

Reaction of Hexamethylphosphorous Triamide with Cotton Cellulose

ARMAND B. PEPPERMAN, JR., and LEON H. CHANCE,
*Southern Regional Research Laboratory, Southern Marketing and
Nutrition Research Division, Agricultural Research Service,
U.S. Department of Agriculture, New Orleans, Louisiana 70179*

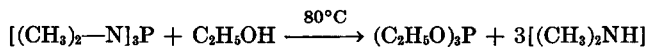
Synopsis

The reactivity of hexamethylphosphorous triamide, $P[N-(CH_3)_2]_3$ (HPT), with cotton cellulose was examined under various conditions. HPT was found to react readily with the cellulose to produce a cellulose phosphite and/or phosphate ester having approximately one acidic hydrogen atom per phosphorus atom. The reaction of HPT with cotton cellulose was efficiently catalyzed by dimethylamine hydrochloride (1%). The phosphorus content imparted by the catalyzed reaction on cotton fabrics was approximately twice that imparted by the uncatalyzed reaction. Flame resistance of the treated fabrics ranged from fair to excellent. The treated fabrics also exhibited ion exchange properties and some crosslinking.

INTRODUCTION

Several workers¹⁻⁵ have discussed the reactions of phosphorous amides and phosphoroamidous acids with alcohols to produce the corresponding esters. In these reactions, the amino, alkylamino, or dialkylamino groups are replaced by the alcohol. The reaction of cellulose with dialkylphosphorous amides in the presence of mineral acids has been reported by Emmons and Wadsworth⁶ in which replacement of the amino groups by cellulose is proposed. The reaction of N,N,N',N' -tetramethylphosphorodiamidic acid both as the chloride and as the ammonium salt has been reported by Jones and Noone.⁷ Neither of these authors proposed that the dialkylamino groups were being replaced by the cellulose.

To our knowledge, no one has considered the reaction of hexaalkylphosphorous amides with cellulose. Hexamethylphosphorous triamide has been shown to be highly reactive to alcohols.³⁻⁵ All three dimethylamino groups can be replaced under appropriate conditions as shown below for ethyl alcohol:



In this paper, we have examined the reaction of cotton with hexamethylphosphorous triamide (HPT); and because of the improved flame resistance of most phosphorous derivatives of cellulose,⁸ the treated fabrics were evaluated for flame retardancy.

EXPERIMENTAL

The hexamethylphosphorous triamide (HPT) used in all these experiments was prepared by the method of Mark⁹ and distilled at water aspirator pressure. The middle fraction was collected and stored under argon in the refrigerator until used. The dimethylformamide (DMF) was reagent grade from Eastman Kodak Co. and was used without further purification. The chloroform was reagent grade from Mallinckrodt and was used without further purification.

Nitrogen was determined by the Kjeldahl method using a mercury catalyst. Phosphorus was determined by an x-ray fluorescence method using a General Electric XRD-5 diffractometer modified to fluorescence analysis.¹⁰ The match test angle,¹¹ which was used to evaluate flame retardancy, consists of igniting the end of a 1-cm-wide strip of fabric held by one end with the fabric surface vertical and determining the angular position at which it must be held for the flame to go out. Samples which have an angle of 135°–180° generally pass the standard vertical flame test.¹³ The fabric used throughout the paper was a standard desized, scoured, and bleached 8-oz white cotton sateen. After reaction with HPT, the fabric was rinsed in excess CHCl_3 to remove the unreacted HPT and then washed in running hot tap water for 30 min.

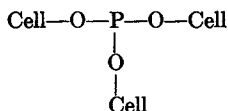
RESULTS AND DISCUSSION

The initial experiments were conducted by immersing the fabric in neat HPT and gently stirring at room temperature for various periods of time. One hour or more was required to yield a fabric having more than 1% phosphorus (Table I). In order to reduce the reaction time, the temperature was raised to 80°C. Again the immersion technique was used, and fabrics were treated at various periods of time. At 80°C, only 10 min were required to yield a fabric containing more than 1% phosphorus. However, even after 1 hr of reaction time, the phosphorus content had

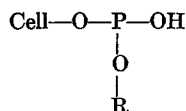
TABLE I
Effect of Temperature

Reaction temp., °C	Reaction time, min	Solvent	Phosphorus, %	Nitrogen, %	Match test angle, degrees
Room temp.	60	none	1.17	—	—
80	10	none	1.04	0.08	45
80	30	none	1.42	0.14	60
80	60	none	1.65	0.27	90
110	5	DMF	1.57	0.36	90
110	20	DMF	1.73	0.34	100
150	5	DMF	0.86	0.47	75
150	15	DMF	1.08	0.44	85

increased only to 1.66%. The very low nitrogen values indicated that essentially all of the dimethylamine groups had been replaced. Reaction of HPT with cellulose is expected to yield a phosphite ester represented by the formula



where Cell is cellulose. This product would be expected if the reaction of HPT and cellulose goes to completion. If the reaction does not go to completion, then the remaining dimethylamino groups can be replaced during the hot water wash to give a partial cellulose ester represented by the formula



where R is either cellulose or hydrogen.

Treatment was also carried out in dimethylformamide solution (DMF) at elevated temperatures. A 40% solution of HPT in DMF was prepared and used to treat several cotton samples. The samples treated at 110°C showed only slight discoloration and had little effect on the color of the solution. However, the samples treated at 150°C caused the solution to turn a dark reddish-orange, which became progressively darker as each sample was added. The 150°C samples were extremely discolored after treatment, but most of the color was removed by washing in running hot water. Typical results are shown in Table I. Only slightly better results were obtained at 110°C than had been obtained at 80°C, but at 150°C, results were actually poorer than at the lower temperatures. The use of DMF considerably reduced the odor of the HPT and also acted as a swelling agent for the cellulose.

In the room temperature experiments, drying of the fabric before treatment with HPT greatly reduced the reactivity and resultant phosphorus content. However, when the reaction was conducted at elevated temperature in DMF solution, the drying of the fabric had very little effect. For example, a dried sample treated in 40% HPT (DMF solution) for 30 min at 110°C had 1.73% P, 0.32% N, and a 100° match test angle. The air-equilibrated sample had 2.19% P, 0.25% N, and a 100° match test angle.

Thus, the drying of the fabric which causes shrinkage of the fibers and consequent reduced accessibility is not a factor at 100°C in DMF solution. Furthermore, that reaction does occur to the same degree in the absence of water as it does in its presence eliminates any ambiguity on the mode of reaction. The possibility that the HPT is converted by reaction with water to the corresponding acid, which would then be reactive to cellulose,

had been considered but has now been ruled out on the basis of this evidence.

Catalyzed Reaction

It has been shown⁵ that dimethylamine hydrochloride (DMA·HCl) is a particularly effective catalyst for the alcoholysis of trivalent phosphorus acid amides. The use of DMA·HCl at the 1% level in the treating bath caused a considerable increase in the phosphorus that reacted with the cotton fabric. Samples were treated in a 40% HPT solution in DMF at 110°C. The results are shown in Table II for samples treated under identical conditions with and without the catalyst.

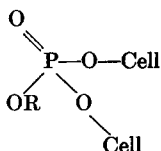
TABLE II
Effect of Catalyst

Reaction time, min	Catalyst, 1%	Phosphorus, %	Match test angle, degrees
5	none	1.33	120
5	DMA·HCl	2.74	150
10	none	1.72	110
10	DMA·HCl	3.26	150
20	none	1.91	110
20	DMA·HCl	3.65	180

In each case where the catalyst was used, the fabric sample contained phosphorus and consequently had a higher match test angle. In experiments where the catalyst was used, the fabrics would be expected to pass the standard vertical flame test.

Properties of the Treated Fabrics

The ion exchange properties of the fabrics were determined by the method of Hoffpauir and Guthrie.¹² Samples treated in 40% HPT in DMF both with and without catalysis by DMA·HCl were evaluated. Eight samples gave a range of 0.79 to 0.93 replaceable hydrogen atom per phosphorus atom. Thus, two of the dimethylamino groups were replaced by cellulose and slightly less than one by water. Some oxidation occurred during the reaction as evidenced by a strong band at 8.25 μ in the infrared spectrum of the treated fabric. The proper structure for the cellulose ester of HPT is thus designated as



where R is H in 79% to 93% of the ester molecules and R is Cell in 7% to 21% of the ester molecules, if one neglects the few remaining dimethylamino

groups. Also some of the esters exist in the phosphate form and others in the phosphite form.

As would be expected from this structure, the fabrics treated with HPT were crosslinked as illustrated by their insolubility in cupriethylenediamine. The fibers were observed under the microscope to swell but not to dissolve. The crosslinking was not uniform as evidenced by areas of the fiber that swelled very little while other areas ballooned. Crosslinking was not reflected in conditioned wrinkle-recovery angles (WRA) because the fabrics were treated in hot DMF, which would cause swelling of the fibers. There was a slight increase in wet WRA as might be expected for a fabric treated in the swollen state.

The match test angle of a treated sample was increased from 135° to 180° by soaking for 1 hr in 5% NH₄OH and air drying. This was attributed to the ion exchange properties of the fabric, in which hydrogen was exchanged for NH₄.

Since the treatment was carried out in DMF at 110°C, losses in breaking strength might be expected. Losses were small, however, ranging from 0 to 15%, which was quite good compared to other methods of preparing cellulose-phosphorous esters.

CONCLUSIONS

HPT was shown to react readily with cotton cellulose under a variety of conditions. The reaction proceeds with displacement of the dimethylamino groups by the cellulose, with the production of a cellulose phosphite and/or phosphate ester having approximately one acidic hydrogen atom per phosphorus atom.

The flame resistance of the treated fabrics ranged from fair to excellent. The fabrics treated by the catalyzed reaction exhibited excellent flame resistance. Some crosslinking is evident from the insolubility of the fabrics in cupriethylenediamine and from the increased wet wrinkle recovery angles.

The best treatment appears to be that which utilizes a 40% HPT in DMF solution heated at 110°C with 1% DMA·HCl as a catalyst.

References

1. K. A. Petrov, E. E. Nifant'ev, T. N. Lysenko, and V. P. Evdakov, *Zh. Obshch. Khim.*, **31**, 2377 (1961).
2. D. Houalla, M. Sanchez, and R. Wolf, *Bull. Soc. Chim. France*, 2368 (1965).
3. Hans J. Vetter and H. Noeth, *Ber.*, **96**, 1308 (1963).
4. R. Burgada, *Ann. Chim.*, **8**, 347 (1963).
5. E. E. Nifant'ev, N. L. Ivanova, and N. K. Bliznyuk, *Zh. Obshch. Khim.*, **36**, 765 (1966).
6. W. D. Emmons and W. S. Wadsworth, Jr., U.S. Pat. 3,068,060 (Dec. 11, 1962).
7. D. M. Jones and T. M. Noone, *J. Appl. Chem.*, **12**, 397 (1962).
8. G. L. Drake, Jr., *Kirk-Othmer Encyclopedia of Chem. Technology*, 2nd ed., Vol. 9, Interscience, New York, 1966, p. 300-311.
9. V. Mark, *Organic Synthesis*, Wiley, New York, 1966, pp. 42-44.

10. V. W. Tripp, B. Piccolo, D. Mitcham, and R. T. O'Connor, *Text. Res. J.*, **34**, 773 (1964).
11. W. A. Reeves, O. J. McMillan, Jr., and J. D. Guthrie, *Text. Res. J.*, **23**, 527 (1953).
12. C. L. Hoffpauir and J. D. Guthrie, *Text. Res. J.*, **20**, 617 (1950).
13. U.S. Federal Supply Service, *Textile Test Methods*, Federal Specification CCC-T-191b, Method 5902, Government Printing Office, Washington, D.C., 20402, 1951.

Received December 10, 1971

Revised February 23, 1972