

## Flame-Retardant Properties and Thermal Behavior of Selected Flame-Retardant Cotton Fabrics\*

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### Synopsis

The flame-retardant properties and the thermal behavior of cotton cellulose finished with THPC-amide, THPOH-amide, THPOH-NH<sub>2</sub>, and THPC-cyanamide were investigated before and after five washes. Phosphorus and nitrogen content, N/P ratios, and total add-on of finish were determined. Flammability properties were evaluated by the 45° angle, the vertical strip, and oxygen index tests. Differential scanning calorimetry and thermogravimetric analysis were used to study the thermal behavior of the fabrics during pyrolysis. Infrared spectra of samples before pyrolysis and at significant points in the pyrolysis reaction were used to obtain further information regarding the pyrolysis reaction. The THPC-amide, THPOH-amide, and THPC-cyanamide finishes appeared to react in a similar manner to impart flame-retardant properties to the fabrics. During pyrolysis, the finished fabrics apparently decomposed first by an acid catalyzed dehydration and chain breakdown. The second step of the pyrolysis probably involved phosphorylation of the C-6 hydroxyl of the anhydroglucose unit occurring around the temperature range of 345°–350°C. The final step was char formation. The THPOH-NH<sub>2</sub> finished fabric decomposed with a strong exothermic reaction under nitrogen which suggested that the reaction was initiated by a base catalyzed dehydration and chain breakdown. This seemed to be followed by phosphorylation at the C-6 hydroxyl of the anhydroglucose units and then char formation. An inverse relationship between  $\Delta H$  and the residue remaining after pyrolysis was observed.  $\Delta H$  was also linearly related to the N/P ratios. All of the fabrics except the THPC-cyanamide-finished fabric had good flammability properties before and after laundry.

### INTRODUCTION

Cotton cellulose, when exposed to an ignition source, will decompose and produce gases which ignite, propagate the flame and heat, and further decompose the cellulose until only a feathery ash remains. Various flame retardants have been used to change the thermal degradation of cellulose, but their reaction mechanisms are not fully understood. Recent legislation has increased the need to understand the action of compounds which decrease the flammability of cotton fabrics.

The primary role of a flame retardant is to alter the decomposition process in some way so that a smaller amount of flammable gases is produced and, correspondingly, a larger char is formed.<sup>1</sup> Phosphorus-containing com-

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pounds in combination with nitrogen or with a halogen are the most widely used durable flame retardants for cotton. Schuyten, Weaver, and Reid<sup>2</sup> proposed that the flameproofing of cellulose was due to a dehydration process operating by acid or basic catalysis through a carbonium or carbanion mechanism. Schwenker and Beck<sup>3</sup> pyrolyzed cellulose in different atmospheres and at different rates and reported that cellulose appeared to decompose by a common mechanism which was nonoxidative and essentially thermal. Schwenker and Pacsu<sup>4</sup> showed that the prevention of levoglucosan formation, one of the products of thermal decomposition, would decrease the flammability of cellulose.

Recently, Hendrix et al.<sup>5</sup> studied cotton finished with phosphoric acid and some of its derivatives and suggested that phosphorylation followed by an acid-catalyzed dehydration and thermal decomposition of the treated cotton occurred. The probable site for phosphorylation was the C-6 hydroxyl of the anhydroglucose units, thereby preventing the formation of levoglucosan. Tesoro and co-workers<sup>6-8</sup> reported that nitrogen has a synergistic effect in the flame-retardant effectiveness of organophosphorus compounds. When nitrogen was added to the system, the per cent phosphorus could be decreased without decreasing the efficiency of the flame retardant. Hendrix et al.<sup>5</sup> suggested that the phosphorus-nitrogen synergistic effect may be due to the formation of a more effective catalyst for cellulose degradation by the interaction of the phosphorus and nitrogen compounds, or the nitrogen may react directly with the products of the cellulose decomposition.

Kilzer and Broido<sup>9</sup> proposed that a base may change the pyrolysis mechanism of cellulose so that levoglucosan is not formed. Mack and Donaldson<sup>10</sup> used thermal analysis to investigate the effects of bases on the pyrolysis of cotton cellulose. They found that the basic additive lowered the heat of reaction, caused a reversal from an endothermic to an exothermic reaction, lowered the temperature of decomposition, lowered the energy of activation, and increased the per cent residue remaining after pyrolysis.

In this research, the flame-retardant properties and the thermal behavior of cotton cellulose finished with four phosphorus-containing flame-retardant compounds were investigated. The thermal behavior of the finished cotton was examined by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and infrared analysis. DSC and TGA thermograms were used to identify the decomposition temperature or decomposition temperature range of the finished cotton. Infrared spectra of samples heated to the significant temperature of pyrolysis, determined from the DSC and TGA thermograms, were obtained. The data were analyzed in an effort to obtain more information concerning the flame-retardant mechanisms of the four finishes studied.

## EXPERIMENTAL

The fabric used in this study was a bleached, mercerized, 160 × 160 combed cotton twill weighing 6.3 oz/sq yd, which was obtained from Test

Fabrics, Inc. Samples of the fabric were finished with four different flame-retardant finishes by the Southern Utilization Research and Development Division of the U.S. Department of Agriculture. The fabrics were finished by the dip-and-nip method using the following treatments:

**THPC-Amide.** 17.2% Tetrakis(hydroxymethyl)phosphonium chloride, 10.9% urea, 9.7% trimethylolmelamine, 4.3% triethanolamine, 0.5% Triton X-100 (trade name of Rohm & Haas Co.) and 57.4% H<sub>2</sub>O. Dry: 85°C/2 min; cure: 140°C/4 min.

**THPOH-Amide.** 16.2% Tetrakis(hydroxymethyl)phosphonium hydroxide, 11.4% urea, 10.2% trimethylolmelamine, 0.5% Triton X-100, 61.7% H<sub>2</sub>O. Dry: 85°C/2 min; cure: 140°C/4 min.

**THPOH-NH<sub>3</sub>.** 35% Tetrakis(hydroxymethyl)phosphonium hydroxide, 0.5% Triton X-100, 64.5% H<sub>2</sub>O. Dry: 85°C/3 min; cure: NH<sub>3</sub> vapors/4-6 min.

**THPC-Cyanamide.** 712.5 g Tetrakis(hydroxymethyl)phosphonium hydroxide, 504.0 g cyanamide, 70.0 g H<sub>3</sub>PO<sub>4</sub>, 14.4 g Velvetol OE (trade name of Quaker Chemical Corp.) 3.0 g Triton X-100, 2116.2 g H<sub>2</sub>O. Dry: 85°C/2 min; cure: 160°C/3 min.

Samples of each of the finished fabrics and the cotton control were laundered five times following the AATCC 124-1967 test method using AATCC Standard Detergent without an optical brightener and then dried in a tumble dryer at the high-temperature setting for 40 min.<sup>11</sup>

The following fabric properties were determined before and after the fabrics were laundered using ASTM methods<sup>12</sup>: weight and per cent addition of finish, ASTM D629-59T; tear resistance, ASTM D1424-63; breaking load, ASTM D1682-64; flame retardance by the 45-degree angle test, ASTM D1230-61, and the vertical strip test, ASTM D626-55T. Flammability was also determined by the oxygen index method<sup>13</sup> on a General Electric tester using 6 in × 2<sup>1</sup>/<sub>2</sub> in. samples. The nitrogen flow rate was maintained at 88 psig = 132.3 cc/sec.

Phosphorus present in the samples was determined by a colorimetric analysis of the phosphomolybdate complex after Kjeldahl digestion.<sup>14</sup> Nitrogen content was determined by a micro-Kjeldahl method following the procedure of the Association of Official Agricultural Chemists.<sup>15</sup>

**Differential Scanning Calorimetry.** DSC thermograms for each of the fabric samples were obtained before and after laundry. Samples were cut with a #2 cork borer and placed in tared aluminum sample pans, weighed, covered with an aluminum lid, and crimped, and weighed again on a Cahn electrobalance. The sealed samples were dried under vacuum over P<sub>2</sub>O<sub>5</sub> for six days and weighed to determine the dry weight of the sample. The solid components of the finishes were treated in the same manner except that 0.5- to 6.0-mg samples were used. All thermograms were run on a Perkin-Elmer Model DSC-1B differential scanning calorimeter in an atmosphere of nitrogen using a sample pan sealed with two lids as a reference. The program parameters were set at a range of 16 mcJ/sec, scan speed of 40°C/min, and chart speed of 1 in./min.

Reaction temperatures, pyrolysis range, nadir of the reaction, type of reaction (endothermic or exothermic), per cent residue, heat of reaction, and activation energy were obtained from the thermograms. Activation energies were estimated from the DSC thermograms using the method described by Rogers and Morris<sup>16</sup> and were reported as an average of five determinations. The heat of reaction was calculated from the area under the curve of the reaction, measured with a planimeter, as compared to the weight of the sample using indium as a standard:

$$\Delta H = \frac{\text{heat of fusion of standard} \times \text{weight of standard} \times \text{sample peak area} \times \text{chart speed of standard} \times \text{range setting of standard}}{\text{standard peak area} \times \text{chart speed of sample} \times \text{range setting of sample} \times \text{weight of sample}}$$

Data were reported as the average of five determinations.

Samples of each of the treated fabrics were pyrolyzed in the DSC by heating at a scan rate of 40°C/min from room temperature (25°C) to 450°C under an inert atmosphere of nitrogen. A quantitative microanalysis of the char was obtained to determine the per cent carbon, hydrogen, nitrogen, and phosphorus by weight in the pyrolyzed samples. Quantitative microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

**Thermogravimetric Analysis.** TGA analysis of the samples before and after laundry was done with a du Pont 950 thermogravimetric analyzer, using a constant heating rate of 5°C/min and a scale sensitivity of 2 mg/in. All measurements were made in an atmosphere of nitrogen at a flow rate of 0.2 l./min. Thermogravimetric analyses were done at Clemson University, Clemson, South Carolina, under the direction of Dr. Robert H. Barker.

**Infrared Analysis.** Infrared spectra of the treated fabric samples, ground in a Wiley Mill to pass a 20-mesh screen, were obtained on a Perkin-Elmer Model 421 grating spectrophotometer using a KBr pellet technique.<sup>17</sup> Spectra of pyrolyzed samples taken directly from the DSC pans and mixed with KBr were obtained at the initial point of the reaction curve, the nadir(s) of the reaction, and the endpoint. All samples were run from 3900 to 600 cm<sup>-1</sup> using a blank KBr pellet in the reference beam.

## RESULTS AND DISCUSSION

The finished fabrics before and after laundry are characterized in Table I. The cotton control gained weight (5.92%) after five washes. This was attributed chiefly to shrinkage (7.5%), but the control did pick up phosphorus (0.13%) from the laundry detergent. Each of the finished fabrics gained weight after five washes which may be attributed to shrinkage and to a pickup of phosphorus or some other component of the detergent. Both the THPC-amide- and the THPOH-amide-treated fabrics gained phosphorus and nitrogen during laundry, but this did not result in an appreciable change in their N/P ratios, which were very close to 2:1 both before and after laundry. The THPOH-NH<sub>2</sub>-treated fabric lost an appreciable

TABLE I  
Characterization of Fabric Finish

Fabric finish	Weight, oz/sq yd	Add-on of finish, %	Phos- phorus, %	Nitrogen, %	N/P ratio
Before Laundry					
Control	6.31	0	0.03	0.03	1.00
THPC-amide	7.14	13.20	1.64	2.82	1.72
THPOH-amide	7.23	14.53	1.68	3.06	1.82
THPOH-NH <sub>3</sub>	7.19	13.87	4.86	1.25	0.26
THPC-cyanamide	6.70	6.06	2.06	1.50	0.73
After Laundry					
Control	6.69	0	0.16	0.03	0.18
THPC-amide	7.62	13.98	1.99	3.79	1.91
THPOH-amide	7.51	12.30	1.88	3.45	1.84
THPOH-NH <sub>3</sub>	7.50	12.15	3.72	1.40	0.38
THPC-cyanamide	6.76	1.02	1.59	1.46	0.92

TABLE II  
Breaking Strength and Tear Resistance

Fabric finish	Breaking strength, lb/sq in. avg. W + F	Tear resistance, g avg. W + F
Before Laundry		
Control	106	2641
THPC-amide	104	2352
THPOH-amide	104	2186
THPOH-NH <sub>3</sub>	107	2614
THPC-cyanamide	46	1414
After Laundry		
Control	111	2191
THPC-amide	97	1822
THPOH-amide	105	1845
THPOH-NH <sub>3</sub>	107	2093
THPC-cyanamide	50	1103

amount of phosphorus but gained nitrogen during laundry because of shrinkage which changed the N/P ratio of 1:4 before laundering to 1:3 after laundry. A large portion of the THPC-cyanamide finish was lost after five washes, and the N/P ratio changed from 3:4 initially to about 1:1 after laundering.

The breaking load and tear strength of the fabrics are given in Table II. The THPC-amide, THPOH-amide, and THPOH-NH<sub>3</sub> finishes had very little effect on the breaking load and only a small effect on the tear resistance of the cotton before and after laundering. This was not true for the THPC-cyanamide-treated fabric, which showed large breaking and tear strength losses in both the warp and filling directions after treatment.

TABLE III  
Flammability Test Results

Fabric finish	Vertical Strip Test				
	Average char length, in.	Maximum char length, in.	After-flame, sec	Afterglow, sec	Oxygen Index
Before Laundry					
Control	12.0	12.0	14.0	117.2	0.184
THPC-amide	3.1	3.8	0	0	0.287
THPOH-amide	2.1	2.8	0	0	0.298
THPOH-NH <sub>3</sub>	2.7	3.0	0	0	0.300
THPC-cyanamide	4.4	5.5	0	0	0.269
After Laundry					
Control	12.0	12.0	23.9	12.6	0.182
THPC-amide	2.7	3.2	0	0	0.296
THPOH-amide	2.5	3.8	0	0	0.300
THPOH-NH <sub>3</sub>	3.0	3.5	0	0	0.290
THPC-cyanamide	4.8	5.8	0	0	0.258

Flammability properties of the fabrics were measured by the 45° angle test, the vertical strip test, and the oxygen index. All of the fabrics, including the cotton control, passed the 45° angle test. Of the finished fabrics, THPC-amide, THPOH-amide, and THPOH-NH<sub>3</sub> passed the vertical strip test before and after laundering. The THPC-cyanamide-finished fabric and the cotton control failed the vertical strip test both before and after laundering. Char lengths, afterflame, and afterglow are compared in Table III. Oxygen index data for the treated fabrics both before and after five washes are also given in Table III.

All fabric samples were pyrolyzed in the DSC under a nitrogen atmosphere both before and after laundry. The cotton control pyrolyzed with an endothermic reaction which began at 264°C and ran to 411°C with the nadir of the reaction at 390°C. The THPC-amide and the THPOH-amide finishes caused the reaction to be first endothermic and then exothermic. The THPOH-NH<sub>3</sub> and THPC-cyanamide treatments changed the pyrolysis to a double exothermic reaction. All the finishes, except the original THPC-cyanamide, lowered the initial temperature of pyrolysis, and the nadir of the reaction was lowered in all cases (Table IV).

Thermogravimetric analyses (TGA) indicated the temperature of first weight loss, the temperature range of major weight loss, and the half-volatilization temperature. The cotton control began to lose weight at 260°C, with the major weight loss occurring between 317°C and 351°C. The half-volatilization point was 334°C. All of the finishes lowered the temperature of initial weight loss and the half-volatilization point. The TGA data are summarized in Table V.

TABLE IV  
DSC Thermal Analysis

Fabric finish	Type of reaction	Temp. of pyrolysis, °C		Nadir of reaction, °C
		Initial	Final	
Before Laundry				
Control	endothermic	264	411	390
THPC-amide	endothermic	199		300
	exothermic		381	349
THPOH-amide	endothermic	185		278
	exothermic		379	351
THPOH-NH <sub>3</sub>	exothermic	240		319
	exothermic		346	333
THPC-cyanamide	exothermic	294		328
	exothermic		364	352
After Laundry				
Control	endothermic	281	404	383
THPC-amide	endothermic	204		299
	exothermic		378	351
THPOH-amide	endothermic	194		269
	exothermic		379	352
THPOH-NH <sub>3</sub>	exothermic	218		318
	exothermic		346	337
THPC-cyanamide	exothermic	262		330
	exothermic		398	355

TABLE V  
Thermogravimetric Analysis

Fabric finish	First	First	Half-	End of	Final	Temp.
	wt. loss,	major wt.	wt. volatile	first maj.	temp.,	span
	°C	loss, °C	point, °C	wt. loss,	°C	°C
Before Laundry						
Control	260	317	334	351	360	100
THPC-amide	215	297	308	319	325	110
THPOH-amide	215	295	307	319	325	110
THPOH-NH <sub>3</sub>	215	270	280	290	295	80
THPC-cyanamide	205	277	290	302	305	100
After Laundry						
Control	280	320	335	350	360	80
THPC-amide	245	298	308	318	325	80
THPOH-amide	250	300	312	323	325	75
THPOH-NH <sub>3</sub>	245	278	289	299	295	50
THPC-cyanamide	260	280	293	306	315	55

TABLE VI  
Per Cent Residue After Pyrolysis

Fabric control	Residue DSC		Residue TGA	
	Before laundry, %	After laundry, %	Before laundry, %	After laundry, %
Control	8.91	11.12	8.05	7.59
THPC-amide	36.01	39.96	37.65	39.78
THPOH-amide	39.13	37.97	37.57	38.16
THPOH-NH <sub>3</sub>	50.33	46.05	47.62	47.83
THPC-cyanamide	38.51	40.70	38.89	37.08

TABLE VII  
Comparative Elemental Analysis of the Fabric Before and After Pyrolysis

Fabric finish	Phosphorus, %		Nitrogen, %		N/P Ratio	
	Initial	Pyrolyzed	Initial	Pyrolyzed	Initial	Pyro-
						lyzed
Control	0.03	0.17	0.03	trace	0.83	—
THPC-amide	1.64	2.54	2.82	4.10	1.72	1.61
THPOH-amide	1.68	3.49	3.06	6.32	1.82	1.81
THPOH-NH <sub>3</sub>	4.86	6.42	1.25	2.76	0.26	0.42
THPC-cyanamide	2.06	3.27	1.50	3.33	0.72	1.02

The final temperatures of pyrolysis observed during TGA analysis were somewhat lower than the temperatures obtained with the DSC. The higher scan rate of 40°C/min for the DSC as compared to 5°C/min for the TGA accounted for the increased temperature.

The residue or the amount of char remaining after pyrolysis was determined from both the DSC and the TGA thermograms (Table VI). In order to be effective, a flame retardant should reduce the amount of combustible tar-like products formed and increase the amount of solid char formed. All of the treated fabrics had a higher per cent residue than the cotton control both before and after laundering. The THPOH-NH<sub>3</sub>-finished fabric had an appreciably higher residue than the other finished fabrics.

Quantitative microanalysis of the char showed that the per cent by weight of phosphorus and nitrogen was greater in the char than in the starting fabric, but the N/P ratios did not change very much (Table VII). The one exception to the trend was the THPOH-NH<sub>3</sub> treatment. The N/P ratio initially was 1:4, but after pyrolysis it was about 1:2. During pyrolysis this fabric lost 33.5% phosphorus but no nitrogen. If about 25% of the THPOH compound was volatile tris(hydroxymethyl)phosphine oxide, this would explain the loss of phosphorus during pyrolysis and account for the 1:2 N/P ratio in the char.

The heat of reaction,  $\Delta H$ , can be defined as the amount of heat (energy) absorbed or released during a reaction. The heats of reaction (Table VIII)



TABLE VIII  
Heats of Reaction and Activation Energies

Fabric finish	Heats of reaction, cal/g		Activation energy, kcal/mole	
	Before laundry	After laundry	Before laundry	After laundry
Cotton	100	108	64	61
THPC-amide	27	27	12	13
THPOH-amide	-16	-23	-182	not clear
THPOH-NH <sub>3</sub>	32	24	10	not clear
THPC-cyanamide	-15	-19	-102	-118
	-77	-83	-63	-37
	-33	-52	-98	-61

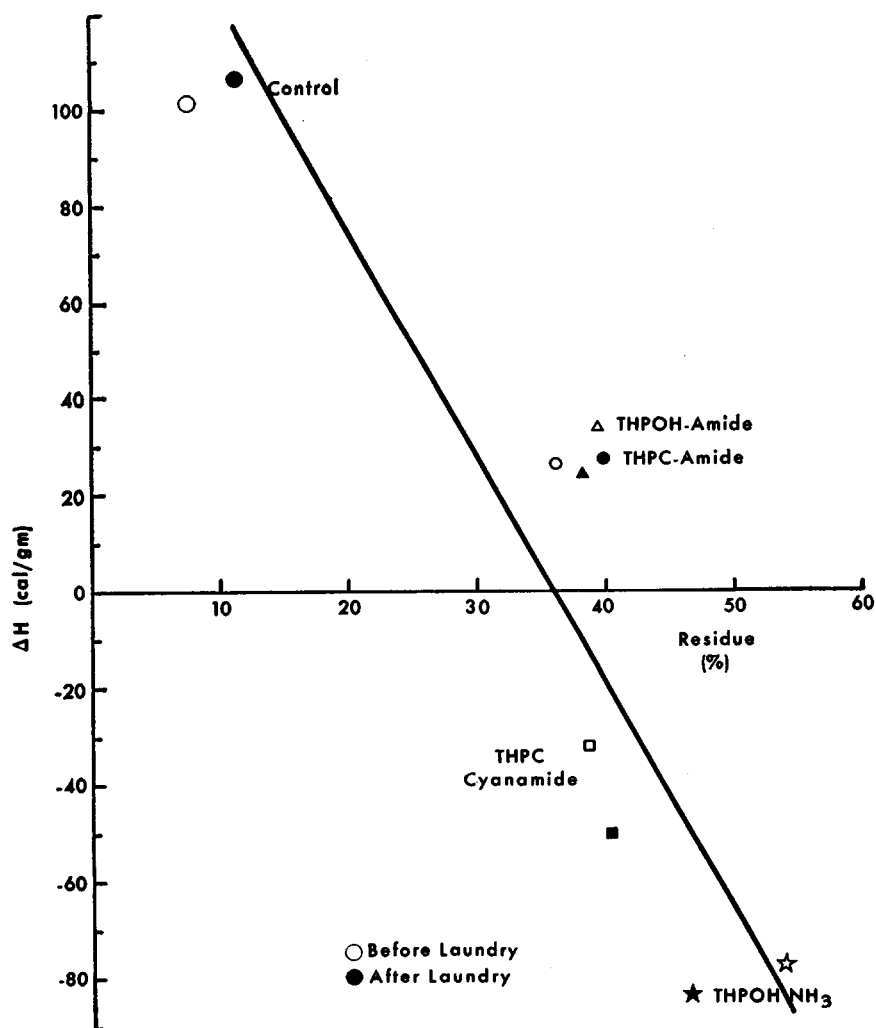


Fig. 1.  $\Delta H$  vs. per cent residue after pyrolysis.

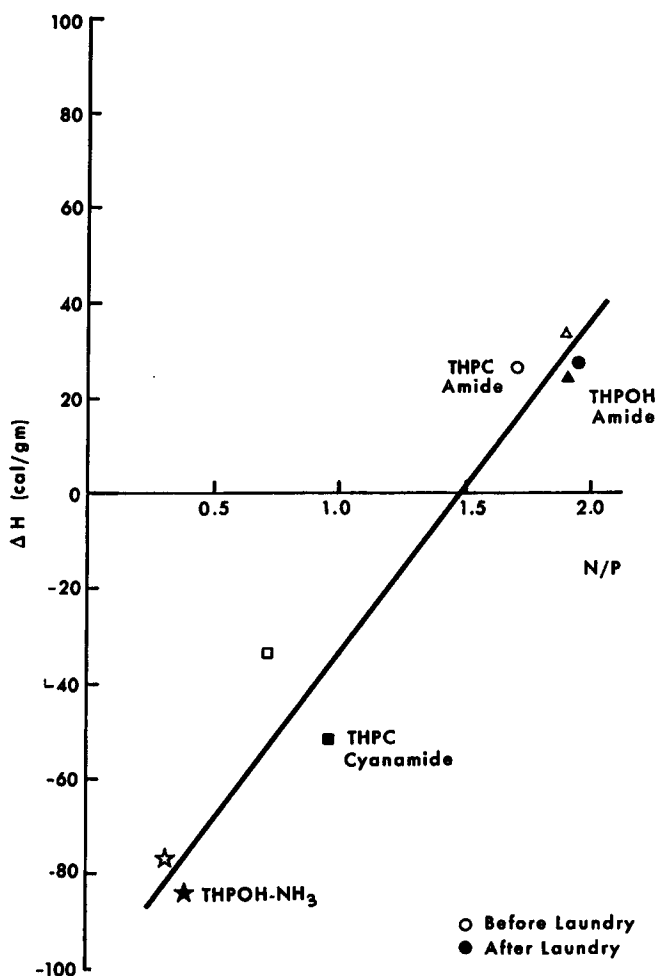


Fig. 2.  $\Delta H$  vs. N/P ratio.

were calculated directly from the DSC thermograms using the area under the curve and the weight of the sample in relation to a known standard. The  $\Delta H$  of the five treated fabrics were all lower than the  $\Delta H$  of the cotton control. As  $\Delta H$  decreased, the per cent residue remaining after pyrolysis increased (Fig. 1). There seemed to be an inverse relationship between the amount of heat absorbed during decomposition and the per cent residue produced. Those finished cottons which pyrolyzed by only an exothermic reaction, THPOH-NH<sub>3</sub> and THPC-cyanamide, produced the highest per cent residue. A linear relationship between  $\Delta H$  and the N/P ratio was observed for the finishes (Fig. 2).

The rate of absorption or evolution of heat during a reaction was measured directly in terms of calories per second as a function of temperature

with the DSC. Energies of activation,  $E_{act}$ , for the finished fabrics were estimated (Table VIII), but no apparent relationships were evident.

Infrared analysis was used to examine the structural changes which occurred during thermal decomposition. The following bands in the infrared spectrum of the original cellulose were identified<sup>17</sup> and used for comparisons with the treated fabrics: 2.9  $\mu$ , OH stretch; 3.4  $\mu$ , CH stretch; 6.13  $\mu$ , C=C stretch and/or absorbed water; 7.0  $\mu$ , HCH deformation; 8.6  $\mu$ , glucopyranose ring vibration; 9.5  $\mu$ , OH deformation; and 11.2  $\mu$ , CH deformation.

### Cotton Control

The infrared spectrum of the cotton control (Fig. 3) heated to 264°C, the beginning of the reaction curve from the DSC thermogram (Table IV), was the same as that for the original control before heating. The spectrum of the sample heated to 390°C, the nadir of the pyrolysis reaction, gave evidence of structural changes. The peak at 3.4  $\mu$  (CH stretch) decreased, and peaks at 5.8  $\mu$  (C=O stretch) and 6.1  $\mu$  (C=C stretch) appeared. The CH deformation peak at 11.2  $\mu$  and the CH<sub>2</sub> bend at 7.0  $\mu$  were almost gone. The sample heated to 411°C, the end of the pyrolysis reaction, gave a spectrum which was used to define the char pattern. Bands were present at 2.9  $\mu$  (OH stretch), 3.4  $\mu$  (CH stretch), 5.8  $\mu$  (C=O stretch), and 6.2  $\mu$  (C=C stretch). The peaks at 7.0  $\mu$ , 8.6  $\mu$ , 9.5  $\mu$ , and 11.2  $\mu$  were gone.

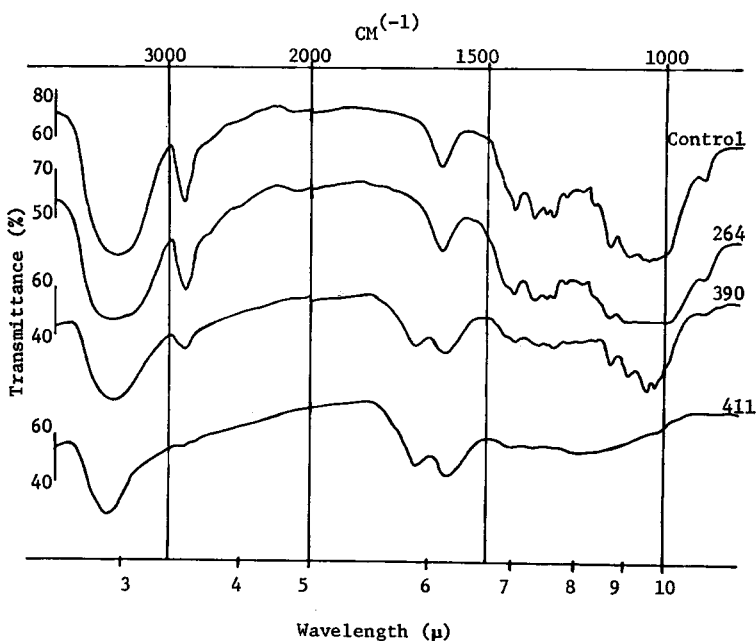


Fig. 3. Infrared spectra of cotton before pyrolysis (control) and at significant points in the pyrolysis reaction (°C).

Thermal decomposition of cellulose is believed to proceed by a two-step mechanism. The first step involves glycosidic bond scission, depolymerization, intramolecular rearrangement, and subsequent formation of 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan). Secondly, the levoglucosan decomposes into volatile and flammable products.

### THPC-Amide and THPOH-Amide

The THPC-amide and the THPO-amide finishes were effective in reducing the flammability of the cotton cellulose and lowering the temperature of decomposition. The DSC thermograms for both finishes showed first an endotherm and then a double-peak exothermic reaction. The unmodified tetrakis(hydroxymethyl)phosphonium chloride decomposed with first an endothermic and then an exothermic reaction. The finished fabric appeared to have a pyrolysis reaction related to the decomposition of the finish polymer.

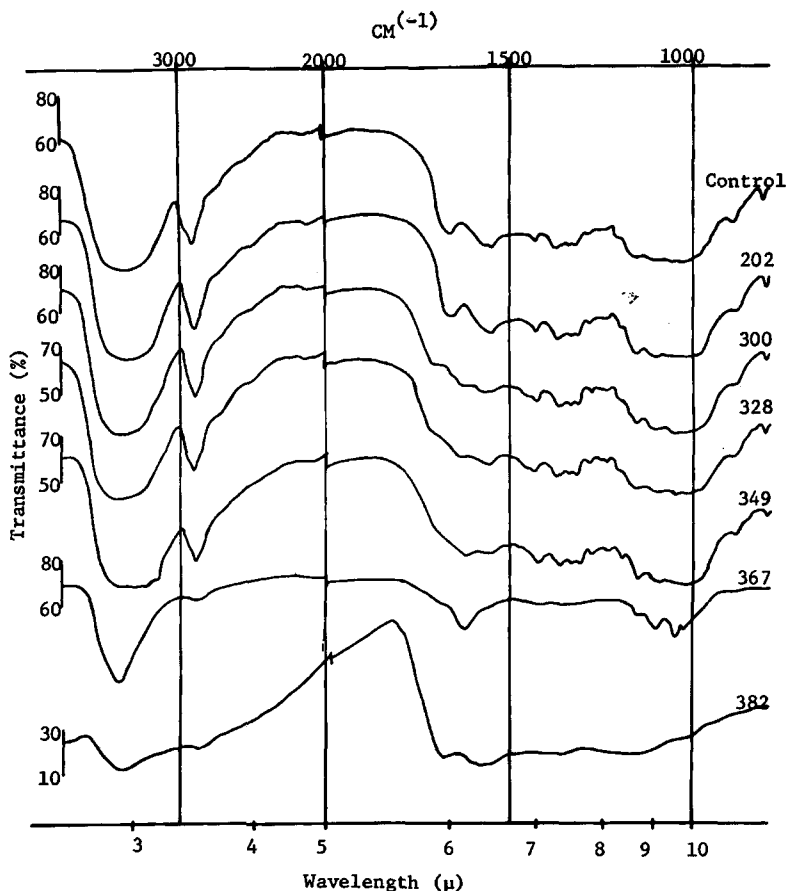


Fig. 4. Infrared spectra of THPC-amide-treated cotton before pyrolysis (control) and at significant points in the pyrolysis reaction ( $^{\circ}\text{C}$ ).

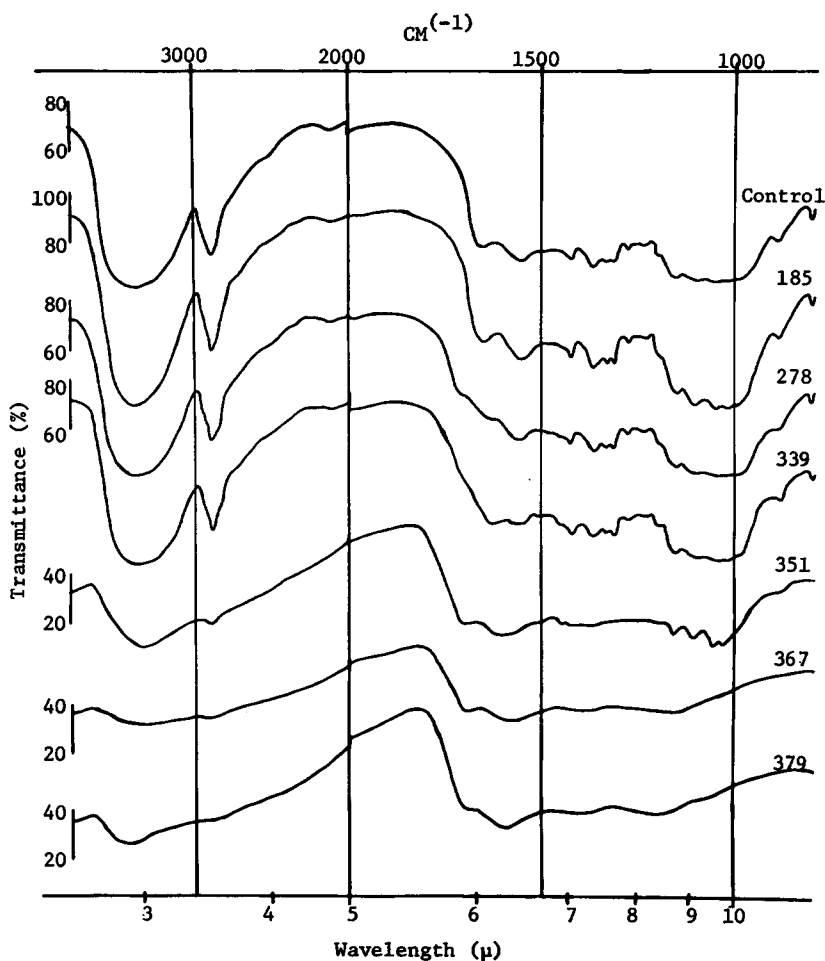


Fig. 5. Infrared spectra of THPOH-amide-treated cotton before pyrolysis (control) and at significant points in the pyrolysis reaction ( $^{\circ}\text{C}$ ).

These two treated fabrics seemed to decompose in two steps. A breakdown or depolymerization of the finish, a catalyzed dehydration of the cellulose, and some bond formation occurred during the first step shown as an endotherm on the DSC thermograms. This was shown on the infrared spectra as the appearance of carbonyl and double-bond formation (Figs. 4 and 5). The second step involved a breakdown of the cellulose chain, evolution of gases from both the cellulose and the finish polymer, and continuation of bond formation. The bond formation was probably due to a phosphorylation reaction at the C-6 hydroxyl of the anhydroglucose unit as suggested by Hendrix.<sup>5</sup> Phosphorylation at this position would inhibit the formation of levoglucosan and prevent further breakdown to flammable gases. This would account for the increased amount of char formed over that for the cotton control.

### THPOH-NH<sub>3</sub>

The THPOH-NH<sub>3</sub> finish effectively lowered the temperature of pyrolysis, changed the decomposition process from an endothermic to an exothermic reaction, and greatly increased the per cent residue. The double-exothermic decomposition observed on the DSC thermograms (Table IV) and the infrared spectra (Fig. 6) described the pyrolysis process. During the first part of the exothermic reaction, there seemed to be a depolymerization of the finish, an evolution of gases, and some bond formation. The second nadir of the exotherm appeared to represent bond formation and char formation. The infrared spectra showed very little structural change at the first exothermic peak (319°C), but at the second peak (333°C) the char pattern appeared.

A chain reaction started at 240°C which gave off heat as it proceeded instead of absorbing it as the THPC-amide-treated fabric did initially. If the THPOH and the NH<sub>3</sub> were polymerized within the cellulose structure but not crosslinked with the fibers, it might explain the ease with which the phosphorus compound was converted to a compound which could react with the anhydroglucose units. Fodor<sup>18</sup> showed that  $(\text{HOCH}_2)_4\text{P}^+$  could decompose to  $(\text{HOCH}_2)_3\text{P}^+\text{CH}_2\text{O}^-$ . This may be the active phosphorus compound which reacts with the C-6 hydroxyl group. Fodor also reported that early work by Hoffman showed that THPC decomposes in

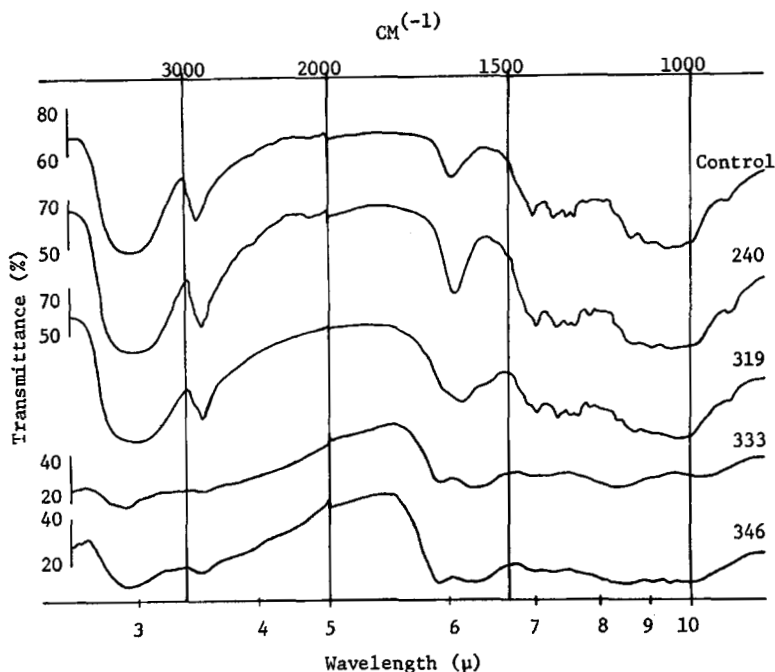


Fig. 6. Infrared spectra of THPOH-NH<sub>3</sub>-treated cotton before pyrolysis (control) and at significant points in the pyrolysis reaction (°C).

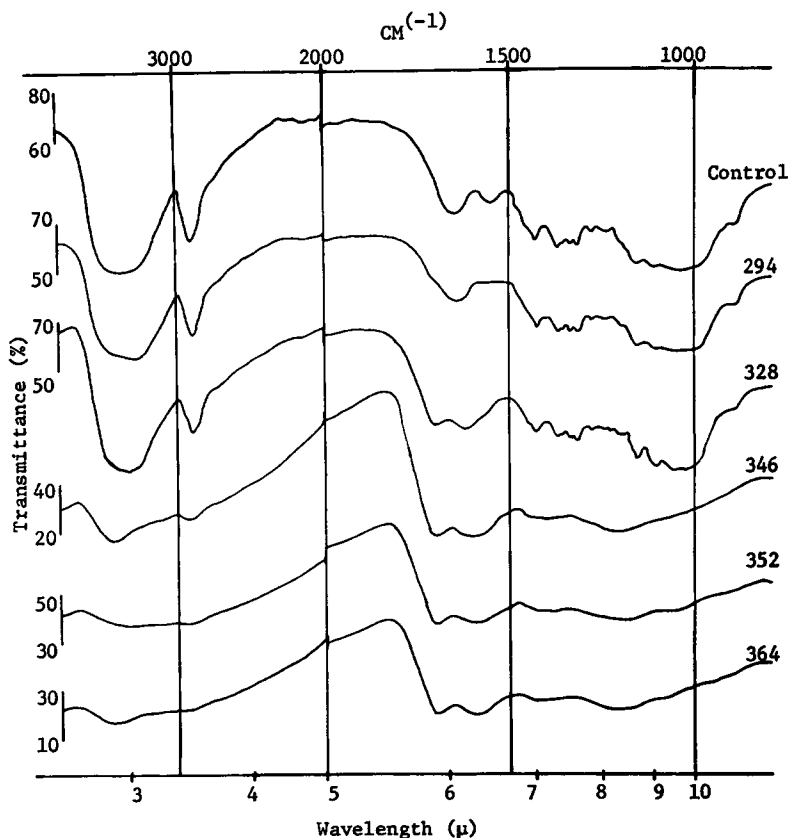


Fig. 7. Infrared spectra of THPC-cyanamide-treated cotton before pyrolysis (control) and at significant points in the pyrolysis reaction ( $^{\circ}\text{C}$ ).

ammonia to form a polymeric product containing 15% nitrogen and 27–30% phosphorus. Elemental analysis of the char of the THPOH-NH<sub>3</sub>-treated fabric gave a N/P ratio of 1:2 which agrees with Hoffman's work for THPC-NH<sub>3</sub>. The active phosphorus compound may polymerize with the nitrogen and then react through transesterification with the cellulose at C-6.

The THPOH-NH<sub>3</sub> finish caused the cellulose to pyrolyze with an exothermic reaction. The cotton modified with THPC-amide and with THPOH-amide pyrolyzed with an endothermic and then an exothermic reaction. The THPOH-NH<sub>3</sub> was the only finish applied from a basic medium. The pad baths of the THPC-amide and the THPOH-amide were both acidic. Mack and Donaldson have shown<sup>10</sup> that bases change the endotherm of cotton degradation to an exotherm. This may account for the strong exothermic reaction of the THPOH-NH<sub>3</sub> finish.

#### THPC-Cyanamide

The structure of the polymer on the finished fabric is not understood, but the finished fabric has wash-wear properties which would indicate cross-

linking of the cellulose.<sup>19</sup> There was no C=N stretch in the infrared spectra (Fig. 7) which suggested that possibly a reaction between formaldehyde from the THPC compound and the cyanamide occurred before the finish reacted with the cellulose.

The DSC data (Table IV) explained the pyrolysis reaction as two exothermic peaks. The first reaction appeared to represent depolymerization of the finish, evolution of gases, and cellulose dehydration. The infrared spectra showed a loss of nitrogen and the appearance of carbonyl groups representing dehydration. When the fabric was burned, a large amount of yellow smoke and irritating odors were produced. Nitrogen in the form of a gas was probably lost in this early stage of the pyrolysis.

The second reaction involved char formation and possibly phosphorylation. It occurred at 352°C, about the same temperature as the exotherm for the THPC-amide- and THPOH-amide-treated fabrics. This temperature range may be associated with phosphorylation of C-6 anhydroglucose units.

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