be present in the compositions as such or in the form of their salts or addition products. Especially good results are obtained with ammonium salts of phosphoric acid which decompose at higher temperatures with the formation of ammonia and steam, which assist in the desired foam production. Also, the addition products of phosphoric acid, or boric acid, and the aldehyde condensation products have been found to give good results.

It has been found that especially good results are obtained when the fire extinguishing composition according to the invention contains 1 to about 6 parts of phosphoric or boric acids, or their compounds, per part of aldehyde condensation product.

In some instances, it has also been found desirable to increase the carbon content of the foam formed, when employing the fire extinguishing compositions according to the invention, by incorporating carbohydrates, such as starch, sugar, dextrin or cellulosic compounds, or proteinaceous materials, such as glue, casein, gelatine and other glue like proteins, in such compositions. The quantity of such carbohydrates or proteinaceous material should not exceed .7 part per part of the phosphoric acid or boric acid component.

In addition to the materials already mentioned, the fire extinguishing compositions, according to the invention, can also contain other inorganic crust forming materials in finely divided form, such as asbestos flour, kieselguhr, gypsum, barite and the like. Furthermore, they also can contain the substances employed in dry chemical fire extinguishers, such as sodium bicarbonate.

The fire extinguishing compositions, according to the invention, are preferably used in dry powder form, but they also can be employed as suspensions in water or non-combustible organic liquids, although their use may be limited to combatting certain types of fires. In the event they are employed as suspensions, it is advisable to incorporate wetting agents in order to provide for a better distribution of the liquid on the burning materials. Also, in order to render the liquid compositions more stable during storage, it is advisable to include emulsifiers or dispersing agents to prevent settling of any solid undissolved components. Preferably such dispersing agents are employed, such as Turkey red oil or saponin, which in themselves assist in foam formation.

When the fire extinguishing compositions are to be employed in dry powdered form, it has been found desirable, in some instances, to treat such composition to prevent agglomeration of the particles and insure that it remains a free-flowing powder during storage, as some of the compositions have a tendency to take up moisture from the air with agglomeration of the powdery components into lumps. The tendency of the dry compositions to become lumpy during storage can be avoided by incorporating other materials which improve the free-flowing characteristics of the powdery composition and prevent agglomeration of the particles. Suitable materials for this purpose are finely divided materials which physically prevent agglomeration of the powdery composition, for example, finely divided silicon dioxide obtained as an aerogel by vapor phase decomposition of volatile silicon compounds, for example, by hydrolysis of silicon tetrachloride in the vapor phase at temperatures of about 600° C. and above, carbon black, talcum powder or lycopodium, and materials which render the surface of the powdery materials hydrophobic, for example, water insoluble salts of the higher saturated or unsaturated fatty acids, such as magnesium, aluminum or zinc stearates or oleates, or the free higher fatty acids, their esters, waxes or other water repellent higher hydrocarbons, and silicones. The materials serving to prevent agglomeration of the dry finely divided fire extinguishing compositions are expediently incorporated in such compositions either during or after the fire extinguishing compounds are ground to finely divided form. The finely divided materials, such as silicon dioxide and the like, are preferably incorporated when the fire extinguishing components are ground. The water repellent materials can be easily incorporated in the powdery fire extinguishing compositions in the form of a dispersion or solution in volatile non-aqueous solvents. Upon drying of such mixtures, water repellent films are formed upon the individual particles of the fire extinguishing compositions. The water repellent materials can also be formed in situ on the fire extinguishing composition itself, for example, by treating the composition first with an aluminum salt and then with a fatty acid. Water repellent materials can also be applied to the fire extinguishing compositions as gases, for example, the fire extinguishing compositions can be rendered water repellent by treatment with a vapor of a silicone.

The condensation products which form an essential ingredient of the fire extinguishing compositions according to the invention can be produced separately and can, after hardening and grinding, be mixed with the other powdered components of the composition. On the other hand, the condensation products can also be produced in the presence of some or all of the other solid ingredients of the fire extinguishing compositions, and then grinding the resulting hardened mixture.

The dry powdered fire extinguishing compositions which are preferred according to the invention have not only been found admirably suited for extinguishing class B and C fires, but have also been found suited for deep seated class A fires and in the latter instance their fire extinguishing action even exceeds that of soda-acid fire extinguishers which are approved for class A fires. Fur-

thermore, the dry powdered fire extinguishing compositions according to the invention can also be used for special types of fires not coming within classes A, B and C fires, such as, for example, magnesium fires and rubber fires.

The following examples illustrate a number of fire extinguishing compositions according to the invention and the method of their use.

Example 1

A solid urea-formaldehyde resin obtained by condensing 1 mol of urea with 2.5 mols of formaldehyde in the form of paraformaldehyde in the presence of ½ mol of phosphoric acid was thoroughly ground until it passed without residue through a DIN 40 screen (1600 meshes per cm.²) and then intimately mixed in a proportion of 1:2.5 with mono ammonium phosphate of the same grain size with the addition of about 7% of powdered dextrin.

Example 2

600 grams of a solid condensation product of dicyandiamide and formaldehyde were ground together with 1200 grams of diammonium phosphate, 50 grams of boric acid and 140 grams of soluble starch until the mixture passed through a sieve having 1400 meshes per cm.² and this mixture was then mixed with 70 grams of gypsum of similar small grain size.

Example 3

500 grams of extremely finely ground fully condensed urea-formaldehyde condensation product, 90 grams of starch and 60 grams of silica aerosol were suspended in 5 liters of an aqueous solution containing 1100 grams of mono ammonium phosphate. 50 grams of a partial decomposition product of albumen and 20 grams of a wetting agent, such as sodium lauryl sulfate, and the pH of the mixture was adjusted to 6 to 7 by the addition of ammonia.

Example 4

100 grams of dimethylol urea, 200 grams of diammonium phosphate, 50 grams of soluble starch and 30 grams of kieselguhr were mixed and finely ground until the mixture passed through a sieve having 1600 meshes per cm.² The mixture was then suspended in 2 liters of carbon tetrachloride.

Example 5

300 grams of dimethylol urea, 50 grams of urea-orthophosphate, 350 grams of mono ammonium phosphate, 75 grams of asbestos flour and 150 grams of dextrin were thoroughly mixed and ground until the mixture passed through a sieve having 1600 meshes per cm.²

Example 6

A resin obtained by condensation of 1 mol of urea, 2.1 mol of formaldehyde as paraformaldehyde and 0.4 mol of acrolein in the presence of ½ mol of phosphoric acid was thoroughly ground until it is passed without residue through a DIN 40 screen (1600 meshes per cm.²) and then intimately mixed (in a proportion of 1:2.5) with mono ammonium phosphate of the same grain size with the addition of about 7% of powdered dextrin.

Example 7

600 grams of a condensation product of dicyandiamide and formaldehyde were mixed with 1200 grams of diammonium phosphate, 50 grams of boric acid, 140 grams of soluble starch and 20 grams of silica aerogel obtained by the vapor phase by hydrolysis of silicon tetrachloride at elevated temperatures and such mixture was finely ground until it passed through a sieve containing 1400 meshes per cm.² The incorporation of the silica aerogel prevented agglomeration of the dry powdery composition during storage.

Example 8

100 grams of dimethylol urea, 200 grams of diam-

monium phosphate, 50 grams of soluble starch and 30 grams of kieselguhr were mixed and finely ground until the mixture passed through a sieve containing 1600 meshes per cm.² The powdery mixture was then sprayed with a solution of 4 grams of paraffin in benzine and dried to coat the individual particles with a thin film of paraffin wax and thus render them water repellent.

Each of the compositions given in the examples above had excellent fire extinguishing qualities when applied to burning materials, as they produced a firmly adherent coating of foam which smothered the flames. The application of such compositions to the burning materials can be by any conventional methods, for example, by spraying those in liquid form or by blowing those in solid powdery form with the aid of CO₂ under pressure.

Example 9

A urea formaldehyde resin was prepared by dissolving 85 kg. of disodium phosphate in 800 kg. of 30% aqueous formaldehyde and sufficient concentrated sodium hydroxide added (about ½ kg.) to adjust the pH of the solution to 8.2. Thereupon, the solution was stirred while adding 242 kg. of urea. At the beginning, the temperature of the solution dropped, but upon initiation of the condensation it began to rise and water cooling was employed to maintain a reaction temperature not above 35° C. Stirring was continued for three hours, at the end of which the reaction mixture was in the form of a relatively thick white paste containing the precondensate. Stirring was then ceased and the mass permitted to stand overnight. During such standing, the mass became relatively solid and it was heated for about a half an hour with steam to liquify the mass sufficiently to permit operation of the stirring mechanism. As soon as the stirring mechanism operated properly, the vessel containing the mass was closed and the mass heated while stirring to a temperature of about 50 to 60° C. under vacuum of between 0.8 and 0.95 atmospheres for 8 to 9 hours to evaporate the excess water contained in the mass. Thereupon, the heated mass which had become viscid was passed into shallow pans and these were placed in a vacuum drying cupboard and allowed to remain therein for 24 hours to dry the resin further. When the resin was sufficiently dry it became very brittle and was easily removed from the pans.

The resulting resin was ground to a fine powder and 18 kg. thereof were thoroughly mixed with 0.5 kg. of magnesium stearate and this mixture was thoroughly mixed with a mixture of 93 kg. of monoammoniumphosphate and 2 kg. of magnesium stearate and thereafter 4 kg. of tricalcium phosphate, 48 kg. of starch, 4 kg. of boric acid and 32 kg. of heavy spar (barite) were added with further mixing. The resulting mixture was then ground until it passed through a sieve having 1600 meshes per cm.² and thereafter 0.4 kg. of Milori blue (coloring) and a further 1.5 kg. of magnesium stearate were added to the ground mixture and the mixture again thoroughly mixed.

The resulting mixture was of the following composition:

	Kg.
Urea formaldehyde resin -----	18
Monoammoniumphosphate -----	93
Tricalcium phosphate -----	4
Starch -----	48
Boric acid -----	4
Heavy spar -----	32
Magnesium stearate -----	4
Milori blue -----	0.4

The fire extinguishing composition thus prepared is stable over a temperature range between minus 40° F. to 120° F.

30 pounds of this powdery composition (about 13.5 kg.) were placed in a standard dry chemical fire extinguisher and blown on a wood crib class A fire in accordance with Underwriters' Laboratories specifications. The

flame was extinguished in 20 seconds and there was no evidence of embers or reignition.

In another test, 20 pounds of this powdery composition (about 9 kg.) were placed in a standard dry chemical fire extinguisher and used to extinguish the fire on a 10' x 10' wooden panel class A fire in accordance with Underwriters' Laboratories specifications. Two spots were not completely extinguished and a second fire extinguisher containing 20 pounds of the powdery composition was used and the fire was extinguished after using about 10 pounds, so that the fire was totally extinguished with a total of 30 pounds of the composition according to the invention.

In still another test, and 800 x 15 automobile rubber tire was placed on the ground and the open center was filled with rubber linings, slit rubber inner tubes and the whole sprayed with gasoline and ignited. The fire was allowed to burn until the entire mass was completely involved, giving off tremendous heat. A 30 pound standard dry chemical fire extinguisher filled with the powdery composition according to the invention was employed and the fire was extinguished in 12 seconds. The full discharge of the 30 pounds fire extinguisher into the mass of hot rubber prevented reignition.

This application is a continuation-in-part of my pending application Serial No. 430,438, filed May 17, 1954, now abandoned.

I claim:

1. A method of combatting fires of burning combustible material which comprises applying to said burning combustible material a solid dry chemical fire extinguishing composition comprising a finely divided solid urea formaldehyde condensation product and a solid finely divided ammonium phosphate, the proportion of the condensation product to said phosphate being between 1:1 and 1:6.

2. A method of combatting fires of burning combustible material which comprises applying to said burning combustible material a solid dry chemical fire extinguishing composition comprising a finely divided solid urea-formaldehyde condensation product in which the ratio of urea to formaldehyde resin is 1 mol of urea per 2 to 2.5 mols of formaldehyde, and a solid finely divided ammonium phosphate, the proportion of the resin to said phosphate being between 1:1 and 1:6.

3. A method of combatting fires of burning combustible material which comprises applying to said burning combustible material a solid dry chemical fire extinguishing composition comprising a powdered solid condensation product of an aldehyde selected from the group consisting of formaldehyde and acrolein and an amino compound selected from the group consisting of urea, thio-urea, guanidine, dicyandiamide and melamine in admixture with at least one solid finely divided foam forming material selected from the group consisting of ammonium phosphates, boric acid and boric acid salts, the proportion of the condensation product to said material being between 1:1 and 1:6.

4. The method according to claim 3 in which the solid dry chemical fire extinguishing composition contains a finely divided solid carbohydrate selected from the group consisting of starch, sugar, dextrin and cellulosic compounds in a quantity less than 0.7 part per part of said foam forming material.

5. The method according to claim 3 in which the solid dry chemical fire extinguishing composition contains a finely divided solid proteinaceous material selected from the group consisting of glue, casein, gelatine and other glue-like proteins in a quantity less than 0.7 part per part of said foam forming material.

6. The method according to claim 3 in which the surfaces of the individual grains of the solid dry chemical fire extinguishing composition are water repellent.

7. The method according to claim 3 in which the individual grains of the solid dry chemical fire extinguishing

composition carry a film of a water insoluble salt of a higher fatty acid to render them water repellent.
 8. The method according to claim 3 in which the individual grains of the solid dry chemical fire extinguishing composition carry a film of paraffin to render them water repellent.

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