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PROCESS FOR FLAMEPROOFING CELLULOSIC MATERIAL

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ABSTRACT OF THE DISCLOSURE

Flame retardant cotton fabric, durable to laundering, was prepared by treatment with aqueous precondensates of tetrakis(hydroxymethyl)phosphonium chloride (THPC) and phosphoroxytriamide (PTA) or dimethylamidophosphoroxydiamide (DPDA) in mole ratios of THPC to PTA or DPDA of 0.5:1 to 6:1.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention, together with the invention disclosed in Ser. No. 443,108 filed of even date, is a further improvement in or modification of the invention claimed in U.S. Patents No. 2,772,188, No. 2,983,623, and No. 3,276,897. More particularly, this invention relates to the treatment of cellulosic materials with a partially polymerized water soluble product containing a further polymerizable polymer which contains phosphorus and nitrogen, and which is insolubilized within the cellulosic material with ammonia, or with heat, thereby producing a flame-retardant cellulosic material have improved strength retention after chlorine bleaching and scorching.

U.S. Patent No. 2,772,188 defines the nature of the further-polymerizable compounds as methylol-phosphorus polymers in one of the water soluble stages when applied to the cellulosic materials. The invention then describes a process to further polymerize methylol-phosphorus-polymers without the use of heat. This further polymerization is accomplished by using ammonia, in the form of gaseous ammonia, ammonium hydroxide, a solution of ammonia in an inert solvent, or as ammonia released in situ by the reaction of a compound capable of releasing ammonia, e.g., an ammonium salt of a weak acid, such as ammonium acetate.

U.S. Patent 2,983,623 claims an improved method of insolubilizing the further-polymerizable methylol-phosphorus polymeric materials by treating with gaseous ammonia first and aqueous ammonia afterwards. The process described in Patent 2,983,623 is briefly: impregnation of a cellulosic material with an aqueous solution or dispersion of a further-polymerizable methylol-phosphorus polymeric material; drying the cellulosic material; treating the cellulosic material in ammonia gas; treating the cellulosic material in aqueous ammonia; washing, rinsing, and drying the cellulosic material.

Whereas any of the further-polymerizable methylol-phosphorus polymeric materials referred to in Patent 2,772,188 are satisfactory for the processes of Patent

2,983,623, a particularly suitable polymeric material is claimed to be the reaction product of tetrakis(hydroxymethyl)phosphonium chloride (THPC) and urea. Scoured and bleached cotton fabric treated by this process was flame resistant, passing the standard vertical flame test (Fed. Spec. CCC–T–191b). The treated fabric was fairly stiff, and when given a chlorine bleach turned yellow. Furthermore, after chlorine bleaching and scorching, the fabric retained only 25–30% of its warp breaking strength.

Particularly suitable precondensates referred to in U.S. Patent No. 3,276,897 are claimed to be the reaction products of (THPC) and tris(carbamoylethyl)amine or ethyl carbamate. Cellulosic materials which contain these polymers are claimed to show virtually no discoloration and very little strength loss after chlorine bleaching and scorching.

It is the object of this invention to provide a method of preparation of new precondensates and a process for the application of the precondensate to impart improved flame resistance to cellulosic materials.

Another object of this invention is to provide white cellulosic materials which retain essentially all of their breaking strength after chlorine bleaching and scorching.

Still another object of this invention is to provide a method of producing cellulosic materials which retain their flame-retarding properties after frequent washings.

These and other objects of this invention will be apparent to those skilled in the art of making flame retardant cellulosic materials.

Methylol-phosphorus polymeric materials are produced by reacting at least one compound of the group tetrakis(hydroxymethyl)phosphonium chloride, tris(hydroxymethyl)phosphine oxide, and phosphorus-linked methylol-group-containing derivatives thereof, with compounds containing a plurality of groups which yield condensation products with a phosphorus-linked methylol group.

The process of this invention is particularly useful in the insolubilization of nitrogen methylol-phosphorus polymers with ammonia. Preferred nitrogen methylol-phosphorus polymers are produced by reacting at least one phosphorus compound of THPC and/or THPO with a compound from the group consisting of phosphoroxytriamide and dimethylamidophosphoroxydiamide.

In accordance with this invention, any cellulosic material, such as cotton, rayon, paper, jute, ramie, and the like, may be treated, but the invention is particularly effective when applied to the treatment of cellulosic textiles.

In preparing the further polymerizable nitrogen methylol-phosphorus polymers, the aforementioned compounds are mixed with water and partially polymerized to form a precondensate. This may be at any temperature from room temperature to the reflux temperature. When the partial polymerization takes place at the reflux temperature, one-half hour is usually adequate. A particularly suitable polymeric material is the reaction product of tetrakis(hydroxymethyl)phosphonium chloride (THPC) and phosphoroxytriamide (PTA), in mole ratios of THPC:PTA of 0.5:1 to 6:1.

The cellulosic material is impregnated with the aqueous solution of the precondensate, preferably by padding, although other impregnating techniques may be used; the

excess solution is removed by passing the cellulosic material through squeeze rolls, centrifuging, or other methods. The impregnated cellulosic material is then dried. The drying temperature can vary about from room temperature to 145° C., although 80–90° C. is preferred; the drying time varies from several hours (at room temperature) to a few minutes at the higher temperatures. For example, drying of the cellulosic material can be effected in a conventional forced hot air oven for five minutes at 80° C.

Insolubilization of the precondensate with ammonia is accomplished in two steps. First, the dried cellulosic material containing the further polymerizable methylolphosphorus polymer is exposed to gaseous ammonia and then to ammonium hydroxide. The gaseous ammonia may be applied at temperatures of about from 25° C. to 100° C.; the aqueous ammonia may be from about 10–29% ammonium hydroxide.

In cases where insolubilization with ammonia is not used, the material is cured at temperatures about from 80° C. to 155° C. The treated cellulosic materials are then washed and dried.

Cellulosic materials treated in accordance with this invention have improved flame-retardant properties which are retained after repeated launderings. When cellulosic materials treated in accordance with this invention are given a chlorine bleach and subsequently scorched, the warp breaking strength retention is more than 90%.

The following examples illustrate the methods of carrying out the invention but the invention is not restricted to these examples. Treated fabrics were tested by the standard methods of the American Society for Testing Materials, Philadelphia, Pa., Committee D–13. Breaking strength was determined by the one-inch strip method, ASTM designation, D39–59; tearing strength by the Elmendorf method, ASTM designation, D1295–60T; damage by chlorine, by ASA Method, No. 1, 14.126–1961; and flame resistance by the standard vertical method, Fed. Spec. CCC–T–191b. The percentages and parts are by weight.

Example 1

Solutions were prepared by dissolving tetrakis(hydroxymethyl)phosphonium chloride (THPC) and phosphoroxytriamide (PTA) in water as indicated in Table I.

TABLE I

Solution No.	Parts of THPC	Parts of PTA	Parts of H_2O	Mole ratio THPC:PTA	pH of solution
1	9.55	4.75	29.0	1:1	2.90
2	9.55	2.38	24.3	2:1	2.65
3	14.32	2.38	33.9	3:1	1.75
4	19.10	2.38	43.6	4:1	1.75
5	23.88	2.38	53.3	5:1	2.15
6	28.65	2.38	63.0	6:1	3.20
7	4.78	4.75	38.1	0.5:1	4.30

Solution No. 1 gelled within 2–3 hours, so it was necessary to apply it to cotton fabric before gelling, preferably within one hour after mixing. Solution No. 7 gelled within 20–25 minutes after mixing. It also had the unusual property of reliquifying after about 5–6 hours, and regelling within several days. Best results with these two solutions were obtained by applying to fabric immediately after preparation. All of the other solutions were stable for extended periods of time without gelling.

The solutions in Table I were padded onto OD sateen and each sample of fabric dried for five minutes at 85° C. The samples treated with solutions 3, 4, 5, and 6 were then exposed to NH_3 gas for three minutes at room temperature (about 25° C.) and then immersed in 10% NH_4OH for three minutes at room temperature. Samples of fabric treated with Solutions 1 and 2 were not exposed to NH_3 gas or to NH_4OH solution, but were allowed to stand at room temperature (26° C.) for 24 hours. The sample of fabric treated with solution No. 7 was not exposed to NH_3 gas or to NH_4OH solution but was cured for five minutes at 155° C. All of the fabric samples were washed thoroughly in hot running tap water. The results are shown in Table II before and after ten home laundering cycles.

TABLE II

Solution used, No.	Add-on, percent	Before laundering		After ten laundering cycles	
		P content, percent	N content, percent	P content, percent	N content, percent
1	7.4	2.07	0.86	1.08	0.47
2	3.3	0.74	0.39	0.54	0.23
3	9.2	2.18	1.29	1.03	0.55
4	10.1	2.13	1.35	1.07	0.58
5	10.3	2.41	1.38		
6	9.7	2.33	1.36	1.27	0.70
7	5.6	1.32		1.40	

All samples in Table II had good flame resistance except samples treated with Solutions 2 and 7. This was due to the low add-on. Most samples retained considerable phosphorus and nitrogen after ten home laundering cycles. The sample treated with solution No. 7 retained all of its phosphorus after ten home laundering cycles.

Example 2

A solution was prepared containing 23.88 parts of THPC, 2.38 parts of PTA, and 53.30 parts of water. The pH of the solution was 2.7. After standing for two hours, the solution was padded onto two samples of OD sateen. The samples were dried five minutes at 85° C. One sample was exposed to NH_3 gas for three minutes at 25° C. and then immersed in 10% NH_4OH for three minutes at 65–70° C. The other sample was exposed to NH_3 gas for five minutes at 25° C. and immersed in 10% NH_4OH for five minutes at 65–70° C. The samples were washed and dried. The former sample had an add-on of 8.6%, a phosphorus content of 1.82%, and a char length of 3.75 inches; the latter had an add-on of 9.5%, a phosphorus content of 2.24%, and a char length of 3.25 inches.

Example 3

Solution No. 6 (see Example 1) was padded on two samples of OD sateen fabric and the samples dried for five minutes at 85° C. One sample was exposed to NH_3 gas at room temperature for five minutes and then immersed in 10% NH_4OH for five minutes. The other sample was exposed to NH_3 gas at room temperature for one minute, and then immersed in 10% NH_4OH for one minute. The former sample had an add-on of 9.9% and a phosphorus content of 2.19%. The latter sample had an add-on of 10.2% and a phosphorus content of 2.36%. Both samples had good flame resistance. After ten laundering cycles, the phosphorus content was 1.22% and 1.30%, respectively, and the retained flame resistance was moderate.

Example 4

Solutions No. 5 and 6 (see Table I) were allowed to age for seven days and five days, respectively, at room temperature and applied to sateen fabric as described in Example 1. Similar results were obtained.

Example 5

A solution was prepared containing 28.65 parts THPC, 2.38 parts PTA, and 63.00 parts water. Two samples of sateen fabric were padded with the solution. The first sample was dried for five minutes at 85° C., exposed to NH_3 gas for three minutes at room temperature, and then immersed in 29% NH_4OH for three minutes. The second sample was dried for five minutes at 145° C., exposed to NH_3 gas for three minutes at room temperature, and then immersed in 10% NH_4OH for three minutes. The data before and after ten laundering cycles are shown in Table III.

TABLE III

Sample No.	Add-on, percent	Before laundering			After ten laundering cycles		
		Percent N	Percent P	Char length, in.	Percent N	Percent P	Char length, in.
1	10.3	1.42	2.31	3.6	0.72	1.27	BEL [1]
2	5.3	0.69	2.13			1.77	

[1] BEL means sample burned the entire length.

The flame resistance of both samples was only moderate after ten laundering cycles.

Example 6

Solutions were prepared by dissolving dimethylamidophosphoroxydiamide (DPDA) and THPC in water as indicated in Table IV.

TABLE IV

Solution No.	Parts of THPC	Parts of DPDA	Parts of water	Mole ratio of THPC:DPDA
1	1.91	1.23	12.6	1:1
2	1.91	2.46	17.5	0.5:1
3	3.82	1.23	20.1	2:1
4	5.73	1.23	27.8	3:1
5	7.64	1.23	35.5	4:1

Solution No. 1 formed an opaque gel within three hours. Solution No. 2 began to gel within one hour, but then reliquified within a short time. The other solutions were stable for extended periods of time without gelling.

Solutions 3, 4, and 5 were padded on samples of sateen fabric. The samples were dried for five minutes at 85° C., exposed to NH_3 gas for five minutes, and then immersed in 10% NH_4OH for five minutes, and washed. The samples had reduced flammability.

Example 7

A solution was prepared containing 57.3 parts THPC, 7.14 parts PTA, and 130.8 parts water. The pH was 1.6. The solution was padded on two samples of white printcloth. Both samples were dried for five minutes at 85° C., exposed to ammonia gas for three minutes at room temperature and then immersed in 10% ammonium hydroxide for three minutes at room temperature. One of the samples (Sample No. 1) was then washed. The other sample (Sample No. 2) was passed through squeeze rolls to remove excess ammonium hydroxide, cured in an oven for five minutes at 140–145° C., and finally washed. Data are shown in Table V before and after ten home laundering cycles.

TABLE V

Sample No.	Resin add-on, percent	Before laundering			After ten laundering cycles		
		(a)	Breaking Str. (warp), lbs.		(d)	Breaking Str. (warp), lbs.	
			(b)	(c)		(e)	(f)
1	16.2	827	41.1	42.1	633	39.8	37.4
2	15.6	770	42.7	39.8	627	39.5	35.6
Control		1,180	46.9		660	46.2	

(a) Tearing strength (warp) gms.
(b) Bleached.
(c) Bleached and scorched.
(d) Tearing strength (warp) gms.
(e) Bleached.
(f) Bleached and scorched.

The strength losses of the treated fabrics after the bleaching and scorching tests are small. The strength retention is good even after ten laundering cycles.

Example 8

A solution was prepared as in Example 7. The solution was then refluxed for thirty minutes and allowed to stand overnight. The acidity of the solution was greater than pH 1. A sample of white printcloth was treated in the same manner as sample 1, in Example 7. The resin add-on was 9.8%, the percent N was 1.16%, the percent P was 2.03%, and the tearing strength was 23.5 lbs. after chlorine bleaching, and 26.8 lbs. after chlorine bleaching and scorching.

Example 9

A solution was prepared as in Example 7 and allowed to stand at room temperature for 24 hours. The pH was 1.5. The solution was padded onto two samples of printcloth, dried five minutes at 85° C., immersed in 10% ammonium hydroxide for three minutes, and then washed. One of the samples (Sample No. 1 in Table VI) was then cured for five minutes at 140–145° C. The other sample (Sample No. 2) was not cured. The data before and after ten home laundering cycles are shown in Table VI.

TABLE VI

Sample No.	Resin add-on	Before laundering		After ten laundering cycles	
		Percent P	Percent N	Percent P	Percent N
1	11.5	2.51	1.30	2.01	1.05
2	14.8	3.25	1.79	1.73	1.32

The percent loss of nitrogen and phosphorus after laundering is less for the sample which was cured.

We claim:

1. A process for treating cellulosic material which comprises:
   (a) treating said cellulosic material with an aqueous solution of a further-polymerizable methylol phosphorus polymeric material containing at least one free methylol group attached to a phosphorus atom, said polymeric material prepared by treating a precondensate comprising a partially polymerized mixture of tetrakis(hydroxymethyl)phosphonium chloride and a phosphorus-containing amide from the group consisting of phosphoroxytriamide and dimethylamidophosphoroxydiamide, the mole ratio of said chloride to said amide being about from 0.5:1 to 6:1 respectively,
   (b) drying the treated material,
   (c) exposing the treated material to gaseous ammonia for a period of time about from one to five minutes, at a temperature of about from 25° C.–100° C.,
   (d) immersing the material in a 10% to 29% aqueous ammonia solution for periods of time about from one to five minutes, at about from room temperature to 70° C., the longer periods of time being applicable to the lower temperatures, and
   (e) washing and drying the material.

2. The process of claim 1 wherein the phosphorus-containing amide is phosphoroxytriamide.

3. The process of claim 1 wherein the phosphorus-containing amide is dimethylamidophosphoroxydiamide.

4. A process for treating cellulosic material which comprises:
   (a) treating said cellulosic material with an aqueous solution of a further-polymerizable methylol phos-

phorus polymeric material containing at least one free methylol group attached to a phosphorus atom, said polymeric material prepared by treating a precondensate comprising a partially polymerized mixture of tetrakis(hydroxymethyl)phosphonium chloride and a phosphorus-containing amide selected from the group consisting of phosphoroxytriamide and dimethylamidophosphoroxydiamide, the mole ratio of said chloride to said amide being about from 0.5:1 to 6:1, respectively, and

(b) curing the treated material at a temperature of about from 80° to 155° C., for periods of time about from five minutes to 24 hours, the longer periods of time being applicable to the lower temperatures.

5. The process of claim **4** wherein the phosphorus-containing amide is phosphoroxytriamide.

6. The process of claim **4** wherein the phosphorus-containing amide is dimethylamidophosphoroxydiamide.

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