Durable Flame Resistance Via Reaction of Cotton Cellulose Bearing Aromatic Amino Groups with Tetrakis(Hydroxymethyl)phosphonium Chloride

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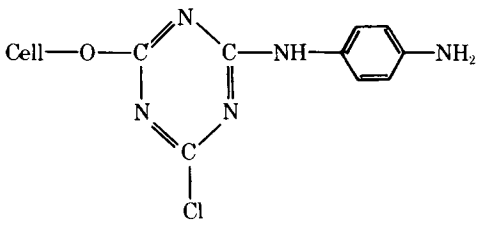
Synopsis

Chemically modified cotton fabric samples having different amounts of aromatic amino groups were prepared. These modified samples were reacted with tetrakis(hydroxymethyl)phosphonium chloride (THPC) under a variety of conditions using the pad-dry–thermofixation technique. The extent of the reaction (expressed as %P) was dependent of the degree of chemical modification of cotton, temperature and time of heating, and pH of the treating bath as well as incorporation of Lyofix CHN (N-methylol finishing agent), $MgCl_2 \cdot 6H_2O$ (catalyst), and urea at various concentrations. THPC did react with the modified cotton having a nitrogen content over a range of 0.4%–1.3% even in the absence of catalyst at a temperature as low as 30°C for 10 min to impart durable flame resistance to cotton. Increasing the temperature up to 80°C enhanced considerably the extent of reaction; the latter remained practically constant upon further increase in temperature. The reaction was favored in acidic media (pH 4–6), whereas alkaline media (pH 9–11) inhibited it. Incorporation of Lyofix CHN (9%), $MgCl_2 \cdot 6H_2O$ (1%), and urea (5%) along with THPC (25%) in the treating bath required a curing temperature of 120°C and a curing time of 5 min to achieve a fabric containing as much as 2.7% phosphorus with excellent durable flame resistance. A tentative mechanism of the reaction between THPC and the modified cotton was also elicited.

INTRODUCTION

Recently we have described a novel method for the preparation of cellulose bearing aromatic amino groups by reacting cotton cellulose with 2,4-dichloro-6-(*p*-nitroaniline)-S-triazine in the presence of alkali and subsequent reduction of nitro groups to amino groups.[1] The chemical structure of the modified cellulose so obtained was represented as follows:



In the present work, this modified cellulose was reacted with THPC with a view of studying (a) factors affecting the extent of reaction, (b) the mechanism of the

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reaction, and (c) the durability of flame resistance properties imparted to the modified cotton.

EXPERIMENTAL

A plain-weave grey cotton fabric (305 g/m^2) (21/cm ends, 22/cm picks) was given a mild alkaline scouring. The latter involved treating the fabric in a solution containing 20 g/l. sodium carbonate and 5 g/l. soap for 6 hr at the boil. The fabric was then thoroughly washed till free of alkalinity and then air dried.

The scoured cotton fabric was chemically modified through introduction of aromatic amino groups. The experimental technique adopted is described elsewhere.[1]

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) (Hooker Industrial Chemicals) and Lyofix CHN, based on trimethylol melamine (Ciba-Geigy), were of technical grade. Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and urea were of laboratory grade.

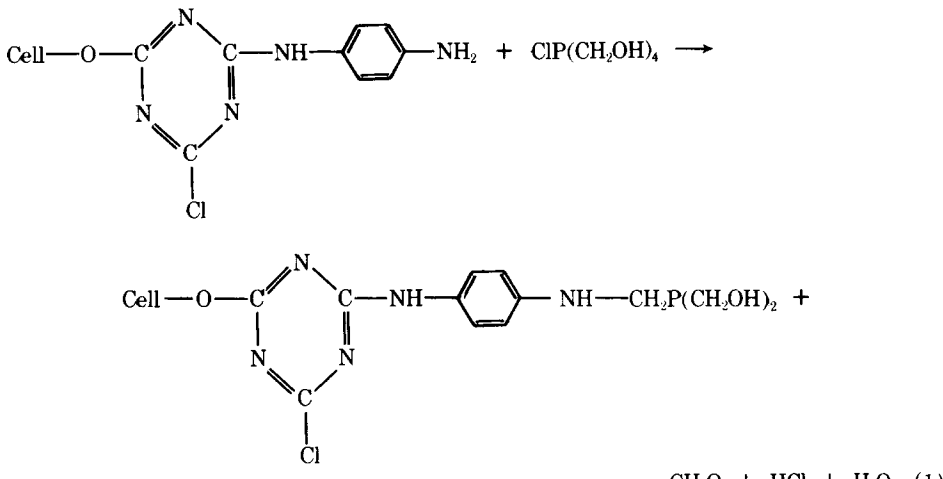
Unless otherwise indicated, samples of the modified cotton fabric were padded through two dips and two nips in a solution containing THPC (25%) to a wet pickup of ca. 70%. The samples were dried in air and then subjected to heat treatments. Details of the conditions used are given below. After heat treatment, the samples were rinsed in running tap water for 15 min, squeezed, and finally air dried.

Durability of the finish was assessed by monitoring the phosphorus content and char diameter before and after repeated washing and drying of the treated samples. Washing for 30 min at the boil was performed in a solution containing soap chips (0.5%) and anhydrous sodium carbonate (0.3%), followed by a thorough rinsing and drying under ambient conditions. The effectiveness of three of such washes is comparable with that of the soap soda boil (SSB).[2]

Phosphorus content was determined via a previously reported method.[3] The test method described in DIN 53907 was used for the flame resistance properties of the treated samples. The conditioned fabric sample was mounted in a specimen holder, which was placed in a horizontal position in a draught-free burning cabinet. Under the rack holding the specimen, 0.3 ml pure ethyl alcohol was ignited. When the alcohol flame was extinguished, the diameter of the charing circle caused by the flame was measured.

RESULTS AND DISCUSSION

Besides the hydroxyl groups, the chain molecules of the modified cotton cellulose in question bear aromatic amino groups. Reactions of this modified cellulose with THPC is anticipated to occur through a condensation reaction between the aromatic amino group and the methylol groups of THPC, in a manner similar to aminized cotton,[4] as shown in the mechanism suggested by eq. (1):



$$CH_2O + HCl + H_2O \quad (1)$$

A condensation reaction between the hydroxyl groups of the modified cellulose and the methylol groups of THPC is also possible as shown in the mechanism suggested by eq. (2):

$$\text{Cell-OH} + ClP(CH_2OH)_4 \rightarrow \text{Cell-O}—CH_2P(CH_2OH)_2 + CH_2O + HCl + H_2O \quad (2)$$

To check the validity of this mechanism, modified cotton fabrics having different amounts of aromatic amino groups (expressed as %N) were padded with a solution of THPC (25%) at pH 2.8 to a wet pickup of ca. 70%, dried in air, and then subjected to different temperatures for 10 min. The fabrics were then rinsed and air dried. The extent of the reaction was expressed as percent phosphorus (%P). Durability of the finish was determined as described in the experimental section.

The results obtained are set out in Table I. It is clear that regardless of the amount of aromatic amino groups of the modified cotton or the temperature used, THPC reacts with the modified cotton. However, the extent of the reaction (expressed as %P) is dependent on the degree of chemical modification of cotton and the reaction temperature. A significant enhancement in the extent of reaction can be achieved upon increasing the nitrogen content of the modified cotton from 0.4% to 0.8%. Further increase in nitrogen content (up to 1.3%) does not cause any improvement in the extent of reaction. The same holds true for the reaction temperature. There is an increase in the extent of reaction as the temperature rises from 30° to 80°C.

Thereafter, the temperature has no effect on the extent of reaction. This is not the case with unmodified cotton, since much higher temperatures (150°–170°C) have been reported.[2] Hence, it is reasonable to conclude that reaction of THPC with the said modified cotton occurs primarily via combination of the amino groups with the tetrakis compound, as shown in eq. (1).

Besides reaction of THPC with the modified cotton, self-polymerization of THPC is very likely to take place. Indeed, the marked fall in phosphorus content after washing (Table I) substantiates this, since the resultant polymeric products are not chemically bound to cotton and tend to be removed during washing.

TABLE I
Effect of the Degree of Chemical Modification of Cotton on its Reaction with THPC at Different Temperatures[a]

%N of modified cotton	%P														
	30°C			50°C			80°C			100°C			120°C		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
0.4	1.1	0.5	0.5	1.3	0.7	0.7	1.5	0.9	0.9	1.6	0.9	0.85	1.5	0.8	0.75
	(3)	(4.7)	(4.7)	(3)	(4.2)	(4.2)	(2.9)	(3.6)	(3.6)	(2.8)	(3.4)	(3.4)	(3)	(3.6)	(3.9)
0.8	1.6	0.9	0.85	1.7	0.9	0.9	1.8	1.1	1	1.8	1.1	1	1.8	0.9	0.82
	(2.8)	(3.6)	(3.6)	(2.8)	(3.6)	(3.6)	(2.6)	(3)	(3)	(2.7)	(3)	(3)	(2.8)	(3.7)	(3.7)
1.3	1.6	0.9	0.85	1.9	1	1	1.9	1.3	1.3	1.9	1.6	1.6	1.8	0.9	0.9
	(2.5)	(3.4)	(3.4)	(2.5)	(3)	(3)	(2.5)	(2.8)	(2.8)	(2.4)	(2.6)	(2.6)	(2.5)	(3.4)	(3.4)

[a] (A) Initial; (B) after five washings; (C) after ten washings. Values in brackets present char diameter, in cm. [THPC], 25%; pH, 2.8; reaction time, 10 min.

The durability of the flame resistance properties of THPC-treated chemically modified cotton may be realized from Table I. Obviously, the modified cotton in question can be made permanently flame resistant by reacting it with THPC. The treated samples pass the standard flame test even after being subjected to up to ten severe washings. An interesting feature is that though there is a significant decrease in the phosphorus content after washing, the increase in char diameter is not as striking. This indicates that the nitrogen of the modified cotton seems to contribute to the flame resistance. That is, the flame resistance is not solely due to the phosphorus content but to a combined effect of phosphorus and nitrogen.

Effect of Curing Temperature

Previous reports have disclosed the advantages of using N-methylol finishing agents, urea, and catalysts together with THPC.[4-7] It appears therefore of interest to conduct further experiments on the modified cotton under similar conditions. For this purpose samples of modified cotton fabric having a nitrogen content of 1.3% were padded in a solution containing THPC (25%), Lyofix CHN (9%), urea (5%), and $MgCl_2 \cdot 6H_2O$ (1%) to a wet pickup of ca. 70%. The samples were dried and then cured at the temperatures indicated in Table II for 5 min. They were then rinsed, air dried, and subjected to several washings and dryings as described above.

Table II shows that raising the curing temperature from 100° to 120°C is accompanied by a significant increase in phosphorus content and a substantial reduction in char diameter. Further increase in curing temperature leaves both properties practically unaltered. The advantages of using the additives cited above is quite obvious. A comparison between Tables I and II indicates (a) that the presence of the additives increase the extent of reaction of THPC with the modified cotton and (b) that the reaction product in the presence of these additives resists severe washings better than the corresponding product in their absence. For instance, in the presence of the additives, curing at 120°C produces a fabric with a phosphorus content of 2.7% and 2.6% before and after washing, respectively. This contrasts with corresponding phosphorus contents of 1.8% and 0.9% in the absence of the additives. Similarly, the char diameter of the treated fabric in the presence of the additives amounted to 2.2 cm before and after the washings, whereas in the absence of the additives the char diameters were 2.5 and 3.4 cm before and after ten washings, respectively.

TABLE II
Effect of Curing Temperature on Phosphorus Content and Char Diameter[a]

Temp.,	%P			Char diameter, cm		
°C	A	B	C	A	B	C
100	1.6	1.3	1.3	2.8	3.4	3.4
120	2.7	2.7	2.6	2.2	2.2	2.2
140	2.7	2.6	2.6	2.2	2.2	2.2
160	2.7	2.6	2.6	2.2	2.2	2.2

[a] (A) Initial; (B) after five washings; (C) after ten washings; fabric, cotton bearing aromatic amino groups (1.3% N); [THPC], 25%, [Lyofix CHN], 9%; [urea], 5%; [$MgCl_2 \cdot 6H_2O$], 1%; curing time, 5 min.

It is believed that reaction of the N-methylol finishing agent (Lyofix CHN) with cellulose and/or with THPC would improve the magnitude of the retention of the THPC polymeric product within the modified cotton matrix. These reactions, together with the reaction of THPC with the modified cotton, may be considerably favored under the catalytic influence of $MgCl_2 \cdot 6H_2O$. The presence of urea along with Lyofix CHN and the catalyst may be rather beneficial since urea would act as an acid acceptor. HCl is liberated via a decomposition reaction of THPC during application and also as a by-product, as shown in eq. (1). In the absence of urea, HCl would hydrolyze the $NH–CH_2P(CH_2OH)_2$ bond, see eq. (1), as well as degrade the polymeric products of THPC. The data presented below are consistent with this assumption.

Effect of Curing Time

In order to investigate the effect of curing time on the extent of the reaction occurring between THPC and the modified cellulose, curing was carried out at 120°C for different lengths of time varying from 1 min to 10 min. The fabric used, the composition of the treating bath employed, and the technique adopted were identical with those described above under the effect of the curing temperature.

Table III shows that the extent of reaction (expressed as %P) increases by increasing the curing time from 1 min to 5 min. Further increase in curing time has no such effect. It is as well to emphasize that the char diameter decreases as the curing time increases from 1 min to 5 min and then remains constant, which rather parallels the extent of reaction. Thus, a curing time of 5 min constitutes the optimal time for curing at 120°C since it is the shortest time within which the highest phosphorus content and the smallest char diameter could be achieved.

Effect of Urea Concentration

Table IV shows the effect of urea concentration on both the extent of reaction (expressed as %P) and char diameter. Samples of the modified cotton fabric having a nitrogen content of 1.3% were padded in solutions containing different concentrations of urea and constant concentrations of THPC (25%), Lyofix CHN

TABLE III
Effect of Curing Time on Phosphorus Content and Char Diameter[a]

Time, min	%P		Char diameter, cm	
	A	B	A	B
1	1.0	0.8	3.2	EB
2	1.3	1.15	3.1	3.3
3	1.8	1.7	2.7	2.8
5	2.7	2.6	2.2	2.2
7	2.7	2.6	2.2	2.2
10	2.7	2.6	2.2	2.2

[a] (A) Initial; (B) after ten washings; EB, entirely burned; fabric, cotton bearing aromatic amino groups (1.3% N); [THPC], 25%; [Lyofix CHN], 9%; [urea], 5%; [$MgCl_2 \cdot 6H_2O$], 1%; curing temperature, 120°C.

TABLE IV
Effect of Urea Concentration on Percent Phosphorus and Char Diameter

% Urea	%P			Char diameter, cm		
	A	B	C	A	B	C
0	2.3	2.2	2.2	2.4	2.3	2.2
3	2.5	2.4	2.4	2.3	2.2	2.2
5	2.7	2.6	2.6	2.2	2.2	2.2
7	2.7	2.6	2.6	2.2	2.2	2.2
10	2.5	2.4	2.4	2.2	2.2	2.2

[a] (A) Initial; (B) after five washings; (C) after ten washings; [THPC], 25%; [Lyofix CHN], 9%, [$MgCl_2 \cdot 6H_2O$], 1%; curing temperature, 120°C; curing time, 5 min; fabric, cotton bearing aromatic amino groups (1.3% N).

(9%), and $MgCl_2 \cdot 6H_2O$ (1%) to a wet pickup of ca. 70%. After being air dried, the fabric was cured at 120°C for 5 min, rinsed, and then washed as previously described.

It is evident (Table IV) that increasing the urea concentration up to 5% in the treating bath has a favorable effect on both the extent of reaction and the char diameter, though this effect is not significant. The slight favorable effect of urea suggests that urea may act as an acid acceptor (HCl liberated during the course of the reactions), a point which validates the assumption postulated earlier.

Effect of Lyofix CHN Concentration

It has been stated above that incorporation of Lyofix CHN in the treating bath of THPC accentuates the properties of the product resulting from the reaction of THPC with the modified cotton in question, most probably via reaction of Lyofix CHN with THPC to form a highly entangled polymeric product within the cellulose and/or with the modified cotton to bring about crosslinked cellulose. To confirm this statement, samples of the modified cotton fabric having 1.3% nitrogen were padded in solutions containing different concentrations of Lyofix CHN and constant concentrations of THPC (25% previously adjusted to pH 6 by NaOH solution) and $MgCl_2 \cdot 6H_2O$ (1%) to a wet pickup of ca. 70%. The samples were dried at ambient conditions, cured for 5 min at 120°C, and then rinsed and washed as usual.

TABLE V
Effect of Incorporation of Different Concentrations of Lyofix CHN in the THPC Treating Bath on Phosphorus Content and Char Diameter[a]

Lyofix CHN, %	%P			Char diameter, cm		
	A	B	C	A	B	C
3	2.2	1.9	1.9	2.3	2.8	2.8
6	2.3	2.1	2.1	2.2	2.3	2.3
9	2.6	2.6	2.6	2.2	2.2	2.2
12	2.5	2.5	2.5	2.2	2.2	2.2
15	2.5	2.5	2.5	2.2	2.2	2.2

[a] (A) Initial; (B) after five washings; (C) after ten washings; fabric, cotton bearing aromatic amino groups (1.3% nitrogen); [THPC], 25%; [$MgCl_2 \cdot 6H_2O$], 1%; curing temperature, 120°C; curing time, 5 min.

TABLE VI
Effect of Treating Bath pH on Phosphorus Content and Char Diameter[a]

pH	%P		Char diameter, cm	
	A	B	A	B
4	2.1	1.9	2.3	2.8
5	2.2	2.1	2.1	2.3
6	2.2	2.0	2.1	2.3
7	1.9	1.7	2.8	3.0
9	0.8	0.3	EB	EB
11	0.8	0.3	EB	EB

[a] (A) Initial; (B) after ten washings; EB, entirely burned; fabric, cotton bearing aromatic amino groups (1.3% N); [THPC], 25%; temperature of curing, 120°C; curing time, 5 min.

Table V reveals clearly that there is considerable enhancement in the extent of reaction (expressed as %P) and a reduction in char diameter when the concentration of Lyofix CHN in the treating bath increases up to 9%, beyond which the extent of reaction remains practically constant. The implication of this is in accordance with the above statement.

Effect of pH of Treating Bath

Reaction of THPC with cotton bearing aromatic amino groups (1.3% N) was carried out at various pH's to determine in particular the effect of pH on the extent of reaction (expressed as %P) and on the char diameter. The experimental technique adopted involved padding samples of the modified cotton in solutions containing THPC (25%) and adjusted to specific pH's to a wet pickup of ca. 70%. The samples were then air dried, cured at 120°C for 5 min, and finally rinsed and washed as previously described.

Table VI indicates that the pH of the treating bath has a significant effect on the extent of reaction, which in turn is reflected in the flame resistance properties of the fabric. Obviously, the reaction is favored in the acidic range till neutrality. Beyond neutrality, that is, in the alkaline range, the extent of the reaction decreases considerably. For instance, samples treated in acidic media showed a phosphorus content of ca. 2% and withstood the flammability test. Conversely, samples treated in alkaline media had a phosphorus content of 0.8% and failed to pass the flammability test. This leads to the conclusion that reaction of THPC with the modified cellulose as well as its self-polymerization reaction is more favored in acid media than in alkaline media.

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