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

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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

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water-soluble salt of an oxygen-containing acid of phosphorus in which phosphorus has a valence of 5, and (4) urea, biuret, ammonium cyanate or ammonium dicyanamide.

5 In a copending application of one of us, Joseph W. Creely, Serial No. 141,852 filed February 1, 1950, use of a similar composition in which (1) may be a finely divided oxide of tin, titanium, antimony, bismuth, or mixtures thereof, (2) is the same, (3) is a water-soluble, metal-free, nitrogen-containing salt of an amino phosphoric acid and (4) is omitted, is described and claimed.

We have now found that by judicious selection of the particular ingredient falling within class (3) of the above-identified applications of Loukowsky, Kienle and Cooke, the necessity for including a member of class (4) in compositions for imparting flame-resistance to cellulosic textiles may be eliminated.

10 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.

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

20 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.

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

30 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 guanidine or guanylurea salt of an oxygen-containing polyacid of phosphorus wherein the phosphorus atom has a valence of 5. 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.

Example 1

312.5 parts of diguanylurea sulfate are reacted in 3257 parts of methyl alcohol-denatured 95% ethyl alcohol with 145 parts of 85% potassium hydroxide. The potassium sulfate which separates out is filtered off and 186 parts of polyphosphoric acid containing 32-50% meta, 47-60% pyro, 3-8% ortho and 82-84% P_2O_5 are added to the filtrate. The mixture is stirred thoroughly and allowed to settle after which the excess alcohol is poured off and the solids dried.

The 32% solution of diguanylurea polyphosphate prepared above (B) is used for padding an 80 x 80 bleached unmercerized cotton fabric. The pH of the bath is about 4.3 and a wet pick-up of about 112% is obtained. The fabric is air dried for 10 minutes at 85° C. in a forced draft oven and cured for 15 minutes at 160° C. After rinsing and drying a dry add-on of about 8.7% is obtained.

A dispersion of 41 parts of titanium dioxide is prepared by mixing it with 57.7 parts of water and 1.3 parts of the sodium salt of disulfodinitrophenylmethane in a homogenizing type of mixer for 10 minutes. The dispersion is then added with stirring to a mixture of 71.0 parts of polyvinyl chloride latex, 55.5% solids, and 329.0 parts of water.

The cloth which has been treated with the diguanylurea polyphosphate is then padded through the bath containing the titanium dioxide dispersion and the polyvinyl chloride (A) to a wet pick-up of about 103% and dried for 10 minutes at 85° C.

After one wash a char length of 2¾ inches is obtained by the vertical flame test and the cloth has an after-glow of 2 seconds. After 5 washes the char length is 3 inches and the after-glow, 15 seconds. Details of both the washing and flame testing procedures used in this and the following examples are given following Example 4.

Example 2

Example 1 is repeated except that the 32% diguanylurea polyphosphate bath contains 2% added hexamethylene tetramine and has a pH of about 4.8. A wet pick-up of about 108% and a dry add-on after rinsing and drying of about 6.7% are obtained. After treatment with bath (A) of Example 1 a wet pick-up of about 114% is obtained.

After one wash a char length of 3 inches is obtained by the vertical flame test, and the cloth has a 2 second after-glow. After five washes there is a 5 inch char length and a 28 second after-glow.

Example 3

A bath (B) is prepared from 131.0 parts of diguanidine carbonate, 132.5 parts of the polyphosphoric acid used in Example 1, 10.0 parts of hexamethylene tetramine and 226.5 parts of water, and 80 x 80 cotton cloth is padded through the bath at 90° C. to a wet pick-up of about 125%. The fabric is dried for 10 minutes at 85° C. and cured for 16 minutes at 160° C. After rinsing

and drying a dry add-on of about 19.5% is obtained.

A bath (A) is prepared using 99.5 parts of polyvinyl chloride latex, 55% solids, 71.0 parts of a metallic oxide dispersion prepared as described in Example 1 but using a 41% antimony oxide dispersion in place of the titanium dioxide, and 329.5 parts of water. The cotton is padded in bath (A) to a wet pick-up of about 90% and dried, giving a dry add-on of about 15%.

After one wash a char length of 4¼ inches is obtained. After 5 washes a char length of 4¾ inches and an after-glow of 11 seconds are obtained.

Example 4

80 parts of diguanylurea polyphosphate prepared as set forth in Example 1, 59 parts of water and 25 parts of 28% aqueous ammonia are stirred together and warmed to dissolve. The solution obtained is added to a mixture of 50 parts of a dispersion prepared as set forth in Example 1 but using a 41% antimony oxide dispersion in place of the titanium dioxide and 36 parts of polyvinyl chloride latex, 55% solids. The resulting solution which has a pH of about 6.7 is padded on 80 x 80 cotton fabric at 40° C. A wet pick-up of about 135% is obtained. After drying 10 minutes at 85° C. and curing 15 minutes at 160° C. a dry add-on of about 35% is obtained.

After one wash the char length is 4 inches and the fabric has an after-glow of 5 seconds. After five washes the char length is 3¾ inches and the after-glow is 20 seconds.

Similar results are obtained when the titanium dioxide and antimony oxide of the examples are replaced by oxides of tin or bismuth. Mixtures of two or more of the metallic oxides may be used if desired.

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.

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

Other guanidine or guanylurea salts of oxygen-containing polyacids of phosphorus wherein the phosphorus atom has a valence of 5 may be used in place of the salts of the specific examples. In general the salts will contain a guanidine or guanylurea nucleus for each phosphorus atom of the polyacid. Thus, some examples of suitable salts are diguanidine pyrophosphate, diguanylurea, pyrophosphate, triguanidine tripolyphosphate, triguanylurea tripolyphosphate, tetraguanidine tetrapolyphosphate, tetraguanylurea tetrapolyphosphate, etc.

The phosphorous acid salt used in the compositions of the present invention is extremely critical for only by selection of certain salts is it possible to formulate a three-ingredient composition at least as effective as the four-ingredient compositions of the Loukowsky, Kienle and Cooke applications referred to above. In the first place, the phosphorous acid must be a polyacid. Guanidine orthophosphate, for example, is ineffective in a three-ingredient composition and requires the presence of cyanamide, dicyandiamide, urea, biuret, ammonium cyanate or ammonium dicyanamide. Secondly, only the guanidine and guanylurea polyphosphates are effective. Thus, we have observed that other salts of polyacids which are effective in the four-ingredient formulations such as, for example, biguanide polyphosphate are not operative in the process and/or compositions of the present invention.

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 guanidine or guanylurea salt of an oxygen-containing polyacid of phosphorus having a valence of 5, 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 material's 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 $\frac{1}{2}$ -% of the total weight of the polyphosphate with which the cellulosic material was initially impregnated. In order to obtain a finished textile containing from 10%-50%, or in those cases where desired up to 65% or 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.

We prefer to employ an aqueous dispersion of the necessary ingredients for treating fibrous cellulosic textile materials in accordance with our invention. The amount of solids in such a dispersion may be varied as desired 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% by 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, 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.

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 our invention properly 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.

We 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 compound selected from the group consisting of the guanidine and guanylurea salts of an oxygen-containing polyacid of phosphorus wherein the phosphorus atom has a valence of 5, 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 titanium dioxide.

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

6. 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 compound selected from the group consisting of the guanidine and guanylurea salts of an oxygen-containing polyacid of phosphorus wherein the phosphorus atom has a valence of 5, 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°-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.

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

8. A method as in claim 6 wherein ingredient (B) is diguanidine pyrophosphate.

9. A method as in claim 6 wherein ingredient (B) is diguanylurea pyrophosphate.

10. A method as in claim 6 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.

11. 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 compound selected from the group consisting of the guanidine and guanylurea salts of an oxygen-containing polyacid of phosphorus wherein the phosphorus atom has a valence of 5; 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.

12. A method as in claim 11 wherein the textile is cotton.

13. A method as in claim 11 wherein ingredient (B) is diguanidine pyrophosphate.

14. A method as in claim 11 wherein ingredient (B) is diguanylurea pyrophosphate.

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

16. A flame-resistant cellulosic textile material obtained in accordance with the method of claim 6.

17. A flame-resistant cellulosic textile material obtained in accordance with the method of claim 11.

18. An aqueous dispersion having a pH of

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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 compound selected from the group consisting of the guanidine and guanyurea salts of an oxygen-containing polyacid of phosphorus wherein the phosphorus atom has a valence of 5, the in-

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redients 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.

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