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DRY-TYPE FIRE-EXTINGUISHER COMPOSITION WITH HIGH ELECTRICAL RESISTANCE

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ABSTRACT OF THE DISCLOSURE

Fire-extinguisher composition in the form of a dry powder containing, in addition to conventional constituents, a mixture of formaldehyde-cresol resin and asbestos powder, the asbestos/resin mixture constituting up to one-fifth by weight of the total.

This application is a continuation-in-part of application Ser. No. 470,591, filed July 8, 1965 now abandoned.

My present invention relates to fire-extinguisher compositions stored and distributed in the form of a powder.

It has long been known that pulverulent fire-extinguisher compositions, containing sodium bicarbonate, are very effective. The sodium bicarbonate has been found, when used to extinguish fire, to exert thereon a negative catalytic action of a heterogeneous character, the so-called wall effect, which inhibits the chain reactions involved in the propagation of fires. More recently, other fire extinguishers in powder form have been made available which contain ammonium phosphate and ammonium sulfate and which are capable of extinguishing fires by evolution of ammonia; the latter also acts as a negative catalyst in the chain reaction of combustion but its action, because of the vapor state of the active substance, is of a homogeneous rather than a heterogeneous character. Moreover, when the mixture of inorganic salts is thrown into a fire, the composition melts and acts as a screen to keep the atmospheric oxygen away from the cinders and the combustibles, so that the quenching action of the powder is due to the combined effect of the ammonia vapors and the molten-salt barrier to atmospheric oxygen.

Although considerable progress has been made in the preparation of pulverulent fire-extinguisher compositions, preparations available up to now still leave a great deal to be desired. Thus, they are not universally applicable and, for example, may fail in the case of electric fires due to low electrical resistance; another disadvantage of the conventional powders is their tendency to agglomerate upon hygroscopic absorption of water.

One object of this invention is the provision of powder which is highly effective in extinguishing fires of any type or origin, including electrical short circuits and those involving organic fluids such as gasoline, oil or natural gas.

Another object of my invention is to provide a fire extinguisher which is inexpensive, which may be stored even at elevated temperatures (e.g. up to about 60° C.) without deterioration (e.g. evolution of gas), which is not poisonous, and which has no tendency to cake or form lumps on standing and, therefore, has a substantially non-hygroscopic character.

A further object is the provision of a dry-type fire-extinguisher composition which may be easily comminuted to the appropriate particle size for easy spreading over a fire.

Still another object of this invention is the provision of a powdered fire extinguisher which does not decompose even when subjected to high voltage, e.g. up to 100,000 volts.

A more particular object of my invention is to provide a composition which, both in its pulverulent state and upon melting at the heat of combustion, has an extremely high electric resistance.

It is also an object of my invention to provide a method of rendering a fire-quenching powder substantially non-conductive electrically.

I have found, in accordance with this invention, that admixture of a combination of formaldehyde-cresol resin and asbestos powder with an otherwise conventional powdered fire extinguisher reduces the electric conductivity of the material, in both its comminuted form and in a molten state, to a surprising extent. Specifically, I have determined that the electric resistance of the basic material is raised thereby to about 10^7 times its original value, provided that the mixture is substantially free from sodium bicarbonate. The use of the formaldehyde-cresol resin/asbestos admixture also markedly reduces the hygroscopicity of the dry-type extinguisher material and renders it suitable for use in fuses or the like as a spark quencher as well as for direct application to burning material. The product can be stored at temperature of 60° C. higher for prolonged periods without deterioration.

The basic powder preferably consists of one or more ammonium compounds, such as ammonium sulfate, monoammonium phosphate, diammonium phosphate or mixtures thereof. Best results are obtained when the ammonium phosphate component is in excess of 60% by weight of the basic powder while the ammonium sulfate content is greater than 10% by weight. Other suitable ingredients include ammonium chloride, ammonium bromide, barium sulfate, melamine (German Auslegeschrift 1,138,323), formaldehyde-urea resin (U.S. Patent No. 2,901,428) and formaldehyde-dicyandiamide resin (U.S. Patent No. 2,901,428). The inclusion of fillers and other additives known per se, such as sulphur, or sodium sulphite, is also possible. Stearic or silicic acid, as well as their salts, may be added in amounts from, say, 0.25% to about 10% by weight in total to improve the hydrophobic property of the mixture.

The resistance-increasing admixture according to the present invention may include between substantially 5 and 95% by weight of its two essential ingredients, i.e. comminuted formaldehyde-cresol resin and asbestos powder with either predominating; best results are obtained when these ingredients are present in approximately equal parts by weight, and departures up to a ratio of about 2:1 (with either ingredient predominating) yield similar suitable results. The amount of admixture preferably ranges between substantially 2 and 20% by weight of the basic powder.

The cresol-formaldehyde resins suitable for use in accordance with the present invention are the well-known stage C resins which are nonthermosoftening and temperature-stable to the highest degree. In general, the cresol-formaldehyde resin are prepared by mixing equimolar quantities of cresol and formaldehyde and then possibly adding to the mixture asbestos powder when, as indicated hereinafter, the additive to the fire-extinguishing mixture is to receive a single powder made up of both the resin and the asbestos. As noted hereinafter, between 5 and 95% of the mass may consist of finely divided asbestos powder thoroughly dispersed in the resin. The polymerization of the resin is catalyzed by acid (hydrochloric acid) or hexamethylenetetramine in the usual manner and is heated through the second-stage transformation to form a solid, stage C cured resin body. The body may be abraded and if it contains the asbestos powder as indicated, the resulting powder can be added in an amount of 2 to 20% to the basic powder as described previously. Best results are obtained when 5–10% by weight of the mixture is made up of the cresol-formaldehyde resin/asbestos com-

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posite. When it is desired to mix the asbestos powder and cresol-formaldehyde resin powder together and then add the mixture to the basic powder, the stage-C resin is cast as indicated earlier and comminuted to a powder (e.g. 50 to 200 U.S. mesh).

I have also found that a market improvement in the flowability and the moisture resistance of the fire-extinguishing powder can be obtained when the cresol-formaldehyde resin and asbestos are added as a single composition to the basic powder by comparison with a system in which individual resin and asbestos-powder ingredients are used. In fact, I have found that powder obtained as detritus or residues of the manufacture of brake linings for automotive-vehicle brake systems, insulation, floor coverings and the like, constituted from a cresol-formaldehyde resin and asbestos meal. In this case, the composite powder is added to the basic powder to make up 5–10% by weight of the fire-extinguishing mixture.

EXAMPLE I

(All quantities being given in parts by weight)

35 parts of diammonium phosphate, 17.5 parts of ammonium sulfate, 35 parts of monammonium phosphate are blended and comminuted to a particle size of about 0.1 mm. and less. The blend is then dried for at least six hours at a temperature not exceeding 60° C. Next, 7 parts of a 1:1 mixture of similarly comminuted stage C formaldehyde-cresol resin (prepared as indicated earlier) and asbestos powder is added together with 3 parts of tricalcium phosphate, 2 parts of magnesium stearate and 0.5 part of a suitable colorant. All the ingredients are thoroughly mixed and then packaged.

It will be noted that, in the foregoing example, the parts by weight of all the ingredients add up to 100 so that they can also be regarded as percent by weight. Possible variations are between about 20 and 70% for the diammonium phospate and also for the monoammonium phosphate, between about 5 and 35% for the ammonium sulfate and, as noted above, between about 2 and 20% for the mixture of formaldehyde-cresol/asbestos powder. The tricalcium phosphate may be present in a range between approximately 1 and 10% whereas the magnesium stearate could account for about 0.2 to 4%. The colorant, which in some cases could also be omitted, should amount to not more than about 1% and can be an inorganic pigment. Naturally, an increase in the quantity of one ingredient will be at the expense of one or more of the other ingredients, the foregoing values indicating merely permissible individual minima and maxima.

While it is preferred that the composition contain ammonium phosphates and ammonium sulfate in addition to the formaldehyde-cresol/asbestos component, it is also possible to make use of conventional dry-type fire-extinguishing material absent ammonia-containing salts or containing small quantities thereof. In all cases, however, the basic powder should be free from sodium bicarbonate.

I list below a number of dry-type fire-extinguishing powders which can be used individually or in mutual admixture together with between 2 and 20% of the composition weight and, preferably between 5 and 10% by weight, of the formaldehyde-cresol/asbestos powder. With the addition of the latter component to any of these powders and to mixtures of them, the electrical resistance is sharply increased both in the dry state of the powder and its molten state; moreover, tendencies to agglomerate appear to be completely eliminated .

EXAMPLE II

Following the technique described in Example I, a fire-extinguishing basic powder was prepared from the following materials:

	Parts by weight
Diammonium phosphate	30
Monoammonium phosphate	36
Ammonium sulfate	22
Barium sulfate	12
Magnesium stearate	1
Tricalcium phosphate	2
Formaldehyde-urea resin (U.S. Patent No. 2,901,428)	1
Finely divided silica	1
Ammonium bromide	2
Milori-blue pigment	1

This powder is combined with between 2 and 20% by weight of the formaldehyde-cresol/asbestos powder consisting of between 5 and 95% of asbestos powder with the balance stage C formaldehyde-cresol resin prepared as described above. The improved fire-extinguishing, electrical and storage properties described above were obtained.

EXAMPLE III

The basic powder consisted of:

	Parts by weight
Monoammonium phosphate	66
Ammonium sulfate	26
Barium sulfate	8
Magnesium stearate	1
Tricalcium phosphate	1
Finely divided silica	1
Formaldehyde-dicyandiamine resin (U.S. Patent No. 2,901,428)	4

This powder was mixed with a stage C formaldehyde-cresol/asbestos component prepared as previosly described of the composition and in the proportions indicated in Example II.

EXAMPLE IV

The basic powder consisted of:

	Parts by weight
Melamine resin (German Auslegeschrift 1,138,323)	60
Diammonium phosphate	25
Tricalcium phosphate	13
Magnesium stearate	2

The additive of the present invention was admixed with the powder as described in Example II.

In place of the two-ingredient powder of the preceding examples, the formaldehyde-cresol/asbestos component is constituted by a powder residue obtained from composite manufacture in the production of brake linings, floor coverings and insulation. In such systems, the composite is made with approximately 30% to 50% by weight asbestos distributed in the formaldehyde-cresol resin constituting the balance of the composition. The formaldehyde-cresol resin is prepared by acid catalysis and after mixture of the asbestos meal therewith is cast and heat-cured until the stage-C resin is obtained. The mass is used for floor coverings, self-supporting insulation for low-temperature applications and brake linings and can be laminated or cast to the desired shape. The dust particles formed during the production of these articles, e.g. upon sawing, are collected and the fraction passing a screen of 1600 mesh per $cm.^2$ is added to any of the mixtures of Examples II–IV in an amount ranging from 5 to 10%. The resulting product has improved flowability and moisture resistance by comparison with the product using formaldehyde-cresol powder and asbestos powder in mutual admixture. The electrical breakdown and resistance properties and flame-quenching character remain undiminished.

A comparative test was made between a composition identified as I and containing 10% of a 1:1 mixture of

formaldehyde-cresol powder and asbestos powder by weight (the basic powder being that given in Example I) and a composition II which is identical in all respects except that 10% by weight of a composite formaldehyde-cresol/asbestos powder (1:1 by weight) and prepared as described in the immediately preceding paragraph is used.

The flowability test involved an hourglass-type apparatus in which 300 g. of the powdered compositions were placed in a narrow-neck Erlenmeyer flask with the volume of 500 ml. The powder was permitted to flow into a second Erlenmeyer flask attached to the first when the assembly was inverted. Ten measurements each for the compositions I and II were taken and the average in the case of composition I for complete passage of the powder was 6 to 8 seconds whereas the average for composition II was 4–6 seconds.

The composition II was also found to have increased rate of dispersion from a fire extinguisher. In this test, 4 kg. of each composition were placed in a pressure-retaining vessel charged with nitrogen at 10 kp./cm.^{2}. The powder is discharged through a coiled tube having a total length of 6 m. with an internal diameter of 8 mm. The composition I was discharged at a rate of about 50–60 g./second while the composition II discharged at 60–70 g./second. Storage tests for one month on a vibrating tray showed that the powder of composition II absorbed less moisture than the powder of composition I.

The basic extinguishing powder is of the type previously disclosed in U.S. Patent No. 2,901,428 and the German publications or Patent Nos. 1,090,963 and 1,138,323, all such basic powders being adapted to be used with the additive of the present invention to yield the improved composition described above.

The invention as described is believed to admit of other modifications, e.g. to use powders other than those found above to be optimum with the additives of the present invention, without the exercise of independent invention; these modifications will be readily apparent to those skilled in the art and are intended to be included within the spirit and scope of the appended claims.

I claim:

1. A fire-extinguisher composition with low hygroscopicity and high electrical resistance in molten and in powder states, said composition being free from sodium bicarbonate and consisting in major part of at least one extinguishing substance selected from the group which consists of ammonium phosphates, ammonium sulfate and melamine resin, and between substantially 2 and 20% by weight of a stage-C formaldehyde-cresol resin/asbestos powder component in intimate admixture with said substance, said component consisting essentially of 5 to 95% by weight asbestos, the balance being constituted by said formaldehyde-cresol resin.

2. The composition defined in claim 1 wherein said component constitutes between substantially 5 and 10% by weight of the composition.

3. The composition defined in claim 1 wherein said substance comprises between substantially 20 and 70% by weight of monoammonium phosphate or diammonium phosphate.

4. The composition defined in claim 1 wherein said substance comprises between substantially 5 and 35% by weight of ammonium sulfate.

5. The composition defined in claim 1 wherein said substance is admixed with between substantially 1 and 10% by weight of tricalcium phosphate.

6. The composition defined in claim 1 wherein said substance is admixed with between substantially 0.2 and 4% by weight of magnesium stearate.

7. The composition defined in claim 1 wherein said substance compirses between 50 and 98% by weight of melamine resin.

8. The composition defined in claim 1 wherein said component consists of a powder made by comminuting a formaldehyde-cresol resin body containing asbestos meal.

9. The composition defined in claim 1 wherein said component is a mixture of formaldehyde-cresol powder with asbestos powder.

10. A method of making a fire-extinguisher composition as defined in claim 1, comprising the steps of forming a body of stage-C formaldehyde-cresol resin and asbestos meal and consisting essentially of 5 to 95% by weight asbestos meal, the balance being formaldehyde-cresol resin; comminuting said body to form a powdered stage-C formaldehyde-cresol resin/asbestos component; and maxing between 2 and 20% by weight of said component with a powder free from sodium bicarbonate and consisting in major part of at least one extinguishing substance selected from the group which consists of ammonium phosphate, ammonium sulfate and melamine resin and constituting the balance of said fire-extinguisher composition.

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