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OFFICE

METHOD OF TREATING FIBROUS CELLULOSIC MATERIALS TO IMPART FLAME RESISTANCE THERETO, COMPOSITION THEREFOR, AND PRODUCTS THEREOF

Joseph W. Creely, East Bound Brook, N. J., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine

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17 Claims. (Cl. 117-103)

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This invention relates to methods of imparting flame resistance to cellulosic material, more particularly natural or regenerated cellulose or mixtures thereof, and specifically to textiles comprising fibers of such cellulosic materials. The invention further relates to the compositions used in such methods and to the flame-resistant cellulosic products thereof.

In the past, various compounds and compositions have been used or suggested for use as agents for treating fibrous cellulosic materials and other normally flammable organic materials in order to render them resistant to flame. Agents or treatments for imparting flame-resistance to ordinarily flammable organic materials may be classified as (1) temporary (2) semi-durable and (3) permanent or durable. This classification is based on the durability of the treatment in providing continued resistance of the treated textile or other material to flame during use.

The durable treatments heretofore used or suggested have been of three general types: (1) urea-phosphate, (2) double bath precipitation, (3) metallic oxide-chlorinated body. One of the main objections to the urea-phosphate type of treatment has been its tendering effect on the cellulosic material whereby its tensile strength is reduced considerably. The double bath precipitation and the metallic oxide-chlorinated body types of treatment generally yield cellulosic textiles having a harsh or stiff hand so that the treated textile has a limited field of utility. The above disadvantages have been overcome by processes for imparting flame-resistance to cellulosic textile materials described in the copending applications of Anne MacMillan Loukowsky, Roy H. Kienle, and Theodore R. Cooke, Serial No. 76,644, filed February 15, 1949, now U. S. Patent No. 2,520,103, and Serial No. 64,416, filed December 9, 1948, now U. S. Patent No. 2,519,388. The first of these applications describes impregnation of fibrous cellulosic materials with a composition containing specified proportions of (1) a finely divided oxide of antimony, (2) a thermally unstable halogen-containing thermoplastic substance, (3) a water-soluble salt of an oxygen-containing acid of phosphorus in which phosphorus has a valence of 5, and (4) either cyanamide, dicyandiamide or mixtures thereof, while the latter application discloses a similar use of a composition containing specified proportions of (1) a finely divided oxide of tin, titanium, antimony or bismuth, (2) a thermally unstable halogen-containing thermoplastic substance, (3) a water-soluble salt of an oxygen-containing acid

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of phosphorus in which phosphorus has a valence of 5, and (4) urea, biuret, ammonium cyanate or ammonium dicyanamide.

Later it was found that by judicious selection of the particular ingredient falling within class (3) of the above identified applications the necessity for including a member of class (4) in compositions for imparting flame-resistance to cellulose textiles might be eliminated. The three component compositions and their use for imparting flame-resistance to textiles are described and claimed in my copending application with Theodore F. Cooke, Serial No. 141,851, filed February 1, 1950, entitled "Permanent Flameproofing Composition and Procedure."

It is an object of the present invention to provide an additional method for imparting flame-resistance to cellulosic textile materials which avoids the disadvantages of the urea phosphate, double bath precipitation or metallic oxide-chlorinated body types of treatment.

It is another object of the present invention to impart flame-resistance to cellulosic textile materials.

It is still another object of the present invention to provide a permanently flame-resistant cellulosic textile material which has an improved hand over that of flame-resistant cellulosic textile materials given a double bath precipitation treatment or a metallic oxide-chlorinated body type of treatment.

Another object of the present invention is to so treat cellulosic textile materials that they become permanently flame-resistant without excessive tendering.

The above and other objects are attained by impregnating a cellulosic textile material with ingredients comprising (1) a finely divided oxide of tin, titanium, antimony, bismuth, or mixtures thereof, (2) a thermoplastic substance containing at least 20% by weight of combined halogen and capable of rupturing under heat at carbon-halogen bonds, the ingredients (1) and (2) together being designated hereinafter as (A), and (B) a water-soluble, metal-free, nitrogen-containing salt of an amino phosphoric acid having an amino nitrogen atom attached directly to a phosphorus atom which salt has a melting point of less than 200° C. The impregnant may be applied to the cellulosic textile material as a single aqueous liquid composition containing the ingredients of both (A) and (B) or as two separately applied aqueous liquid compositions, one containing the ingredients of (A) and the other containing the ingredient (B).

The invention will be described in greater detail in conjunction with the following specific examples in which proportions are given in parts by weight unless otherwise noted. The examples are merely illustrative, and it is not intended that the scope of the invention be limited to the details therein set forth.

ONE BATH APPLICATIONS

Example 1

A bath is prepared containing 75 parts of phosphoric acid product #1 (see below), 6.2 parts of antimony oxide (Sb_2O_3), 5.6 parts of polyvinyl

A bath (b) containing 5.6 parts of polyvinyl chloride, 6.2 parts of antimony oxide (Sb_2O_3) and 88.2 parts of water is prepared and used to impregnate the padded cloth to give a wet pick-up of about 93%. The treated cloth is then dried in an oven with forced air circulation to give a dry add-on of about 10.9%.

After one wash a char length of $3\frac{1}{2}$ inches and no afterglow are observed. After five washes the cloth shows a char length of $3\frac{1}{2}$ inches and an after-glow of 10 seconds.

Example 8 is repeated using different impregnating baths with the following results:

Ex.	Formulation	pH	Bath (a)		Bath (b)		Char Length in Inches		Afterglow in secs.	
			Wet Pick-up	Dry Add-on	Wet Pick-up	Dry Add-on	1 wash	5 washes	1 wash	5 washes
9	98% #1, 2% HMTA ¹ -----	6.9	Per cent	Per cent	Per cent	Per cent				
10	50% #1, 25% urea, 2% HMTA-----	7.1	123	20.9	94	11	$3\frac{1}{2}$	$3\frac{3}{4}$	none	6
11	33 $\frac{1}{3}$ % #2, 66 $\frac{2}{3}$ % H_2O -----	5.7	105	13	100	11.7	$3\frac{1}{2}$	$3\frac{1}{2}$	none	5
12	33 $\frac{1}{3}$ % #2, 2% HMTA-----	6.5	101	13	99	11.6	3	$3\frac{1}{2}$	none	3
13	20% #2, 20% urea, 2% HMTA-----	6.8	111	10.8	98	11.5	$3\frac{1}{2}$	4	none	6
14	#3-----	6.0	121	16.6	93	10.9	$3\frac{1}{2}$	$4\frac{1}{4}$	none	5
15	98% #3, 2% HMTA-----	6.1	123	11.2	97	11.3	5	5	none	3
16	50% #3, 25% urea, 2% HMTA-----	6.4	117	20.3	92	10.8	$3\frac{1}{2}$	$4\frac{1}{2}$	none	5
17	#4-----	6.5	121	15.3	93	10.9	4	4	none	4
18	50% #4, 25% urea, 2% HMTA-----	7.0	119	21	92	10.8	$3\frac{1}{2}$	$3\frac{1}{2}$	none	5
19	50% #4, 25% urea-----	6.9	121	12	90	10.5	$3\frac{1}{2}$	$3\frac{1}{2}$	none	5
20	50% #5, 25% urea-----	7.4	125	19.7	93	10.9	$3\frac{1}{2}$	$3\frac{1}{2}$	none	6
21	12.5% #6, 25% urea-----	4.6	106	8.7	106	12.4	4	$4\frac{3}{4}$	none	2
22	25% #6, 2% HMTA-----	5.4	110	8.0	104	12.2	4	$5\frac{1}{4}$	none	3
23	25% #7, 25% urea, 2% HMTA-----	6.8	124	18	94	11	$3\frac{3}{4}$	5	none	3
24	49% #8, 25% urea, 2% HMTA-----	2.5	118	21	96	11.2	4	4	none	5

¹ HMTA=hexamethylenetetramine.

chloride, and 13.2 parts of water. This solution, which has a pH of about 6.8, is padded on bleached, unmercerized 80 x 80 cotton cloth to give a wet pick-up of about 125%. The padded cloth is air dried, cured for 15 minutes at 160° C., rinsed and again dried to give a dry add-on of about 30%.

After one wash a char length of $3\frac{1}{2}$ inches is obtained by the vertical flame test, and the cloth has no after-glow. After five washes the char length is $3\frac{3}{4}$ inches and the after-glow, 7 secs. Details of both the washing and flame testing procedures used in this and all following examples are given below.

Example 1 is repeated using different impregnating baths with the following results:

Wherever the percentages of ingredients in the formulations appearing in the above tables do not total 100%, the balance is water.

Similar results are obtained when the antimony oxide of the examples is replaced wholly or in part by oxides of bismuth, titanium or tin or by mixtures of two or more of the oxides.

Preparation of phosphoric acid products

1. 2 mols 85% H_3PO_4 and 6 mols urea are mixed in a glass tray and heated in an oven for one hour at 160° C. A 97.7% yield of a glassy substance is obtained. This is dissolved in sufficient water to make about a 59% solution.

2. 0.5 mol (as $\text{H}_4\text{P}_2\text{O}_7$) polyphosphoric acid containing 32-50% meta, 47-60% pyro, 3-8% ortho

Ex.	Bath		Per Cent Wet Pick-up	Per Cent Dry Add-on	One Wash		Five Washes	
	Formulation	pH			Char Length, Inches	After-Glow, Secs.	Char Length, Inches	After-Glow, Secs.
2	37.5% #1, 2% HMTA, ¹ 18.8% urea, 6.2% Sb_2O_3 , 5.6% PVC ² -----	7.3	123	26	$3\frac{3}{4}$	none	4	5
3	75% #3, 6.2% Sb_2O_3 , 5.6% PVC-----	6.2	125	26	$3\frac{3}{4}$	none	4	5
4	37.5% #3, 2% HMTA, 18.8% urea, 6.2% Sb_2O_3 , 5.6% PVC-----	6.8	124	31	$3\frac{1}{2}$	none	$3\frac{1}{2}$	6
5	37.5% #4, 2% HMTA, 18.8% urea, 6.2% Sb_2O_3 , 5.6% PVC-----	6.8	124	31	$3\frac{1}{2}$	none	$3\frac{1}{2}$	6
6	37.5% #4, 18.8% urea, 6.2% Sb_2O_3 , 5.6% PVC-----	6.9	127	30	$3\frac{1}{2}$	none	$3\frac{1}{2}$	7
7	37.5% #8, 2% HMTA, 18.8% urea, 6.2% Sb_2O_3 , 5.6% PVC-----	2.4	125	30	4	none	$3\frac{3}{4}$	7

¹ HMTA=hexamethylenetetramine.

² PVC=polyvinyl chloride.

TWO BATH APPLICATIONS

Example 8

Bleached, unmercerized 80 x 80 cotton cloth is padded with a bath (a) of phosphoric acid product #1 having a pH of about 6.7 to a wet pick-up of about 123%. The cloth is dried in an oven with forced air circulation, cured for 15 minutes at 160° C., rinsed and again dried to give a dry add-on of about 22.6%.

and 82-84% P_2O_5 and 2 mols urea are mixed in a glass tray and heated in an oven for 30 minutes at 160° C. A spongy white solid, having a pH of about 6.1 when dissolved in water, results. The hot solid smells of ammonia. This solid is easily powdered and removed from the glass tray, giving a yield of about 93% based on the weight of the reactants.

3. 1 mol H_3PO_4 (85%), 2 mols urea and 1 mol 75 monoguanidine phosphate are mixed in a glass

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tray and heated for one hour at 160° C. An about 34.7% yield of a glassy product is obtained. A 50% solution of this product in water is made.

4. 2 mols urea and 2 mols monoguanidine phosphate are mixed in a glass tray and heated for one hour at 160° C. An about 89.4% yield of a glassy product is obtained. This is dissolved in an equal weight of water.

5. 2 mols urea and 2 mols monoguanidine phosphate are mixed in a glass tray and heated for 30 minutes at 160° C. in an oven. One-third mol hexamethylenetetramine is stirred in, and the mixture is heated an additional 20 minutes. The foaming melt is cooled and weighed. Yield: about 95.4% white solid. A 50% solution of this in water is prepared.

6. 2 mols (as $H_4P_2O_7$) polyphosphoric acid and 2 mols urea are mixed together and heated at 160° C. in an oven. A white foam forms which solidifies on cooling. Yield: about 87%.

7. 1 mol monoguanidine phosphate, 0.5 mol dicyandiamide and about 6 mols water are heated one hour at 160° C. A white foam results. An about 100% yield on the weight of solid reactants is obtained. The product is dissolved in an equal weight of hot water.

8. 1 mol H_3PO_4 (85%), 0.5 mol dicyandiamide and about 6 mols water are heated one hour at 160° C. A white gummy substance results in about a 94% yield.

FLAME TESTING PROCEDURE

Flame tests on the impregnated cotton fabrics of the examples are made following a procedure which is in general that given in ASTM Tentative Specifications Designation: D626-41T issued 1941. Samples 2½ inches x 10 inches are cut with the long dimension parallel to the warp. The sample of fabric to be tested is suspended vertically in a shield by means of a clamp at the top and bottom thereof. A Bunsen burner previously regulated to a luminous flame 1½ inches high is placed under the suspended sample so that the end of the sample extends ¾ inch into the flame. The flame is held under the sample for 12 seconds and then extinguished. The total length of char in inches is measured by the tear length produced with a tearing weight equal to approximately 10% of the tearing strength of the unburned fabric.

WASHING PROCEDURE

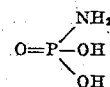
The washings referred to in the preceding examples are effected in small oscillating machines. A one pound load is used for each wash, and the fabrics are washed for 15 minutes intervals using 12 liters of 0.5% neutral soap solution at 65°-75° C. They are spun and rinsed for from 3-5 minutes in lukewarm water and then spun and rinsed further by hand.

The present invention is not limited to the particular polyvinyl chloride of the examples and the thermoplastic substance may be any thermoplastic material containing at least 20%, and preferably at least 40%, by weight of combined halogen which is capable of rupturing under heat at carbon-halogen bonds. Some examples of such thermoplastic materials are the polyvinyl bromides, the polyvinylidene chlorides, the polyvinylidene bromides, copolymers of vinyl halide and vinylidene halides as, for example, of vinyl chloride and vinylidene chloride, copolymers of vinyl halides and acrylic esters as, for example, of vinyl chloride and methyl, ethyl, propyl, butyl or the like acrylates, halogenated paraffins, halogenated diphenyls as pentachlo-

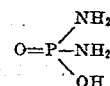
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rodiphenyl, pentabromodiphenyl, and the halogenated naphthalenes including the chlorinated, brominated, etc., naphthalenes. I prefer to use polyvinyl chloride or a vinyl chloride copolymer containing at least 80% by weight of combined vinyl chloride.

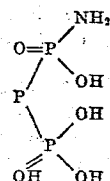
The phosphoric acid products which comprise ingredient (B) of the compositions of the present invention are water-soluble salts of amino phosphoric acids having an amino nitrogen atom attached directly to a phosphorus atom which have a melting point of less than 200° C. and the cations of which contain nitrogen and no metal. Ammonium salts and guanido type salts such as the guanidine, guanyurea and biguanide salts of the following amino phosphoric acids are representative of those which are suitable for use:



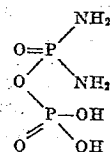
Monoaminophosphoric



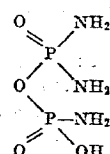
Diaminophosphoric



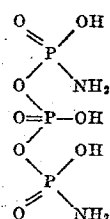
Monoaminodiphosphoric



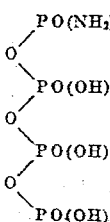
Diaminodiphosphoric



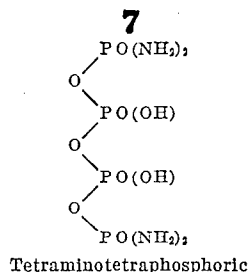
Triaminodiphosphoric



Diaminotriphosphoric



Diaminotetraphosphoric



The mono- and poly-salts may be used. I prefer, in general, the ammonium and guanidine salts and more particularly, salts containing a cationic ammonium or guanidine group for each phosphorus atom in the acid.

The amino phosphoric acid salts may conveniently be prepared by melting together (1) urea or dicyandiamide and (2) phosphoric acid, a polyphosphoric acid or a guanido type salt of phosphoric acid or of a polyphosphoric acid. When the free acid is reacted with urea or dicyandiamide, the ammonium salt of the amino phosphoric acid is obtained. When the urea or dicyandiamide is reacted with the guanido type salt of a phosphoric acid, the corresponding guanido type salt such as the guanidine, biguanide, guanylurea, etc., salt of the amino phosphoric acid is obtained. The invention is not, however, in any way limited to any particular method of preparing the amino phosphoric acid salts.

The cellulosic textile material may be impregnated with the ingredients of the present process in one or more steps or stages as illustrated by the specific examples. It may be impregnated with a dispersion containing all of the necessary ingredients within the range of proportions specified below or it may be given a two-bath treatment. If the latter, the textile must be impregnated first with (B), the aqueous solution containing the water-soluble, metal-free, nitrogen-containing salt of an amino phosphoric acid having an amino nitrogen atom attached directly to a phosphorus atom, and then after drying with (A), the dispersion containing the metallic oxide and the thermally unstable thermoplastic substance.

Regardless of the method of impregnation of the fibrous cellulosic textile material it is important that the ingredients of (A) and (B) be employed in a weight ratio of 1 part of the former to from 0.2-8 parts of the latter just as it is important that ingredients (1) and (2) of (A) be employed in a weight ratio of 1 part of the former to from 0.6-20 parts of the latter.

The total amount of the ingredients of (A) and (B) with which cellulosic textile materials are impregnated according to the present process must be sufficient to impart flame-resistance to the materials after heating them within the range of 135°-200° C. and thereafter washing to remove any residual water-soluble substances. The total amount of the ingredients of (A) and (B) with which the cellulosic material is impregnated is so controlled that the finished flame-resistant textile contains from about 10%-50% by weight or, if the hand of the treated material is relatively unimportant, to as high as about 75% by weight, based on the dry weight of the untreated textile, of wash-fast impregnant. During the heat treatment at 135°-200° C. a substantial loss of solids takes place which may be as much as 1/2-2/3 of the total weight of the phosphate with which the cellulosic material was

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initially impregnated. In order to obtain a finished textile containing from 10%-50%, or in those cases where desired up to 65%-75%, by weight based on the dry weight of the untreated textile, of wash-fast impregnant, the amount of solids in the textile as initially impregnated should be sufficiently high to allow for this weight loss of solids during the heat treating and washing steps.

I prefer to employ an aqueous dispersion of the necessary ingredients for treating fibrous cellulosic textile materials in accordance with my invention. The amount of solids in such a dispersion may be varied as described but they will usually constitute from about 40% to about 70% by weight of the dispersion.

The present invention applies to cellulosic materials of the class consisting of natural celluloses, regenerated celluloses and mixtures thereof and including primarily cotton and viscose rayon.

The textile treating compositions of this invention may be modified by incorporating therein various modifying agents which aid in further improving the flame-resistant characteristics of the treated cellulosic material or which facilitate the technique of application. For instance, the compositions may also contain minor amounts (e. g., from 1% to 30% weight of the total solids content) of such glow retardants as the glow-retarding borates, phosphates, pyrophosphates, etc., e. g., zinc borate, zinc phosphate, zinc ammonium phosphate, stannic phosphate, phenyl diamido phosphate, melamine pyrophosphate, etc. Agents which have a buffering effect on the composition after being applied to the fabric or other textile, e. g., calcium carbonate, magnesium oxide, urea, hexamethylene tetramine and other polyalkylene polyamines boiling above about 200° C., the amount of said polyamines not exceeding about 7% by weight of ingredient (B), etc., may be incorporated into the treating compositions as desired or as conditions may require. It is often advantageous to add an agent such as urea which will convert any aminophosphate which may have been hydrolyzed back to the aminophosphate.

Bath (B) in a two-bath process should be adjusted to a pH (glass electrode pH) within the range of from about 3 to about 7 if it is not initially within that pH range. Preferably the pH of the aqueous composition containing ingredient (B) is between about 4 and 6.

The present invention is applicable to the production of a wide variety of flame-resistant cellulosic materials, e. g., wearing apparel of all kinds, especially children's clothes and clothing used by the armed forces, curtains, draperies, sheeting, furniture coverings, linings for electric blankets, net fabrics, non-woven fabrics, chenilles, etc., which are made of cellulosic textile materials.

The terms "flame resistance" and "flame-resistant" as used herein and in the appended claims with reference to cellulosic textile materials are used generically to include within their meanings treated cellulosic textile materials, which, after ignition, will continue to burn at a relatively slow rate as well as those which, after ignition, will burn over only a limited area beyond that directly exposed to the source of ignition and which may be specifically designated as "fire-resistant" cellulosic textile materials. It will be apparent from the examples herein given that most of the products of my invention prop-

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erly fall within the specific classification of fire-resistant cellulosic textile materials.

The terms "textile" and "textile material" as used generically herein and in the appended claims include within their meanings filaments, fibers, rovings, slivers, threads, yarns, twisted yarns, etc., as such or in woven, felted or otherwise formed fabrics, sheets, cloths and the like.

I claim:

1. A method of imparting flame-resistance to a cellulosic textile material of the class consisting of natural celluloses, regenerated celluloses and mixtures thereof, which comprises impregnating said material with an association of an aqueous liquid composition containing ingredients comprising (1) a finely divided oxide of a metal of the group consisting of antimony, bismuth, tin and titanium and (2) a thermoplastic substance containing at least 20% by weight of combined halogen and capable of rupturing under heat at carbon-halogen bonds, the ingredients of (1) and (2) which together are designated hereinafter as (A) being employed in a weight ratio of 1 part of the former to from 0.6-20 parts of the latter, and of an aqueous liquid composition containing an ingredient comprising (B) a water-soluble, metal-free, nitrogen-containing salt of an amino phosphoric acid having an amino nitrogen atom attached directly to a phosphorus atom, which salt has a melting point of less than 200° C., the ingredients of (A) and (B) being employed in a weight ratio of 1 part of the former to from 0.2-8 parts of the latter, the aqueous composition containing the ingredient (B) having a pH of from about 3 to about 7; heating the impregnated material at a temperature within the range of about 135°-200° C.; and washing the resulting material to remove any residual water-soluble substances therefrom, the total amount of the ingredients of (A) and (B) with which the cellulosic textile material initially is impregnated being such that the finished flame-resistant textile contains from about 10% to about 75% by weight, based on the dry weight of the untreated textile, of wash-fast impregnant.

2. A method as in claim 1 wherein the cellulosic textile material is cotton.

3. A method as in claim 1 wherein the cellulosic textile material is viscose rayon.

4. A method as in claim 1 wherein the metal oxide is antimony oxide.

5. A method of imparting flame-resistance to a textile comprising fibers of a cellulosic material of the class consisting of natural celluloses, regenerated celluloses and mixtures thereof which comprises impregnating said textile with an aqueous dispersion having a pH within the range of 3-7 and comprising (1) a finely divided oxide of a metal of the group consisting of antimony, bismuth, tin and titanium, (2) a thermoplastic substance containing at least 20% by weight of combined halogen and capable of rupturing under heat at carbon-halogen bonds, the ingredients of (1) and (2) which together are designated hereinafter as (A) being employed in a weight ratio of 1 part of the former to from 0.6-20 parts of the latter, and (B) a water-soluble, metal-free, nitrogen-containing salt of an amino phosphoric acid having an amino nitrogen atom attached directly to a phosphorus atom, which salt has a melting point of less than 200° C., the ingredients of (A) and (B) being employed in a weight ratio of 1 part of the former to from 0.2-8 parts of the latter; heating the impregnated textile at a temperature within the range of about 135-

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200° C.; and washing the resulting textile to remove any residual water-soluble substances therefrom, the total amount of the ingredients of (A) and (B) with which the textile initially is impregnated being such that the finished flame-resistant textile contains from about 10% to about 75% by weight, based on the dry weight of the untreated textile, of wash-fast impregnant.

6. A method as in claim 5 wherein ingredient (2) is a vinyl chloride polymerization product.

7. A method as in claim 5 wherein ingredient (B) is the amino phosphoric acid salt obtained by reaction of urea with phosphoric acids.

8. A method as in claim 5 wherein ingredient (B) is the amino phosphoric acid salt obtained by reaction of urea with pyrophosphoric acid.

9. A method as in claim 5 wherein ingredient (B) is the amino phosphoric acid salt obtained by reaction of urea with monoguanidine phosphate.

10. A method as in claim 5 wherein ingredient (B) is the amino phosphoric acid salt obtained by reaction of dicyandiamide with phosphoric acid.

11. A method as in claim 5 wherein ingredient (B) is the amino phosphoric acid salt obtained by the reaction of dicyandiamide with monoguanidine phosphate.

12. A method as in claim 5 wherein the aqueous dispersion contains a small amount, not exceeding about 7% by weight of the ingredient (B), of a polyalkylene polyamine having a boiling point substantially above 200° C.

13. A method of imparting flame-resistance to a textile comprising fibers of a cellulosic material of the class consisting of natural celluloses, regenerated celluloses and mixtures thereof which comprises impregnating said textile with an aqueous solution having a pH within the range of 3-7 and containing (B) a water-soluble, metal-free, nitrogen-containing salt of an amino phosphoric acid having an amino nitrogen atom attached directly to a phosphorus atom, which salt has a melting point of less than 200° C.; heating the impregnated textile at a temperature within the range of 135°-200° C.; washing the resulting textile to remove any residual water-soluble substances therefrom; impregnating the heated and washed textile with ingredients comprising (1) a finely divided oxide of a metal selected from the group consisting of antimony, bismuth, tin and titanium and (2) a thermoplastic substance containing at least 20% by weight of combined halogen and capable of rupturing under heat at carbon-halogen bonds, the ingredients of (1) and (2) which together are designated hereinafter as (A) being employed in a weight ratio of 1 part of the former to from 0.6-20 parts of the latter, the ingredients of (A) and (B) being employed in a weight ratio of 1 part of the former to from 0.2-8 parts of the latter; and heating the impregnated material at a temperature within the range of about 135° C. to 200° C., the total amount of the ingredients of (A) and (B) with which the said textile is impregnated being such that the finished flame-resistant textile contains from about 10% to about 75% by weight, based on the dry weight of the untreated textile, of wash-fast impregnant.

14. A flame-resistant cellulosic textile material obtained in accordance with the method of claim 1.

15. A flame-resistant cellulosic textile material obtained in accordance with the method of claim 5.

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16. A flame-resistant cellulosic textile material obtained in accordance with the method of claim 13.

17. An aqueous dispersion having a pH of from about 3-7 and comprising (1) a finely divided oxide of a metal selected from the group consisting of antimony, bismuth, tin and titanium, (2) a thermoplastic substance containing at least 20% by weight of combined halogen and capable of rupturing under heat at carbon-halogen bonds, the ingredients of (1) and (2) which together are designated hereinafter as (A) being employed in a weight ratio of 1 part of the former to from 0.6-20 parts of the latter and being dispersed in water containing (B) a water-soluble, metal-free, nitrogen-containing salt of

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an amino phosphoric acid having an amino nitrogen atom attached directly to a phosphorus atom, which salt has a melting point of less than 200° C., the ingredients of (A) and (B) being employed in a weight ratio of 1 part of the former to from 0.2-8 parts of the latter.

JOSEPH W. CREELY.

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