

Flame-Retardant Cotton Fabrics by Reaction of Cellulose with Phosphorus Trichloride-DMF Adduct

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Synopsis

Cotton sateen fabric was found to react with the 1:2 adduct of phosphorus trichloride and N,N-dimethylformamide (DMF) in DMF or DMF-chloroform solutions at room temperature. During this reaction, the fabric acquired flame resistance. The introduction of as little as 1.2% phosphorus and 0.4% nitrogen, achieved at adduct concentrations as low as 2-5% in reaction times of 5-30 min, was sufficient to impart a useful level of flame retardancy. The effect of the adduct concentration, reaction time, and wash procedures on the flame resistance and other properties of the resultant cotton fabrics was studied. Moderate increases in the wet and dry wrinkle recovery were imparted by the treatment, but the use of high concentrations of adduct were somewhat detrimental to the tensile strength of the fabric. However, adduct concentrations of 20-25% produced a rather durable finish which passed the standard vertical flame test after 20 home launderings. Gradual loss of flame resistance during repeated laundering is attributable to ion exchange properties gradually acquired by the fabric. Based on analytical and infrared spectral data, the initial reaction of cellulose with the PCl_3 -DMF adduct is thought to involve elimination of one mole of DMF to form cellulose-O-P linkages, as well as some cellulose crosslinking via a second formimidate group of the adduct. Gradual hydrolysis during multiple launderings apparently yields cellulose acid phosphates responsible for the calcium ion uptake and decrease in flame resistance.

INTRODUCTION

The action of certain Vilsmeier-type reagents on cotton cellulose has been the subject of several studies in this laboratory. For example, thionyl chloride and N,N-dimethylformamide (DMF) react with loss of sulfur dioxide to form the well-known¹ intermediate chlorodimethylformiminium chloride, $\text{Cl}-\text{CH}=\overset{+}{\text{N}}\text{Me}_2 \text{Cl}^-$. This compound has been shown² to react rapidly with cellulose at room temperature to give cellulose N,N-dimethylformimidate chloride (cellulose-O- $\text{CH}=\overset{+}{\text{N}}\text{Me}_2 \text{Cl}^-$). The resulting highly reactive cellulose derivative is readily prepared in yarn or fabric form and can be converted in situ or in subsequent treatments to halodecoxycelluloses^{2,3} or to cellulose formate. Little research has been reported on the interaction of phosphorus trichloride-DMF adduct with cotton cellulose. Rath and co-workers⁴ have studied the reaction of cellulose powder with mixtures of red phosphorus and chlorine or bromine

in DMF to produce halodeoxycelluloses having low phosphorus/halogen ratios.

We now wish to report on the reaction of cotton with the adduct of phosphorus trichloride and DMF at room temperature. The structure of the adduct has previously⁵ been established as that of a phosphorus-containing iminium salt, $\text{Cl}-\text{P}(\text{OCH}=\text{NMe}_2)_2^{2+} 2\text{Cl}^-$. Although it can be considered as a Vilsmeier reagent, it differs fundamentally from the thionyl chloride-DMF adduct in structure and, as will be seen, in the types of reactions it undergoes with cellulose. It brings about the introduction of both phosphorus and nitrogen into the cellulose, causing a marked increase in flame resistance of cellulosic fabrics. The nature of the reactions occurring and the influence of processing variables on the product obtained is the subject of the present report.

EXPERIMENTAL

The cellulose used was desized, scoured and bleached cotton sateen fabric (8.2 oz/sq yd). Phosphorus trichloride, DMF, chloroform, and toluene were all reagent-grade materials; the perchloroethylene was a commercial grade. The phosphorus trichloride-DMF adduct was made by the procedure of Smith,⁵ with the exception that the adduct was diluted with DMF or DMF-chloroform for use with cotton.

The fabric samples were immersed in excess DMF for 30 min, put through wringers at 100 lb pressure (wet pickup range of 90-110%), then agitated for 5-60 min in a laboratory shaker with 1-25% solutions of PCl_3 -DMF adduct at 25°C, using DMF or DMF-chloroform as the solvent. In a few cases, other solvents such as toluene or perchloroethylene were employed. Wash procedures utilizing water in the final step were primarily of two types: (a) initial wash with DMF to remove excess adduct, then ice water, then excess tap water for 30 min, or (b) initial wash with DMF to remove excess adduct, then ice water, subsequent soaking in excess 5% aqueous acetic acid for 10 min, and rinsing with excess tap water for 1 min. In either case, the fabrics were allowed to air dry after the final wash. Other special wash procedures and techniques are described in the tables and text.

Elemental analyses for chlorine, calcium, and phosphorus were run by x-ray fluorescence, and nitrogen was determined by the Kjeldahl method. Infrared spectra were recorded on a Perkin-Elmer 137B Infracord spectrophotometer using discs of the modified cellulose in potassium bromide.

Breaking strength in the warp direction was determined by the method of ASTM D-1682-64; wrinkle recovery was by the Monsanto method (ASTM D-1295-67). The standard vertical flame test was that described in U. S. Federal Supply Service "Textile Test Methods," Federal Test Method Std. No. 191., Method 5903.1; the match or clock test is that described by Reeves et al.⁶ Durability to laundering of the treated fabrics was determined by repeated washing and drying in an agitator-type

washer and a tumble dryer under normal conditions for cotton (10 min hot-water wash, 30 min high-temperature drying) using the commercial phosphate detergent Tide XK.

RESULTS AND DISCUSSION

Effect of Adduct Concentration and Wash Procedure on Fabric Flammability

The reaction of the PCl_5 -DMF adduct with cotton sateen was quite rapid at room temperature, but was still quite dependent on several factors: the solvent in which the adduct was dissolved, the adduct concentration, and the reaction time.

Of the solvents screened, only chloroform and DMF were effective media for reaction of the adduct with the cellulose. In nonpolar solvents such as toluene or perchloroethylene, reaction was incomplete. DMF also proved effective for preactivating the cellulose and was therefore used both as pretreatment solvent and as the reaction solvent in these studies, although at high adduct concentrations, chloroform-DMF mixtures were employed to ensure that the adduct would not precipitate from solution. The pretreatment time was held constant at 30 min for all treatments reported; excess DMF was removed by laboratory-type wringers prior to reaction of fabric with the adduct in DMF.

The effects of concentration and reaction time on fabric composition and flame resistance are shown in Table I. Increases in the weight gain and the phosphorus and nitrogen contents, and a decrease in the fabric flammability, were observed with an increase in the concentration of the adduct employed. Under comparable conditions (reaction time constant at 1 hr and use of the HOAc wash procedure), increasing the adduct concentration from 1% to 15% increased the phosphorus and nitrogen contents respectively from 0.87% P and 0.36% N to 3.84% P and 0.78% N (see Table I). Flame resistance of the fabric greatly increased even during treatment with low adduct concentrations. Although 1% of the adduct was not adequate to cause the fabric to pass the standard vertical flame test (BEL), 2% adduct produced a fabric having a char length as low as 2.5 in. and exhibiting no afterglow (1.23% P and 0.56% N). Increasing the adduct concentration from 15% to 25% had no additional beneficial effect on improving the initial flame resistance of the fabric, but did moderately increase the phosphorus content (from 3.84% to 4.73% P). No further increase in the nitrogen content of the fabrics was noted.

Although the wash procedures employed had no noticeable effect on either the weight gain or phosphorus content of the fabrics at a given reaction time and adduct concentration, they did have a marked influence on the resultant flammability of the fabrics (see Table I). Less concentrated solutions of adduct were required to impart a given degree of flame resistance if the fabric was afterwashed with acetic acid than if afterwashed with tap water. For example, sateen fabric treated with 2% adduct solu-

TABLE I
Effect of Adduct Concentration and Sojourn Time on Reaction of PCl_5 -DMF Adduct with Cotton Sateen

% Adduct ^a	Solvent	Reaction time, hr	Wash procedure ^b	% Wt. gain	% P ^c	% Cl ^c	% Ca ^c	% N ^c	Char length, in.
1	DMF	1	HOAc	3.5	0.87	0.00	0.07	0.36	BEL
2	DMF	1/12	HOAc	3.3	0.49	0.07	0.04	0.24	3.5
2	DMF	1/4	HOAc	5.3	1.04	0.03	0.06	0.42	8.5
2	DMF	1	HOAc	7.2	1.23	0.00	0.06	0.56	2.5
5	DMF	1/12	HOAc	6.5	1.34	0.17	0.04	0.40	3.5
5	DMF	1/4	HOAc	10.2	2.33	0.03	0.11	0.57	3
5	DMF	1	HOAc	12.7	2.78	0.18	0.06	0.66	2.75
5	DMF	1	H ₂ O	10.5	2.49	0.17	0.36	0.37	5.5
8	DMF	1	H ₂ O	11.4	2.95	0.24	0.34	0.46	4
10	DMF	1	H ₂ O	12.7	3.23	0.32	0.27	0.55	3.5
15	DMF	1	HOAc	18.2	3.84	0.47	0.06	0.78	2
15	DMF	1	H ₂ O	14.0	3.59	0.40	0.28	0.71	3.5
20	20% CHCl_3	1	H ₂ O	18.6	4.05	0.45	0.54	0.47	3
	80% DMF								
20	33% CHCl_3	1	HOAc	18.3	3.84	0.47	0.06	0.78	1.75
	47% DMF								
25	16% CHCl_3	1	H ₂ O	14.6	3.92	0.39	0.29	0.56	2.5
	59% DMF								
25	16% CHCl_3	1	HOAc	18.8	4.73	0.78	0.05	0.70	2.25
	59% DMF								

^a Cotton sateen fabric, 8.2 oz/yd², was immersed in excess DMF for 30 min, put through wringers, then shaken for times listed above with various concentrations of the adduct (using 40 g of soln. per g of fabric); adduct and solvents are given in wt.-% totaling 100%.

^b HOAc wash procedure consisted in washing with DMF three times, ice water, ice water, ice water, soaking in 5% ac. acetic acid for 10 min, then washing in tap water for 1 min, and air drying; H₂O procedure differs in that, after ice water wash, fabrics were washed for 30 min in tap water prior to air drying.

^c All analyses were done using x-ray fluorescence, except nitrogen, which was done by the Kjeldahl method.

^d Standard vertical flame test; BEL = burned entire length.

tion for 1 hr, then washed by the acetic acid method, easily passed the vertical flame test (2.5 in. char length), while treatment with a 5% adduct solution for 1 hr, followed by a tap water wash, produced a fabric having a char length of 5.5 in. Only at adduct concentrations of 10% or greater were fabrics given a tap water wash comparable in flame resistance to those treated with 2% adduct solution and given an acid wash.

An examination of the calcium and nitrogen contents of fabrics treated at comparable adduct concentration but washed by differing procedures revealed that the fabric given the acid wash had a calcium content of only 0.06% and a nitrogen content of 0.66%, while fabric given a tap water wash took up six times as much calcium (0.36%), and its nitrogen content was low (0.37%). Evidently, the water-washed fabric acquired some ion exchange properties. This point will be discussed in detail later in relation to the mechanism by which the adduct reacts with cellulose and the product structures that result.

Effect of Reaction Time on Fabric Flammability

At a given adduct concentration, an increase in the reaction time resulted in an increase in the weight gain as well as in phosphorus and nitrogen contents. There was a corresponding increase in flame resistance of the cotton fabrics. The effect of varying reaction time was investigated using the acid wash procedure, since this was shown to require the minimum adduct concentration to impart flame resistance; under these conditions the minimum reaction time required could also be determined.

As shown in Table I, an abrupt increase in weight gain, and in phosphorus and nitrogen contents, was observed when the reaction time was increased from 5 min to 15 min (irrespective of the adduct concentration employed). Treatment with a 2% adduct solution for 5 min produced 0.49% P and 0.24% N, while at the same adduct concentration treatment for 15 min approximately doubled the phosphorus and nitrogen contents (1.04% and 0.42%, respectively). However, if the reaction time was increased to 1 hr, the phosphorus content increased to only 1.23% and the nitrogen content, to 0.56%. Similar results were observed with the 5% adduct at comparable reaction times, although the extent of reaction was much greater for a given reaction time than with the 2% adduct (see Table I).

In terms of fabric flammability, reaction with 2% adduct for times of less than 1 hr did not provide adequate flame resistance, since a reversal in char length occurred using the 5-min and 15-min treatments. However, with 5% adduct, a 5-min treatment gave a fabric containing 1.34% P and 0.40% N and was quite adequate in imparting a high degree of flame resistance (char length 3.5 in.).

Durability of Adduct-Treated Cotton Sateens to Home Laundering

The durability of the flame-resistant cotton fabrics to machine laundering and tumble drying was investigated (Table II). The fabrics subjected to

TABLE II. Durability of Adduct-Treated Sateens to Home Laundering

% Adduct ^a	Solvent	Wash procedure ^b	Home Laund., cycles ^c	% Wt. gain ^d	% P ^e	% Cl ^e	% Ca ^e	% N ^e	Char length, f in.
5	DMF	HOAc	0	9.8	1.76	0.02	0.02	0.61	3.75
5	DMF	HOAc	5	7.9	2.18	0.00	0.73	0.17	BEL
20	20% CHCl ₃								
	60% DMF	H ₂ O	0	18.6	4.05	0.45	0.54	0.47	3
20	20% CHCl ₃								
	60% DMF	H ₂ O	10	14.2	4.60	0.34	1.16	0.26	BEL
20	20% CHCl ₃								
	60% DMF	H ₂ O	15	14.0	4.80	0.47	1.29	0.29	2.5
20	33% CHCl ₃								
	47% DMF	HOAc	0	15.8	4.19	0.85	0.05	0.75	2.75
20	33% CHCl ₃								
	47% DMF	HOAc	10	14.0	4.50	0.97	1.21	0.34	2.75
20	33% CHCl ₃								
	47% DMF	HOAc	15	13.7	4.56	0.85	1.33	0.29	BEL
25	16% CHCl ₃								
	59% DMF	H ₂ O	0	14.6	3.92	0.39	0.29	0.56	2.5
25	16% CHCl ₃								
	59% DMF	H ₂ O	5	14.7	4.26	0.31	0.83	0.20	3.5
25	16% CHCl ₃								
	59% DMF	H ₂ O	10	17.2	5.20	0.68	1.08	0.26	3.75
25	16% CHCl ₃								
	59% DMF	H ₂ O	15	15.4	5.03	0.64	1.17	0.26	BEL
25	16% CHCl ₃								
	59% DMF	H ₂ O	20	16.4	5.20	0.83	1.16	0.29	3.5

^a Cotton sateen fabric, 8.2 oz./yd², was immersed in excess DMF for 30 min, put through wringers, then shaken for 1 hr at 25°C in various concentrations of the adduct listed above (using 40 g of soln. per g of fabric), adduct and solvents for expressed in wt-% totaling 100%.

^b Same as described in Table I, footnote b.

^c A cycle consists of a normal wash (10 min, hot water, 1 cup phosphate detergent), followed by drying for 30 min at normal dry cycle and high-temperature setting.

^d Wt.-% gains listed are after the stated number of launderings.

^e Phosphorus, chlorine, and calcium determined by x-ray fluorescence; nitrogen determined by Kjeldahl method; all analyses were taken after specified number of home launderings listed.

^f By standard vertical flame test: BEL = burned entire length.

laundering were previously reacted for 1 hr with 5–25% concentrations of the adduct in DMF or DMF–chloroform and washed by either the acetic acid or tap water procedure.

Although a 5% adduct concentration was quite adequate to impart high initial flame resistance to sateen ($3\frac{3}{4}$ in. char length), the treated fabric failed the vertical flame test after five laundering cycles. This can be attributed to the great increase in calcium content (from 0.02% to 0.73%) and corresponding decrease in the nitrogen content (from 0.61% to 0.17%) after laundering.

Fabrics previously treated with 20% concentrations of the adduct (irrespective of the wash procedure, see Table II) had flame resistance durable for 10–15 launderings. The same problem with increased calcium ion uptake (up to 1.3%) and loss of original nitrogen content (from 0.5–0.8% to 0.3%) was experienced, but in most cases the phosphorus content was great enough (usually over 4.5%) to offset the ion exchange properties to produce fabrics which passed the vertical flame test. For example, sateen fabric containing 4.8% P, 1.3% Ca, and 0.3% N after 15 launderings passed the vertical flame test with a char length of only 2.5 in.

Fabrics treated with 25% adduct concentrations were somewhat more durable to laundering, since a fabric given 20 home launderings and containing 5.2% P, 1.2% Ca, and 0.3% N still passed the vertical flame test (3.5 in. char length). At this stage of development, the fabrics produced had moderate durability to laundering (10–20 cycles), although their initial flame resistance was excellent (achieved using only 5% adduct concentrations).

Tensile and Wrinkle Recovery Properties of Adduct-Treated Cotton Sateens

Treatment of cotton sateen fabrics with the PCl_3 –DMF adduct produced moderate increases (40–60° W+F) in both the wet and dry wrinkle recoveries. The wet wrinkle recovery achieved with low adduct concentrations was not further increased with concentrations above 5% and/or reaction times longer than 5 min. For example, sateen fabric treated with 5% adduct for 5 min gave the same wet wrinkle recovery value (214°) as fabric treated with 5% adduct for 1 hr; treatment for 1 hr with 15% adduct resulted in only a moderate increase (224°). In contrast to this behavior, the conditioned wrinkle recovery increased with an increase in the adduct concentration and reaction time, although, as shown in Table III, it appeared to reach a maximum with 15% adduct concentration (230°). For comparable reaction times (1 hr), using adduct concentrations less than 15% produced dry wrinkle recoveries of 200–222°.

Tensile properties of the adduct-treated fabrics (listed in Table III) were adversely affected by increasing the concentration of the adduct employed. Reaction for 1 hr with 5% adduct produced a fabric having 68–73% strength retention, while a progressive strength reduction to 33% was observed when increasing the adduct concentration to 25%. Re-

TABLE III
Tensile and Wrinkle Recovery Values of Adduct-Treated Sateens

% Adduct ^a	Reaction time, hr	Solvent	Wash procedure ^b	% P ^c	% N ^c	B.S., lb	B.S. retained, ^d %	Wrinkle recovery (warp + fill)	
								Cond.	Wet
5	1/12	DMF	HOAc	1.00	0.35	106.0	77	185	214
5	1/4	DMF	HOAc	1.43	0.54	105.2	77	197	222
5	1/4	DMF	HOAc	1.76	0.61	89.5	65	215	222
5	1/4	15% DMF 80% CHCl ₃	HOAc	2.97	0.25	42.9	31	199	218
5	1/2	DMF	HOAc	1.29	0.57	103.5	75	195	214
5	1	DMF	HOAc	1.77	0.64	100.6	73	200	211
5	1	DMF	HOAc	2.38	0.75	93.8	68	209	218
10	1	DMF	HOAc	3.44	0.80	76.2	55	222	212
15	1	DMF	HOAc	3.84	0.78	68.6	50	230	224
20	1	47% DMF 33% CHCl ₃	HOAc	4.59	0.68	57.0	42	228	212
25	1	59% DMF 16% CHCl ₃	HOAc	4.21	0.71	45.9	33	217	211
None ^e	—	—	HOAc	—	—	133.3	97	149	172
None ^f	—	—	—	—	—	137.3	(100)	183	168

^a Sateen fabrics treated under same conditions described in Tables I and II.

^b HOAc wash procedure consisted in washing with DMF three times, then with ice water, soaking in 5% aq. acetic acid for 10 min, then washing in excess tap water for 1 min, and air drying.

^c Phosphorus determined by x-ray fluorescence; nitrogen determined by the Kjeldahl method.

^d Compared to untreated cotton sateen fabric.

^e Given the DMF pretreatment, then the HOAc wash.

^f Untreated sateen fabric.

action time at a given adduct concentration appeared to have little influence on tensile strength, as evidenced from the time study with 5% adduct shown in Table III. The strength retention observed with 5% adduct for 5–60 min was only 65–77%. The strength retentions obtained with DMF as solvent were superior to those obtained when using chloroform. A mixture of 5% adduct, 15% DMF, and 80% CHCl_3 produced a fabric having only 31% strength retention, compared to a fabric having 65% strength retention (at comparable reaction times) when the solvent was DMF alone. Presumably, the beneficial effects of DMF are due to its effectiveness as an acid scavenger; this is readily demonstrated by the above comparison of tensile properties using DMF and DMF- CHCl_3 as adduct solvents.

Proposed Mechanism of the Adduct Reaction with Cellulose

Elemental analyses of cotton fabrics treated with the PCl_3 -DMF adduct show definite trends in the phosphorus/nitrogen ratio. The ratios proved to be dependent on the wash procedures employed. To a large extent, the phosphorus content is altered very little by change in the wash procedure. On the other hand, fabrics given an acetic acid wash, particularly those treated at low adduct concentrations, have approximately twice the nitrogen content of those treated under comparable conditions and given a tap water wash (see Tables I–III). Chlorine contents are usually negligible at low adduct concentrations (less than 0.3%), but at higher adduct concentrations reach values of 0.5–1.0%, with some dependence on the wash procedure used. As previously observed, the calcium content increases markedly with either a tap water wash or home laundering.

In an effort to elucidate the mechanism by which the PCl_3 -DMF adduct initially reacts with the cotton cellulose and then undergoes partial hydrolysis leading to ion exchange properties in the fabric, sateen fabrics were treated with 5% and 15% solutions of the adduct for 15 min and were later washed by one of three different procedures. The effect of the wash procedure on the P, N, Cl, and Ca contents as well as on the P/N and P/Cl ratios in the fabrics was investigated. The wash procedures employed were as follows: (1) wash with DMF, then chloroform; (2) the acetic acid wash procedure previously described; and (3) the tap water wash procedure previously described. Figures 1 through 4 depict the amounts of these elements remaining in the fabrics after the latter were washed by one of the three methods.

The phosphorus content of the fabrics was basically unaffected by using different wash procedures (Fig. 1), being in the range of 1.8–1.9% for fabrics given the 5% adduct treatment, and 2.7–3.1% in the case of the 15% adduct treatment. The nitrogen contents observed under comparable conditions (Fig. 2) showed a quite different behavior.

In the case of the 5% adduct treatment, the fabric contained 0.9% N after a chloroform wash, 0.55% N after the acetic acid wash, and only 0.2% N after a tap water wash. As shown in Figure 2, similar results

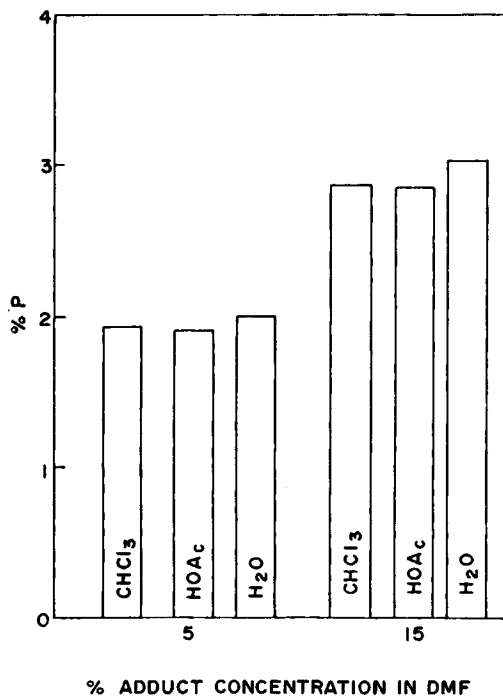


Fig. 1. Effect of wash procedure on phosphorus content of cotton sateen treated with 5% and 15% PCl_3 -DMF in DMF at 25°C.

were obtained at the 15% adduct level. The significance of these observations can best be seen in terms of the P/N ratios obtained. The ratio of phosphorus/nitrogen atoms in the product was essentially unity, irrespective of adduct concentration, for fabrics given a nonaqueous or chloroform wash increased to 1.5–2.0 for an acetic acid wash and further increased to 4.5–5.0 for the tap water wash. The initial reaction of the cotton cellulose with the PCl_3 -DMF adduct apparently yields a product having one P atom for every N atom, and the subsequent hydrolysis is selective, since it removes most of the nitrogen-containing substituents of the cellulosic derivative.

The chlorine contents of the fabrics were quite high (Fig. 3) for those given the chloroform wash (1.6% Cl for the 5% adduct treatment and 2.5% Cl for the 15% adduct treatment). However, exposure to water (either an acetic acid or tap water wash) caused the chlorine content to be reduced by 80% or more. Evaluating this behavior in terms of the P/Cl atomic ratio, fabrics washed with chloroform had a value of 1.3; those given an acetic acid wash, a value of 9.2; and those washed with tap water, values ranging from 8 to 30. Taking into consideration that the chloroform-washed fabrics may have undergone some hydrolysis by moisture in the air, the P/Cl ratio is near to unity. This indicates that the cellulosic reaction product contains not only one P for every N, but one Cl atom as well.

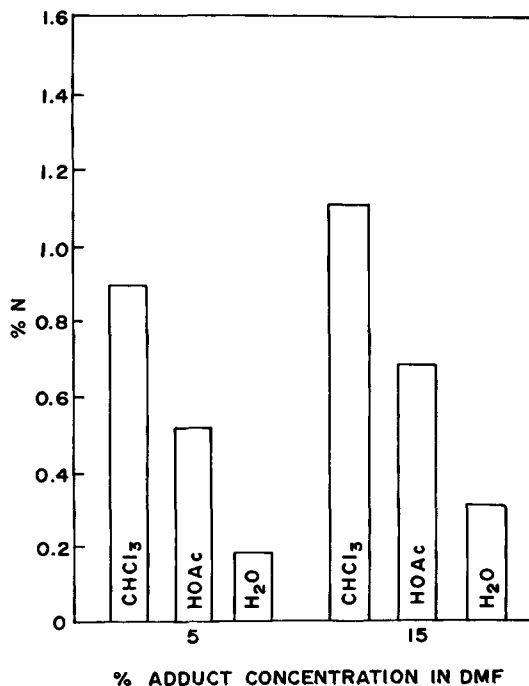
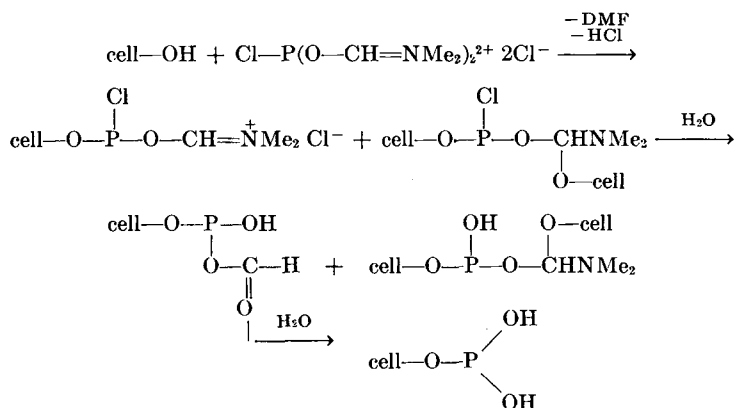


Fig. 2. Effect of wash procedure on nitrogen content of cotton sateen treated with 5% and 15% PCl₃-DMF in DMF at 25°C.

The calcium content (Fig. 4) was essentially negligible (0.01-0.03%) for fabrics washed with either chloroform or acetic acid (irrespective of adduct concentration), but increased markedly on fabrics given a tap water wash (to 0.55%). This behavior is typical of an ion exchange cotton. A mechanism consistent with the reaction of cellulose with the adduct and subsequent hydrolysis of the cellulosic product is as follows:



These reactions are consistent with the analyses shown in Figures 1-4, and are also consistent with the infrared spectra of the cellulosic product

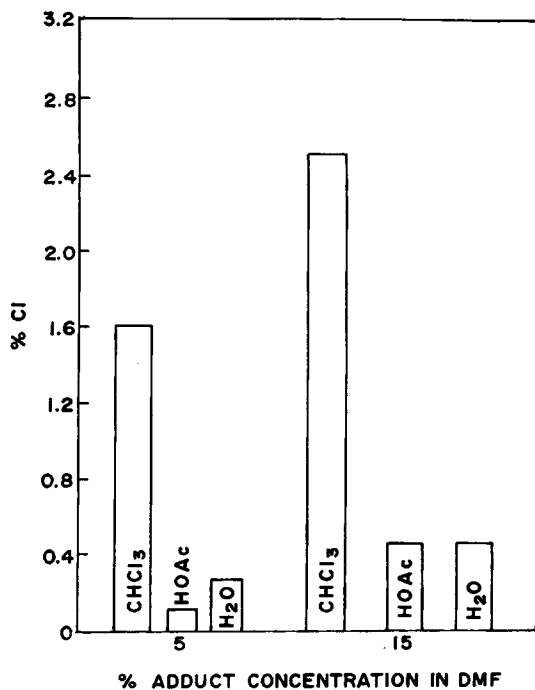


Fig. 3. Effect of wash procedure on chlorine content of cotton sateen treated with 5% and 15% PCl₃-DMF in DMF at 25°C.

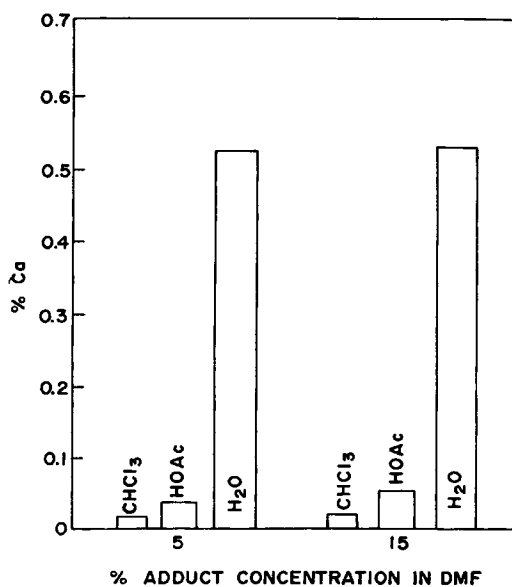


Fig. 4. Effect of wash procedure on calcium content of cotton sateen treated with 5% and 15% PCl₃-DMF in DMF at 25°C.

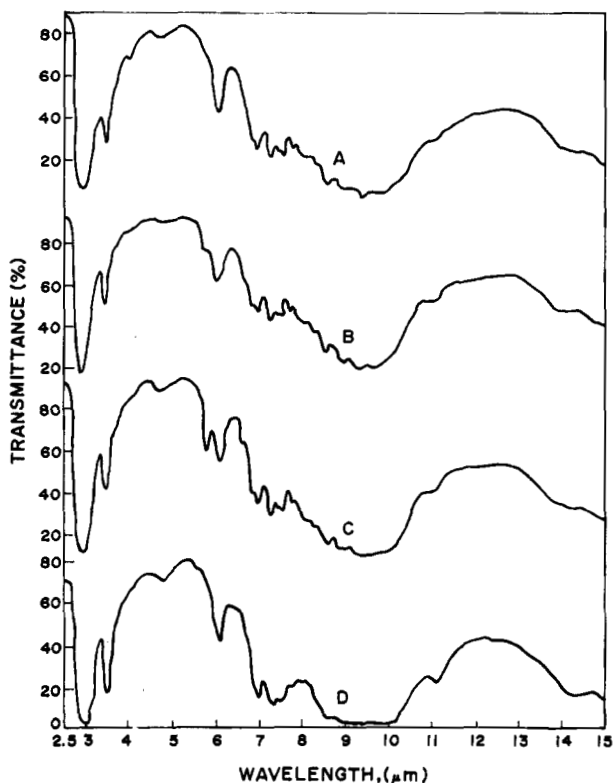


Fig. 5. Infrared spectrum of cotton sateen treated for 15 min at 25°C with 15% PCl_3 -DMF in DMF, then washed with DMF, then with (a) chloroform, (b) ice water, 5% HOAc, and tap water, (c) ice water and tap water: (d) untreated sateen.

taken after each of the three wash procedures. In Figure 5, spectra are shown for fabrics treated with 15% adduct and then washed by each of the three procedures. There is an increase in the carbonyl peak (5.75–5.85 μm) in going from chloroform wash to acetic acid wash to a tap water wash. This peak is thought to be due to the very labile formate ester of the phosphorylated cellulose depicted in the equations above, which hydrolyzes readily to the free phosphoric acid form. The residual nitrogen which is never completely removed (usually about 20–25% of the original) is thought to be due to some crosslinking of the cellulose through the formimidate group of the adduct, as depicted above. Experiments are now in progress to reduce or eliminate ion exchange behavior in the cellulosic product and make it an acceptable flame-retardant finish by modifying the structural features of this material.

The authors wish to thank Biagio Piccolo and John Mason for the determination of the elemental analyses. We wish also to acknowledge the contribution of Louise Bosworth in textile tests made on the fabrics.

Use of a company or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

References

1. H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).
2. T. L. Vigo, D. J. Daigle, and C. M. Welch, *J. Polym. Sci., B*, **10**, 397 (1972).
3. T. L. Vigo and C. M. Welch, *Text. Res. J.*, **40**, 109 (1970).
4. H. Rath, J. H. Rau, and G. Brink, *Melliand Textilber.*, **47**(8), 909 (1966).
5. T. D. Smith, *J. Chem. Soc. (A)*, 841 (1966).
6. W. A. Reeves, O. J. McMillan, Jr., and J. D. Guthrie, *Text. Res. J.*, **23**, 527 (1953).

Received August 15, 1972.