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PROCESS FOR FLAMEPROOFING COMBUSTIBLE CELLULOSIC MATERIAL AND PRODUCT RESULTING THEREFROM

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The present invention relates to a new or improved method of flame-proofing combustible cellulosic materials that enables them to be washed or laundered in hot aqueous media without losing their flame-proof qualities, and to the resulting flame-proofed cellulosic materials. The invention also relates to a new reagent for use as a flame-proofing component according to the aforesaid new or improved method of flame-proofing combustible cellulosic materials.

Amongst the cellulosic materials to which the invention is especially applicable are textile fabrics, for instance woven or pleated fabrics, threads, yarns, filaments and fibres, made of cotton, linen, regenerated cellulose, jute, cellulose acetate and the like.

Various proposals have already been made in connection with the flame-proofing of combustible materials but those proposals for the most part have suffered from such disadvantages as the necessity of having to employ large amounts of reagent to ensure effective flame-proofing thereby stiffening the materials to an undesirable extent, the difficulty experienced in fixing the reagent satisfactorily to the combustible materials so that it will resist laundering operations, and the scarcity or difficulty of production of some of the reagents proposed.

A process has already been disclosed which comprises treating with an acidic-fire-retardant as for example phosphoric acid or calcium phytate a cellulosic material impregnated with polyethyleneimine.

An object of the present invention is to provide a method of flame-proofing combustible cellulosic materials, and a new flame-proofing component used in carrying out the method, yielding flame-proof products that retain their flame-proof qualities subsequent to hot water washing and laundering with hot soap solutions in a more satisfactory degree than heretofore.

It has been found that compositions comprising the novel higher acidic orthophosphoric ester derivative of dipentaerythritol, presumed to be largely dipentaerythritol hexaorthophosphate, can be readily anchored to cellulosic materials impregnated with polyethyleneimine to give flame-proof cellulosic materials which retain their flame-proof characteristics subsequent to their treatment with soap and water washing.

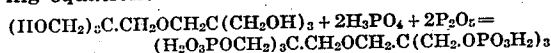
According to the present invention therefore the method of flame-proofing combustible cellulosic materials comprises treating the said materials impregnated with a polyethyleneimine with a solution comprising a higher acidic orthophosphoric ester derivative of dipentaerythritol.

The flame-proofing component according to the present invention for flame-proofing combustible cellulosic materials previously subjected to the action of a polyethyleneimine comprises a

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higher acidic orthophosphoric ester derivative of dipentaerythritol.

A crude higher acidic orthophosphoric ester derivative of dipentaerythritol presumed to be crude dipentaerythritol hexaorthophosphate was prepared from dipentaerythritol, orthophosphoric acid and phosphorus pentoxide as follows, the quantities being employed being based upon the molecular ratio of one part dipentaerythritol, two parts of orthophosphoric acid and two parts phosphorus pentoxide in accordance with the following equation:



Phosphoric acid (15.7 gr. of 88%) was added gradually to phosphorus pentoxide (34.4 gr.) and when the mixture was cooled finely ground dipentaerythritol (26.6 gr.) was added thereto, the whole being well stirred. The mixture was heated in an oil bath at 120-140° C. for 20 hours with exclusion of moisture and occasional stirring. The reaction product thus formed presumably the crude dipentaerythritol hexaorthophosphate product probably contained phosphoric acid and lower orthophosphate derivatives of dipentaerythritol in addition to the dipentaerythritol hexaorthophosphate.

Comparative experiments were carried out to illustrate the differences in behaviour to washing with soap and water of cotton cloth in every case first treated with an aqueous solution of polyethyleneimine in the manner specified and subsequently with aqueous solutions of the resulting reaction product presumed to be crude dipentaerythritol hexaorthophosphate, and aqueous solution of a mixture of the three reactants upon which the heat treatment was omitted, the mixture being immediately dissolved in water and an aqueous solution diluted as required of a mixture of phosphoric acid and phosphorus pentoxide only which were heated together before dissolving in water. Solutions of various concentrations were used.

Experiments were also carried out to see how to improve the handle or feel of the combustible cellulosic materials and yet retain the desired fireproof qualities after soap and water washing.

The handle or feel is found to be often improved by cutting down the quantity of polyethyleneimine with which the combustible cellulosic materials is impregnated, as for example by working with polyethyleneimine solutions of strengths lower than 8 to 12%, but to make certain that in such cases the product remains flame-proof after soap and water washing it is often necessary to treat it subsequent to the dipentaerythritol hexaorthophosphate treatment with an acidified aqueous solution of hexamethyloxymethyl melamine or triethyloxymethyl melamine followed by baking at about 100° C. The

acidification can be effected for example with paratoluene sulphonic acid.

A piece of cotton cloth (12 sq. in.) was soaked in 10 ml. of a boiling aqueous solution of polyethyleneimine for one hour, wrung out and baked in a steam oven overnight. The cloth was then steeped in 15 ml. of an aqueous solution of the resulting reaction product presumed to be crude dipentaerythritol hexaorthophosphate for one hour at room temperature, thoroughly rinsed, and dried. The time given for each operation and quantities used were arbitrarily fixed.

uct to treatment with crude dipentaerythritol hexaorthophosphate prepared by reacting at an elevated temperature a mixture comprising 1 part dipentaerythritol, 2 parts of orthophosphoric acid, and 2 parts of phosphorus pentoxide.

6. A method for flame-proofing a combustible cellulosic textile which comprises initially impregnating said textile with a polyethyleneimine by soaking said textile in a boiling aqueous solution of the polyethyleneimine, steeping the resulting impregnated product for about one hour at room temperature in an aqueous solution con-

Treatment of Cloth	Before Washing	After water washing	After soap and water washing
5% polyethyleneimine, 10% d. p. h. p. ¹	Flameproof.	Flameproof.	Just short of flameproof but showed no afterglow.
10% polyethyleneimine, 10% d. p. h. p.	do.	do.	Flameproof.
10% polyethyleneimine, 10% control ² liquor.....	do.	do.	Not flameproof.
10% polyethyleneimine, 10% phosphoric acid.....	do.	do.	Do.
5% polyethyleneimine, 10% d. p. h. p. Final treatment with a solution containing 2 grams hexamethoxymethyl melamine+0.05 gram p. toluene sulphonie acid in 18 cc. water (for 12 sq. ins. cloth) followed by baking at 100° C. for 1 hour	do.	do.	Flameproof.
5% polyethyleneimine, 10% d. p. h. p. Final treatment with a solution containing 2 gms. triethoxymethyl melamine+0.05 gm. p. toluene sulphonie acid in 18 cc. water (for 12 sq. ins. cloth) followed by baking at 100° C. for 1 hour.	do.	do.	Do.

¹ d. p. h. p. = a reaction product presumed to be dipentaerythritol hexa-orthophosphate.

= solution of unheated mixture of pentaerythritol phosphoric acid and phosphorus pentoxide.

² Solution of heated mixture of phosphoric acid and phosphorus pentoxide.

Testing of flame-proofness was carried out by holding the cloth in a Bunsen flame for 5 to 10 seconds. Some charring always took place, but if burning was not propagated with any speed in the flame and ceased without afterglow when the cloth was removed from the flame, the cloth was recorded as "flame-proof." If either of these conditions was not satisfied the sample was recorded as "not flame-proof."

The stability of the flame-proofness to washing was tested as follows. The test piece was stirred with 200 ml. water at 40 to 50° C. for 30 minutes and dried. Flame-proofness was then tested as above. The same piece was then stirred with 200 ml. of 0.25% soap solution at 40 to 50° C. for 30 minutes, wrung out, rinsed thoroughly in 3 changes of water and dried. The flame-proofness was again tested.

The results obtained are given in the following table:

We claim:

1. A process for flame-proofing a combustible cellulosic material which comprises impregnating said material with a polyethyleneimine and then treating the impregnated product with an aqueous solution of the reaction product resulting from the interaction of dipentaerythritol, orthophosphoric acid, and phosphorus pentoxide.

2. A method for flame-proofing a combustible cellulosic textile which comprises impregnating said textile with a 8-12% polyethyleneimine solution and then subjecting the impregnated product to treatment with an aqueous solution of the reaction product resulting from the interaction of dipentaerythritol, orthophosphoric acid, and phosphorus pentoxide.

3. A method as claimed in claim 2 wherein the cellulosic material is subsequently treated with an acidified aqueous solution of hexamethoxymethyl melamine followed by baking at about 100° C.

4. A method as claimed in claim 2 wherein the cellulosic material is subsequently treated with an acidified aqueous solution of triethoxymethyl melamine followed by baking at about 100° C.

5. A method for flame-proofing a combustible cellulosic textile which comprises impregnating said textile with a 8-12% polyethyleneimine solution and then subjecting the impregnated prod-

uct to treatment with crude dipentaerythritol hexaorthophosphate as an essential ingredient, and then rinsing and drying the treated, flame-proofed textile.

7. A flame-proofed cellulosic material impregnated with dipentaerythritol hexaorthophosphate, said impregnant being fixed to said material by polyethyleneimine.

8. A process for flame-proofing a combustible cellulosic material which comprises impregnating said material with polyethyleneimine and then treating the impregnated product with a solution containing dipentaerythritol hexaorthophosphate as an essential active ingredient.

9. A process as claimed in claim 8, wherein said impregnation is accomplished with an aqueous polyethyleneimine solution of 8 to 12% concentration.

10. A process for flame-proofing a combustible cellulosic material which comprises impregnating said material with a polyethyleneimine, treating the impregnated product with an aqueous solution of dipentaerythritol hexaorthophosphate, subsequently treating the product with an acidified aqueous solution of a polyalkoxymethyl melamine and then baking at about 100° C.

11. A process as claimed in claim 10, wherein said polyalkoxymethyl melamine is hexamethoxymethyl melamine.

12. A process as claimed in claim 10, wherein said polyalkoxymethyl melamine is triethoxymethyl melamine.

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