United States Patent [19]

Endler

[11] **3,819,518**

[45] **June 25, 1974**

[54] **SCORCH-RESISTANT WATER-SOLUBLE FLAME-RETARDANTS FOR CELLULOSE**

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[22] Filed: **July 31, 1972**

[21] Appl. No.: **276,888**

[52] **U.S. Cl.** ..... **252/8.1,** 8/116 P, 117/137, 161/403

[51] **Int. Cl.** **C09k 3/28**

[58] **Field of Search** ..... 161/403; 8/116 P; 252/8.1

[56] **References Cited**

UNITED STATES PATENTS

3,513,114	5/1970	Hahn et al.	252/8.1

FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

Cellulosic materials are made flame retardant, while minimizing the scorching and loss of strength of such materials when heated, by applying thereto a composition, preferably in aqueous solution, consisting essentially of at least one sodium or potassium salt of orthophosphoric acid or the various polymeric phosphoric acids, and at least one guanidine, guanylurea or biguanide salt of hydrochloric, hydrobromic, sulfuric, sulfamic or phosphoric acid, with the proportion, by weight, of the sodium or potassium salt to the guanidine, guanylurea or biguanide salt being in the range from 1:5 to 5:1, and with the total dry add-on of the composition being from 5 to 30 percent of the weight of the cellulosic material being treated therewith. The guanidine, guanylurea or biguanide salt constituent of the flame retardant composition may be provided in the form of the product of the condensation reaction of dicyandiamide with at least one of ammonium chloride, bromide, sulfamate or sulfate.

4 Claims, No Drawings

SCORCH-RESISTANT WATER-SOLUBLE FLAME-RETARDANTS FOR CELLULOSE

This invention relates generally to flame retardants for application to cellulosic materials, for example, in the form of fibers, yarns, fabrics, papers, paperboard, films and other structures, and more particularly is directed to flame retardants which minimize the scorching or other discoloration and the loss of strength of the treated materials caused by exposure to heat.

A number of ammonium salts of inorganic acids are known to be effective as flame retardants when applied to cellulose fibers. Among the salts well known to be effective are diammonium phosphate, monoammonium phosphate, ammonium sulfamate, ammonium bromide, ammonium chloride, and ammonium sulfate. In general, all of these compounds cause cotton and rayon fabrics, which of course, are composed of cellulose fibers, to turn brown, and lose most of their tensile strength when the treated fabrics are heated for as little as thirty seconds at 400°F., or for only slightly longer periods at lower temperatures, for example, for two minutes at 350°F. Since there are a number of commercially important processes which require that fabric, or other structures containing cellulose fibers, be heated for varying times at elevated temperatures, this loss of strength and discoloration are serious disadvantages of these flame retardants. A number of not wholly satisfactory expedients have been proposed in order to ameliorate the situation. For example, U.S. Pat. No. 2,935,471, discloses the use of nitrogenous buffers, such as urea, together with borate compounds, in conjunction with ammonium salts, such as, diammonium phosphate and ammonium sulfamate. Others have simply proposed combining alkaline buffers, such as borax, with the ammonium salt being used. These expedients are of distinct value, but still permit serious strength loss and serious scorch discoloration of the treated cellulose when the latter is heated for as little as 30 seconds at 400°F.

It is also known to employ various boron-containing mixtures or compounds, such as, borax-boric acid mixtures and sodium polyborate compounds, as flame retardants for cellulose. Although these boron-containing mixtures or compounds do not cause scorching or discoloration of the treated cellulose upon heating of the latter, these flame retardants do cause substantial embrittlement and loss of tensile strength when applied to cotton and/or rayon fabircs. Therefore, the boron-containing compounds and mixtures have little, if any, utility as flame retardants for cellulosic fabrics and their use has been practically restricted to lumber.

It is also known to use guanidine salts of phosphoric, sulfuric, hydrobromic, sulfamic, and other acids as flame retardants for fabrics composed of cellulose. For example, in "An Introduction to Textile Finishing," by J.T. Marsh, published 1950 by Chapman & Hall, Ltd., London, at page 525, quanidine phosphate is included in a listing of so-called fireproofing agents for cotton. The guanylurea salts of the previously mentioned acids have also been proposed as flame retardants for fabrics composed of cellulose. However, these guanidine or guanylurea salts of the listed inorganic acids require fairly high add-ons in order to be effective as flame retardants on materials composed of cellulose and, when used in that manner, are insufficiently resistant to scorching or discoloring at elevated temperatures, for example, as shown specifically in Example II below, and thus are unsuitable for many purposes.

In "Flameproofing Textile Fabrics," Robert W. Little, Reinhold Publishing Corp. 1947, at page 172, the flame retardancies of the sodium salts of orthophosphoric acid are listed. Such listing shows that trisodium phosphate permits a cotton fabric treated therewith to burn completely in the vertical flame test even when a 77 wt. percent dry add-on of the trisodium phosphate is employed. Thus, the trisodium phosphate is ineffective as a flame retardant for cellulosic fabrics in any useful add-on. The disodium phosphate is also shown to be ineffective as a flame retardant, as a 57 wt. percent dry add-on thereof still permitted complete burning of the treated cotton fabric. On the other hand, the acid salt, that is, monosodium phosphate, is shown to be moderately effective as a flame retardant. The foregoing is not surprising as it has been generally well known to those skilled in the art of flameproofing cellulose that acids or acidic salts are frequently the most effective fire retardants. Unfortunately, however, the characteristic of acidity also causes the cellulose impregnated with the chemical to become more sensitive to heat than untreated cellulose, and to scorch more easily when subjected to elevated temperatures. The foregoing is true in respect to fabrics of regenerated cellulose and paper or paperboard composed mostly of cellulose fibers, as well as in respect to cotton fabrics.

Accordingly, it is an object of this invention to provide water-soluble substances which are effective as flame retardants for cellulosic materials in practically useful addons, and which result in less sensitivity to heat of the treated cellulosic materials than the previously available flame retardants.

In accordance with this invention, materials of cellulose or regenerated cellulose are made substantially flame retardant without unduly increasing the heat sensitivity of the treated material by treating the cellulosic material with a composition, preferably in aqueous solution, consisting essentially of at least one sodium or potassium salt of phosphoric acid, that is, orthophosphoric acid, or of the various polymeric phosphoric acids, such as, pyrophosphoric acid, triphosphoric acid and metaphosphoric acid, and at least one guanidine, guanylurea or biguanide salt of hydrochloric, hydrobromic, sulfuric, sulfamic or phosphoric acid.

The last mentioned constituent of the flame retardant composition according to this invention may be provided in the form of the product of the condensation reaction of dicyandiamide with at least one of ammonium chloride, bromide, sulfamate and sulfate, which condensation product is believed to be, for the most part, the guanidine salt of the acid or acids in the ammonium salt reactant. Such condensation product may also contain distinct proportions of guanylurea salts, and possibly even small amounts of biguanide salts, of the acid in the respective ammonium salt reactant, as well as traces of other related compounds. It has been found that the presence of minor amounts of such compounds other than the guanidine, guanylurea and biguanide salts, does not alter the effectiveness of the described condensation products in the flame retardant compositions according to this invention. The condensation reaction is preferably conducted at elevated temperatures, for example, in the range between about 110°C. and 160°C., and preferably involves approxi-

mately from 1 to 2 equivalent weights of the ammonium salt reactant for each mole of the dicyandiamide. In the foregoing, the term "equivalent weight" is intended to mean the molecular weight divided by the number of ammonium groups per molecule of the ammonium salt.

The sodium or potassium salt of orthophosphoric acid or the various polymeric phosphoric acids used in the flame retardant compositions according to this invention are preferably those which, in a 10 percent aqueous solution, provide a pH from approximately 5.2 to 11.1. Thus, for example, commercial sodium hexametaphosphate, which provides a pH of about 5.5 in a 10 percent aqueous solution, and commercial tetrasodium pyrophosphate, which provides a pH of about 11.0 in a 10 percent aqueous solution, may be used in compositions according to the invention which give satisfactory results, both as to flame retardancy and heat sensitivity of the treated cellulosic material. In any particular case, the use of a sodium salt or of a potassium salt may be dictated by reasons of cost, solubility, softness of the treated fabric, or other such reasons which are not connected with the effectiveness of the treatment as a flame retardant or in reducing heat sensitivity. In general, since the potassium salts have a higher formula weight than the corresponding sodium salts, it is necessary to use a proportionally larger amount of the potassium salts than of the sodium salts in order to achieve comparable results. Further, since the potassium salts are normally more costly than the sodium salts the latter will be usually preferred. However, in some cases, the relatively higher solubility of the potassium salts may make their use preferable to the use of the corresponding sodium salts, as when a relatively high concentration of the active components is required in the flame retardant solution with which the cellulosic material is to be treated.

In the composition or mixture of water-soluble substances used as a flame retardant in accordance with this invention, the first essential substance selected from among the sodium and potassium salts of orthophosphoric acid and the various polymeric phosphoric acids and the second essential substance selected from among the guanidine, guanylurea and biguanide salts of hydrochloric, hydrobromic, sulfuric, sulfamic and phosphoric acids and the reaction product of dicyandiamide with ammonium chloride, bromide, sulfate or sulfamate, may be present in the proportions, by weight, lying in the range from 1:5 to 5:1, that is, from 1 to 5 parts, by weight of the first substance and from 1 to 5 parts, by weight, of the second substance. In dependence upon the degree of fire retardancy that is desired and the extent to which changes in the hand or feel of the fabric may be tolerated, the dry add-on of the composition according to the present invention may be in the range between 5 and 30 weight percent, based on the weight of the cellulosic material.

The effectiveness of the mixtures or combinations of substances used as flame retardant compositions according to this invention is quite surprising in view of the fact that the mentioned sodium and potassium salts of phosphoric acid and of polymeric phosphoric acids are, by themselves, quite ineffective as flame retardants for cellulosic materials, for example, as specifically shown in Example I below. Further, although the other component of the mixture or combination, that is, the guanidine, guanylurea and biguanide salts of the mentioned inorganic acids are known as fire retardants, such substances, when used alone, require a fairly high add-on to be effective and further render the treated materials too sensitive to heat for most purposes, for example, as shown specifically in Example II below. Therefore, it is truly surprising that the addition of the sodium or potassium salt of a phosphoric acid to the guanidine, guanylurea or biguanide salt of one of the specified inorganic acids very much reduces the add-on of the latter that is required for effective flame retardance. Thus, the amount of the relatively expensive guanidine or other related salt required for effective flame retardance is reduced for lowering the cost of the treatment as compared with a treatment using the guanidine or the related salt alone. Further, the combination of the sodium or potassium salt of a phosphoric acid with a guanidine or related salt of an inorganic acid, as specifically described above, is effective to very greatly reduce the sensitivity to heat of the treated materials, whereby materials treated according to this invention are strongly resistant to scorching.

In determining the sensitivity to heat of fabrics or other cellulosic materials treated with flame retardants in the following examples, a common heat sensitivity test has been employed which involves subjecting the treated material to hot air in an oven at 400°F. for one minute and then observing or noting the resulting scorching or discoloration, if any, of the treated material as compared with that of the untreated cellulosic material when similarly tested.

The effectiveness of the various flame retardants has been determined by standard tests, as follows:

a. The so-called vertical test identified as AATCC No. 34–1969 and in which a fabric or paper swatch or specimen measuring 2.75 inches by 10 inches is held vertically in a metal frame leaving a 2 inch width of the specimen exposed, and the lower edge of the specimen is ignited by a yellow Bunsen flame, whereupon the vertical extent of the specimen that is burned is measured. If the specimen burns along its entire length, which condition is hereinafter indicated as BEL, it is not considered effectively flame retardant. Obviously, the shorter the distance along the specimen that is burned, the more effective is the flame retardant with which the specimen has been treated.

b. The so-called horizontal test according to Federal Test Method Standard No. 191, Method 5906, in which a fabric specimen is held in a horizontal position and ignited at one end, whereupon the rate at which specimen burns over a length of 10 inches or less is measured.

The invention will now be further described with reference to the following specific examples which are merely illustrative:

EXAMPLE I

Individual specimens or pieces of 80 by 80 cotton print cloth weighing 4 ounces per yard were impregnated with the following aqueous solutions so as to obtain approximately 110 wt. percent add-on in each case:

1. 15 wt.% Disodium Phosphate
2. 20 wt.% Dipotassium Phosphate
3. 15 wt.% Tetrasodium pyrophosphate
4. 20 wt.% Tetrapotassium pyrophosphate
5. 15 wt.% Sodium triphosphate (commonly known as sodium tripolyphosphate)

6. 20wt.% Potassium triphosphate
7. 30 wt.% Sodium hexametaphosphate
8. 30 wt.% Potassium hexametaphosphate

The fabric specimens were dried in a circulating air over at 275°F. for 6 minutes, and were then tested for flame retardance as described above. In all cases the fabrics burned the entire length, indicating that the salt solutions identified at (1)–(8) are all ineffective to impart flame retardancy to the cotton specimens when used alone.

The above tests were repeated with the solutions (1)–(8) impregnating specimens of 4 ounce per yard in viscose rayon taffeta fabric, 11 lb. tissue paper and 40 lb. paper cover stock, and with the same results, that is, the specimens burned the entire length in all cases.

EXAMPLE II

Various aqueous solutions of guanidine sulfamate were applied to 4 ounce cotton print cloth, using the same type of impregnation as in Example I, namely, approximately 110 wt.% wet add-on of each solution, and drying for 6 minutes at 275°F. It was found that a 10 wt.% solution permitted the fabric to burn its entire length; a 15 wt.% solution showed a 7 inch charlength; and a 20 wt.% solution showed a 2.5 inch char-length.

The cotton fabric specimens, impregnated with the varying amounts of guanidine sulfamate indicated above were subjected to the previously described usual test for determining sensitivity to heat, that is, each specimen was subjected to a temperature of 400°F. for one minute in a circulating air oven. In all cases, the fabric specimens impregnated or treated with guanidine sulfamate showed appreciable yellowing in response to the heating thereof, with the specimens treated with the largest amount of guanidine sulfamate, that is, impregnated with the 20 wt.% solution, showing the darkest discoloration.

EXAMPLE III

The following solutions in accordance with the invention were prepared:

a. 10 wt.% guanidine sulfamate, 5 wt.% sodium triphosphate, and the remainder water.

b. 10 wt.% guanidine sulfamate, 5 wt.% sodium hexametaphosphate, and the remainder water.

c. 10 wt.% Guanidine sulfamate, 7 wt.% potassium triphosphate, and the remainder water.

d. 10 wt.% Guanidine sulfamate, 5 wt.% disodium phosphate, and the remainder water.

The above solutions (*a*)–(*d*) were each applied to specimens of 4 ounce rayon woven fabric to provide a 110 wt.% wet add-on in each case, whereupon the specimens were dried at 275°F. for 6 minutes. When subjected to the previously described flame retardant vertical test, all of the treated fabrics were found to be fire-retardant and showed char-lengths of from 2 to 3 inches in all cases. Further, when subjected to the described heat-sensitivity test, that is, to heating at 400°F. for one minute in the circulating air oven, all of the treated specimens showed only very slight discoloration.

The above flame retardant vertical test was repeated on similar cotton fabric specimens also impregnated to provide a 110 wt.% wet add-on and then dried, as described, but using the following solutions:

e. 7.5 wt.% Guanidine sulfamate, 7.5 wt.% sodium triphosphate, and the remainder water.

f. 7.5 wt.% Guanidine sulfamate, 5.0 wt.% sodium triphosphate, and the remainder water.

It was found that solutions (e) and (f) did not provide effective flame retardancy under the strict vertical test in that the specimen impregnated with solution (e) showed a 9 inch charlength and the specimen impregnated with solution (f) burned its entire length. This shows that, for the 1:1 or 1 ½: 1 proportions of guanidine sulfamate and sodium triphosphate, solutions (e) and (f) did not provide an adequate dry add-on of these compositions when applied with a wet add-on of 110 wt.% to withstand the vertical test. However, when cotton fabric specimens impregnated with 110 wt.% wet add-ons of solutions (e) and (f) were subjected to the previously mentioned horizontal test, each specimen burned only about 1 ½ inches along its length and this is accepted as sufficient flame retardancey under the less stringent horizontal test. In this connection, it should be noted that the untreated cotton fabric specimens burned at a rate of about 5.5 inches per minute over the full 10 inch length when subjected to the horizontal test.

Although the guanidine sulfamate component of the guanidine sulfamate-sodium triphosphate composition is the one which, when applied alone, has flame retardant properties and, in spite of the fact that sodium triphosphate alone is shown by Example I to be ineffective as a flame retardant, it has been found that compositions having the same, or even a lesser amount of guanidine sulfamate than in the solutions (e) and (f) can be made truly effective flame retardants under the vertical test merely by increasing the amount of sodium triphosphate in the compositions. Thus, for example, additional cotton fabric specimens were impregnated with 110 wt.% wet add-ons of the following solutions:

g. 7.5 wt.% Guanidine sulfamate, 10 wt.% sodium triphosphate, and the remainder water.

h. 5.0 wt.% Guanidine sulfamate, 15 wt.% sodium triphosphate, and the remainder water.

After drying, and when subjected to the described vertical flame retardant test, the specimen impregnated with solution (g) showed only a 2 inch char-length as compared with the 9 inch char-length of the specimen impregnated with solution (e) which contained the same amount of guanidine sulfamate. The specimen treated with solution (h) also showed only a 2 inch char-length, even though the amount of guanidine sulfamate is smaller than that in solutions (e) and (f).

In order to determine approximately the lower limit of the dry add-ons of the guanidine sulfamate-sodium triphosphate composition required to impart appreciable flameretardant properties to 4-ounce woven cotton fabric, specimens of such fabric were impregnated with 110 wt.% wet add-ons of the following solution:

i. 4.0 wt.% Guanidine sulfamate, 2 wt.% sodium triphosphate, and the remainder water.

After drying, and when subjected to the described horizontal test for flame retardant properties, the specimen impregnated with solution (i) burned for only 1 ½ inches from its ignited end, that is, experienced self-extinguishing after burning only 1 ½ inches from its ignited end. However, when the amount of guanidine sulfamate in solution (i) was further reduced to 3.0 wt.% and the tests repeated, the cotton fabric specimen burned at the rate of 5 inches per minute which is only

slightly less than the rate of burning for this fabric in the untreated state.

It should be noted that the amount of fire retardant required to impart fire retardant properties to fabric is generally reduced as the weight of the fabric is increased. Thus, it may be expected that woven cotton fabric specimens heavier than the 4-ounce fabric tested will require even slightly smaller dry add-ons of the compositions according to this invention than are indicated above.

EXAMPLE IV

In order to determine the importance of using a guanidine or related salt in compositions according to this invention rather than the more commonly used ammonium salt, a cotton specimen was impregnated with a 110 wt.% wet add-on of the following solution:

5.0 wt.% ammonium sulfamate, 15 wt.% sodium triphosphate and the remainder water.

After drying the specimen, as previously described, the specimen was subjected to the flame retardant vertical test and burned its entire length (BEL), which is to be compared with Example III(h) according to this invention showing only a 2 inch char-length in the case of a composition containing the same amount of guanidine sulfamate in place of the ammonium sulfamate of the present example.

EXAMPLE V

Specimens of cotton fabric and of rayon fabric were impregnated with 110 wt.% wet add-ons of 20 wt.% aqueous solutions of guanidine hydrochloride. When such specimens were dried, as previously described, and then subjected to the flame retardant vertical test, each of the specimens burned its entire length (BEL). Further, when subjected to the heat sensitivity test, each of the treated specimens showed considerable darkening

EXAMPLE VI

The experiments of Example V were repeated, but using each of the following solutions:

a. 20 wt.% Guanidine hydrochloride, 10 wt.% sodium hexametaphosphate, and the remainder water.

b. 10 wt.% Guanidine hydrochloride, 15 wt.% sodium hexametaphosphate, and the remainder water.

It was found that the specimens treated with solution (a) showed a char-length of 2.0 inches in the vertical test for flame retardance, and that the specimens treated with solution (b) showed a char-length of 2.5 inches in that test. Further, the specimens treated with solutions (a) and (b) according to this invention exhibited only very slight discoloration when subjected to the heat sensitivity test.

EXAMPLE VII

A specimen of cotton fabric was impregnated with a 110 wt.% wet add-on of a 10 wt.% aqueous solution of guanidine phosphate. When such specimen was dried, as described above, and then subjected to the flame retardant vertical test, the specimen burned its entire length (BET). Further, the specimen showed marked discoloration when subjected to the heat sensitivity test.

EXAMPLE VIII

The experiments of Example VII were repeated, but using each of the following solutions:

a. 10 wt.% Guanidine phosphate, 5 wt.% sodium triphosphate, and the remainder water.

b. 10 wt.% Guanidine phosphate, 6 wt.% tetrapotassium pyrophosphate, and the remainder water.

These two specimens showed only slight discoloration in the heat sensitivity test, and such specimens (a) and (b) showed char-lengths of 2.2 inches and 2.5 inches, respectively, in the vertical test for flame retardance.

EXAMPLE IX

A specimen of rayon fabric was impregnated with 110 wt.% wet add-on of a 10 wt.% aqueous solution of guanylurea phosphate. When such specimen was dried, as previously described, and then subjected to the flame retardant vertical test, the specimen burned its entire length (BEL).

EXAMPLE X

The experiment of Example IX was repeated, but using each of the following solutions:

a. 10 wt.% guanylurea phosphate, 10 wt.% sodium hexametaphosphate, and the remainder water.

b. 10 wt.% guanylurea phosphate, 10 wt.% potassium triphosphate, and the remainder water.

It was found that the specimen treated with solution (a) showed a char-length of 3.0 inches in the vertical test for flame retardance, and that the specimen treated with solution (b) showed a char-length of 2.5 inches in that test.

EXAMPLE XI

A specimen of cotton fabric was impregnated with a 110 wt.% wet add-on of a 15 wt.% aqueous solution of guanylurea sulfate. When such specimen was dried, as previously described, and then subjected to the flame retardant vertical test, the specimen burned its entire length (BEL). Further, when subjected to the heat sensitivity test, the treated specimen showed considerable darkening.

EXAMPLE XII

The experiments of Example XI were repeated, but using the following solution:

15 wt.% guanylurea sulfate, 5 wt.% sodium hexametaphosphate, and the remainder water.

It was found that the specimen treated with the above solution according to this invention showed a char-length of 2.5 inches in the vertical test for flame retardance, and that such specimen exhibited only very slight discoloration when subjected to the heat sensitivity test.

EXAMPLE XIII

276 grams of dicyandiamide, 600 grams of ammonium bromide, and 1,000 grams of water were mixed together, and the mixture was heated with stirring to a temperature of 150°C., in a closed, pressure-resistant reactor, using due care to employ cooling if and when the reaction heat tended to make the temperature rise above 150°. After 2 hours at 150°C. the mixture was cooled and removed from the reactor. It was found to be a clear liquid, containing 46 to 47 percent solids. On

storage at room temperature, some crystalline material separated from the liquid, but this could be redissolved by warming the mixture above 50°C. It is believed that the reaction product is essentially guanidine hydrobromide, with small amounts of other chemicals which do not affect the working properties of the product for the purpose of impregnating textile fabrics, papers, and the like for flame retardance.

A 15 wt.% solution of the above reaction product in water was used to impregnate a cotton fabric specimen for achieving a wet add-on of 110 wt.%. After drying of the specimen, as in the previous examples, the specimen was subjected to the flame retardant vertical test and burned for its entire length.

EXAMPLE XIV

In place of the solution employed in Example XIII a cotton fabric specimen was impregnated, to a wet add-on of 110 wt.%, with the following solution:

15 wt.% of the reaction product of Example XIII, 10 wt.% of potassium triphosphate, and the remainder water.

After drying of the specimen, as described above, the treated specimen was found to have a char-length of 2.5 inches when subjected to the flame retardant vertical test.

EXAMPLE XV

378 grams of dicyandiamide, 392 grams ammonium bromide, 456 grams ammonium sulfamate, were mixed together with 100 grams water in a laboratory reactor. This mixture was held at 150°C. for 2 hours, then cooled and removed from the reactor. The reaction product was a faintly hazy liquid above 90°C., and became a crystalline paste when stored at temperatures about 20°C. The active content of this product was found to be 92%, and is believed to be essentially all guanidine hydrobromide and guanidine sulfamate, together with relatively small amounts of guanylurea salts of the same acids.

a. A 21 wt.% aqueous solution of the above reaction product was applied to 100 lb. paper board poster stock to provide a 70 wt.% wet add-on. The impregnated paper board was then dried to provide approximately a 14.5 wt.% dry add-on of the reaction product. The paperboard thus treated burned its entire length (BEL) when subjected to the vertical test for flame retardance.

b. The solution of paragraph (a) above was similarly applied to 11 lb. tissue paper with the same result, that is, the treated tissue paper burned its entire length when subjected to the flame retardant vertical test.

EXAMPLE XVI

The experiments of paragraph (a) and (b) of Example XV were repeated, but using the following solution:

21 wt.% of the reaction product from Example XV, 6 wt.% sodium triphosphate, and the remainder water.

In each instance, the latter solution in accordance with this invention afforded effective flame retarding properties to the paperboard and tissue paper, respectively. More specifically the char-length in the flame retardant vertical test was reduced to about 3.5 inches. Further, in each case, when subjected to the heat sensitivity test, neither the paperboard nor the tissue paper treated in accordance with this invention showed any appreciable discoloration.

EXAMPLE XVII

378 grams of dicyandiamide, 912 grams of ammonium sulfamate, and 100 grams of water were mixed together and slowly brought to 150°C. and held at this temperature in a closed reactor for 2 hours, and then cooled to 90°C. and removed from the reactor. The product is a faintly hazy liquid above 90°C., but begins to crystallize below this temperature, and becomes a crystalline paste when stored at room temperature. The active content of this product was found to be 92 percent, and is believed to be, for the most part, composed of guanidine sulfamate, together with small amounts of guanylurea sulfamate and possibley also biguanide sulfamate.

The above condensation reaction product was made up into the following solutions:

a. 12 wt.% of condensation product, and 88 wt.% water.

b. 10 wt.% of condensation product, 5 wt.% sodium hexametaphosphate and the remainder water.

c. 10 wt.% of condensation product, 5 wt.% tetrasodium pyrophosphate, and the remainder water.

d. 10 wt.% of condensation product, 6.5 wt.% tetrapotassium pyrophosphate, and the remainder water.

e. 10 wt.% of condensation product, 5 wt.% trisodium phosphate anhydrous and the remainder water.

Specimens of cotton fabric and of viscose rayon fabric were impregnated with a 110 wt.% wet add-on of each of the above solutions (a)–(e) and, after suitable drying, subjected to the flame retardant vertical test with the following results:

It was found that, for both the cotton and rayon fabric specimens, treatment with solution (a) permitted the fabric to burn the entire length when tested. Treatment with solutions (b),(c) and (d) resulted in char-lengths between 2 inches and 3 inches. Treatment with solution (e) resulted in a 6 inch char length. This last result is consistent with the earlier statement herein to the effect that the sodium or potassium salt of orthophosphoric acid or of the various polymeric phosphoric acids which is included in the composition according to this invention is preferably one which, in a 10% aqueous solution, provides a pH in the range from approximately 5.2 to 11.1. Actually, trisodium phosphate included in solution (e) of this example gives a higher pH than 11.1 in a 10% aqueous solution, and thus is not one of the preferred salts. Although it is clear that solution (e) above affords some benefit as a flame retardant, such solution is shown not to be as advantageous as the solutions including the sodium or potassium salts of phosphoric acids which are included in the preferred salts.

EXAMPLE XVIII

378 grams of dicyandiamide, 214 grams ammonium chloride, 456 grams of ammonium sulfamate and 100 grams of water were mixed together and slowly brought to 150°C. and held at this temperature in a closed reactor for 2 hours, and then cooled to 90°C. and removed from the reactor. The product was a faintly hazy liquid above 80°C., but when stored at room temperature it became a crystalline paste. The active content of this product was 92 wt.%, and is believed to be a mixture of guanidine hydrochloride with guanidine sulfamate,

together with minor amounts of the corresponding guanylurea and biguanide salts.

The following solutions were made up with this condensation product, and were applied to cotton and to viscose rayon fabrics, with 110 wt.% wet add-ons:

a. 12 wt.% of the condensation product, and 88 wt% water.

b. 12 wt.% of the condensation product, 8 wt.% potassium triphosphate, and the remainder water.

c. 10 wt.% of the condensation product, 6 wt.% disodium phosphate, and the remainder water.

d. 10 wt.% of the condensation product, 6 wt.% sodium hexametaphosphate, and the remainder water.

e. 10 wt.% of the condensation product, 6 wt.% of the sodium metaphosphate available commercially under the trade name "Quadrafos," and which is represented to be a tetramer, and the remainder water.

When the cotton fabric specimens and the rayon fabric specimens treated with solution (a) were subjected to the flame retardant vertical test, each of these specimens burned its entire length. However, all of the other solutions (b)–(e) gave fully satisfactory flame retardant properties to all of the specimens treated therewith, giving in each case a char-length of less than 3.5 inches.

EXAMPLE XIX

The following solutions were prepared from the condensation or reaction product of Example XVIII:

a. 18 wt.% of the condensation product of Example XVIII, and 82 wt.% water.

b. 6 wt.% of the condensation product of Example XVIII, 30 wt.% sodium hexametaphosphate, and the remainder water.

c. 15 wt.% of the condensation product of Example XVIII, 3 wt.% sodium hexametaphosphate, and the remainder water.

Specimens of 4-ounce cotton fabric and of 4-ounce viscose rayon fabric were impregnated with each of the above solutions to a wet add-on or pickup of 110 wt.%, whereupon, as previously, each specimen was dried in a circulating air oven for 6 minutes at 275°F. When the various specimens were subjected to the flame retardant vertical test, it was found that the fabrics treated with solution (a) burned the entire length when tested, while the fabrics treated with solutions (b) and (c) did not continue to burn when the igniting flame was removed, and showed only a two-inch char length. Solution (b) which has a high concentration of sodium hexametaphosphate, produces fabric which is quite stiff, and which would have limited usefulness due to that stiffness. However, the effectiveness of solutions (b) and (c) illustrates the range of proportions of the constitutents that may be included in flame retardant compositions according to this invention. Thus, in solution (b) there is one part of the guanidine salt component to five parts of the phosphate salt component, whereas, in solution (c) the proportions are reversed, that is, there are five parts of the guanidine salt component to each part of the phosphate salt component. Further, solution (a) of this Example, when compared with solution (c), demonstrates that even a relatively higher add-on of the guanidine salt alone does not achieve as effective a flame retardant property as is obtained when a lesser amount of the guanidine salt is combined with a small amount of the phosphate salt.

Having described the invention with particular reference to precise examples thereof, it is to be understood that the invention is not limited to those examples, and that various modifications and changes may be made by one skilled in the art without departing from the scope or spirit of the invention.

What is claimed is:

1. A composition useful as a flame retardant and consisting essentially of from 1 to 5 parts, by weight, of a first substance selected from the group consisting of potassium and sodium triphosphate and mixtures thereof, and from 1 to 5 parts, by weight, of a second substance selected from the group consisting of guanidine sulfamate, guanidine sulfate, guanidine hydrobromide, guanidine hydrochloride, guanidine phosphate, guanylurea sulfamate, guanylurea hydrobromide, guanylurea hydrochloride, guanylurea phosphate, and mixtures thereof.

2. A composition useful as a flame retardant and consisting essentially of from 1 to 5 parts, by weight, of a first substance selected from the group consisting of disodium phosphate, dipotassium phosphate and mixtures thereof, and from 1 to 5 parts, by weight, of a second substance selected from the group consisting of guanidine sulfamate, guanidine sulfate, guanidine hydrobromide, guanidine hydrochloride, guanidine phosphate, guanylurea sulfamate, guanylurea hydrobromide, guanylurea hydrochloride, guanylurea phosphate, and mixtures thereof.

3. A composition useful as a flame retardant and consisting essentially of from 1 to 5 parts, by weight, of a first substance selected from the group consisting of tetrasodium pyrophosphate, tetrapotassium pyrophosphate and mixtures thereof, and from 1 to 5 parts, by weight, of a second substance selected from the group consisting of guanidine sulfamate, guanidine sulfate, guanidine hydrobromide, guanidine hydrochloride, guanidine phosphate, guanylurea sulfamate, guanylurea hydrobromide, guanylurea hydrochloride, guanylurea phosphate, and mixtures thereof.

4. A composition useful as a flame retardant and consisting essentially of from 1 to 5 parts, by weight, of a first substance selected from the group consisting of sodium and potassium tetraphosphates and hexametaphosphates and mixtures thereof, and from 1 to 5 parts, by weight, of a second substance selected from the group consisting of guanidine sulfamate, guanidine sulfate, guanidine hydrobromide, guanidine hydrochloride, guanidine phosphate, guanylurea sulfamate, guanylurea hydrobromide, guanylurea hydrochloride, guanylurea phosphate, and mixtures thereof.

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