Nitrogen–Phosphorous Antagonism in Flame-Retardant Cotton

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Synopsis

Phosphorous, as sodium dihydrogen phosphate, and nitrogen, in the form of a urea–formaldehyde condensate, were applied to cotton fabric. The flame-retarding character of each treated fabric was assessed by determining the respective limiting oxygen index. Analysis of the results showed that at the lowest levels of applied phosphorous (P = 2%), the presence of nitrogen produced less than an additive combined flame-retarding effect. At higher phosphorous levels, this deviation from additivity increased until at P > 6%, the presence of nitrogen antagonized the flame-retarding effect of the phosphorous. These observations are discussed within the current ideas of nitrogen–phosphorous interaction in flame-retardant systems, for cotton-containing fabrics.

INTRODUCTION

The use of phosphorous-containing compounds as durable flame retardants for cellulosic material has been widely reported.[1-3] Incorporation of a nitrogenous component to these finishes has the advantage of minimizing acid degradation of the cellulose by released phosphoric acid and also enhances flame retardation.[4]

Using a combination of urea and phosphoric acid, Little,[5] in 1947, observed that a comparable level of flame retardance could be achieved using a smaller add-on of a phosphorous/nitrogen mixture than with phosphorous or nitrogen alone. His results suggested that urea could effectively replace much of the phosphoric acid in an additive manner and hence produce a less expensive durable finish.

In contrast, Tesoro.[6,7] reported that nitrogen, applied to phosphorous-based compounds, increased the flame resistance properties of the finish above and beyond the level expected from the additive behavior of the individual components. She concluded that a synergistic effect occurs between phorphorous and nitrogen with respect to their ability to flame-retard cotton fabrics.

In a later study,[8] using triazine formaldehyde and trimethylol melamine on diammonium-phosphate-treated cotton, the synergistic effect was found to be dependent on the type of nitrogen present. Reeves et al.[9] suggested that, in fact, amide and amine nitrogen generally increase flame retardance whereas nitrile nitrogen can cause a reduction.

The importance of the chemical character of nitrogen present in a flame retardant has been further studied by Hendrix et al.[2,10] and reviewed by Weil.[11]

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The aim of this study is to investigate the flame-retardant behavior of nitrogen and phosphorous, both alone and together, applied to cotton using chemically simple agents. In this way, the individual flame-retarding contributions of phosphorous and nitrogen may be determined in a given formulation, and hence their combined effect may be assessed as additive, synergistic, or antagonistic in character.

EXPERIMENTAL

A plain weave 187 g/m^2 cotton fabric was alkaline–peroxide scour-bleached to give an ash content of 0.80%. Fabric samples were impregnated with sodium dihydrogen orthophosphate at nominal percentage concentrations equivalent to 2, 4, 6, 8, and 10 wt % phosphorous. To each phosphate-impregnated fabric, nitrogen in the form of a prepared urea–formaldehyde, (1:1.6 molar ratio) precondensate was applied at respective nominal weight percentages of nitrogen of 2, 5, and 10%. After drying, the actual sample levels of applied phosphorous and nitrogen were analyzed in the laboratories of Albright and Wilson Ltd., Warley, U.K., and the results are shown in Table I.

The limiting oxygen index values of all samples were assessed using a Stanton Redcroft 671B apparatus in accordance with standard procedure.[12] All samples were conditioned at 65% RH and 20°C prior to testing and the results are shown in Table I and designated $LOI_{P,N}$.

RESULTS AND DISCUSSION

The LOI results obtained from the samples impregnated with phosphorous alone show a linear dependence on phosphorous content as shown in Figure 1. Also included in Figure 1 are the results of other published values of LOI at varying levels of phosphorous-containing cotton fabrics.[13-15] The combined results in Figure 1 suggest that a linear dependence of LOI on phosphorous content occurs, irrespective of the chemical character of the phosphorous present.

A similar plot for samples impregnated with nitrogen only again shows a linear dependence of LOI on nitrogen content. However, when the results obtained in this study are compared to those obtained by other workers, it is apparent that little correlation occurs, as shown in Figure 2. It is apparent from the results in Figure 2 that the performance of nitrogen alone as a flame retardant on cotton is largely determined by the chemical nature of the nitrogen present, as suggested by Tesoro[8] and reviewed by Weil.[11] It is interesting to note that the reported results[8,13] in Figure 2 for apparently the same basic melamine-based resin source of nitrogen in the absence of phosphorous give nonsuperimposable plots. This shows that the source and mode of application of nitrogen-containing agents may influence the observed degree of flame retardancy at a given nitrogen concentration.

The actual dependence of LOI on phosphorous and nitrogen concentrations of cotton fabrics derived from results found in this study can be obtained by linear regression. From our results in Figure 1 for phosphorous,

$$LOI_P = 0.320[P] + 0.187 \pm 0.007 \quad (1)$$

TABLE I
Experimental and Calculated LOI Values for Cotton Fabrics Containing Various Concentrations of Phosphorous and Nitrogen

Nominal levels (% w/w)		Actual levels (% w/w)							
P	N	P	N	$LOI_{N,P}$	LOI_P	LOI_N	$LOI_{(P,N-P)}$ (effect of N)	$LOI_{(P,N-N)}$ (effect of P)	$LOI_{(P+N)}$
0	0	0	< 0.01	0.179					
0	1	0	0.96	0.203					
0	2	0	1.72	0.212					
0	4	0	2.81	0.223					
0	6	0	3.49	0.232					
0	8	0	5.46	0.256					
2	0	1.80	< 0.01	0.258					
2	2	2.03	2.11	0.270	0.252	0.214	0.018	0.056	0.280
2	5	2.04	4.73	0.279	0.253	0.249	0.026	0.030	0.316
2	10	1.53	8.08	0.282	0.236	0.293	0.046	-0.011	0.332
4	0	3.40	< 0.01	0.299					
4	2	3.85	1.93	0.303	0.310	0.212	-0.070	0.091	0.336
4	5	3.53	4.77	0.310	0.300	0.249	0.010	0.061	0.363
4	10	2.93	7.67	0.313	0.281	0.288	0.032	0.025	0.383
6	0	4.66	< 0.01	0.332					
6	2	5.00	1.75	0.359	0.347	0.209	0.012	0.150	0.370
6	5	4.69	4.00	0.361	0.337	0.239	0.024	0.122	0.390
6	10	3.89	7.63	0.361	0.311	0.287	0.050	0.074	0.412
8	0	6.19	< 0.01	0.378					
8	2	6.34	1.70	0.366	0.390	0.209	-0.024	0.157	0.413
8	5	6.20	3.72	0.364	0.385	0.235	-0.021	0.129	0.434
8	10	5.23	7.11	0.356	0.354	0.281	0.002	0.075	0.449
10	0	6.93	< 0.01	0.415					
10	2	7.33	1.80	0.376	0.422	0.210	-0.046	0.166	0.446
10	5	7.38	4.11	0.373	0.423	0.241	-0.050	0.132	0.478
10	10	7.21	7.07	0.354	0.418	0.280	-0.064	0.074	0.512

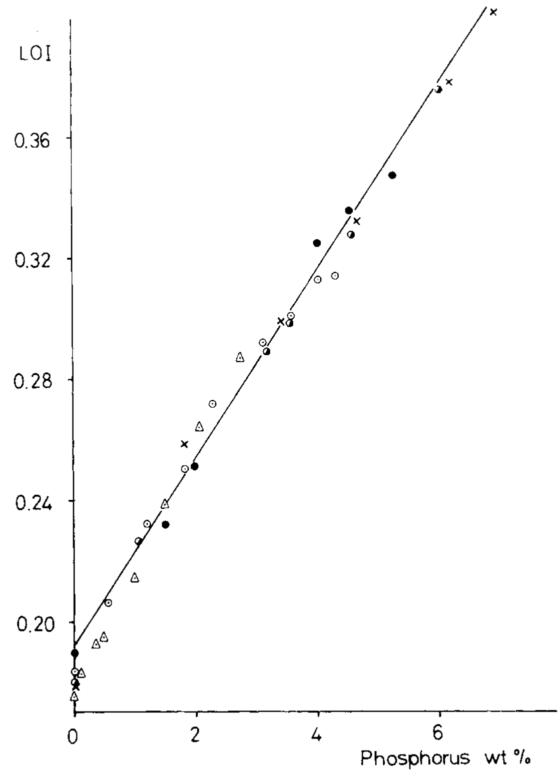

Fig. 1. The limiting oxygen index values for cotton samples treated with phosphorous-containing flame retardants as a function of percentage phosphorous content by weight: (⊙) Willard and Wondra;[13] (△) Franklin and Rowland;[14] (●) NaH_2PO_4 and (◑) H_3PO_4, Inagaki et al.[15]; (×) this study. The straight line is defined by eq. (1).

where LOI_P is the expected oxygen index value for a given percentage phosphorous [P]. Similar analysis of the results in Figure 2 for fabrics prepared in this study show that for nitrogen

$$LOI_N = 0.0133[N] + 0.186 \pm 0.004 \quad (2)$$

where LOI_N is the expected oxygen index for a given percentage nitrogen [N]. Correlation coefficients for both empirical relationships are of the order of 0.99. Equation (1) is similar to the linear relationships found by Inagaki et al.[15] for both phosphoric acid and sodium dihydrogen phosphate included in Figure 1. No similar relation for nitrogen was reported by these workers.

Using the predictive nature of these relationships, it is possible to assess the influence of nitrogen on the flame-retarding properties of each of the phosphorous- and nitrogen-containing fabrics. If the predicted LOI value for the phosphorous fraction LOI_P, of a phosphorous- and nitrogen-containing fabric is substracted from the actual limiting oxygen index value of that fabric, $LOI_{P,N}$, then the resulting difference, $LOI_{(P,N-P)}$, can be attributed to the change in burning behavior resulting from the addition of nitrogen.

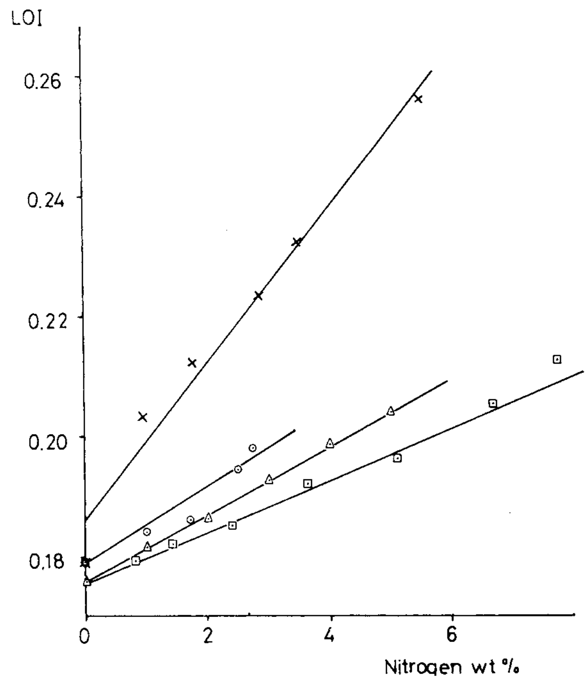

Fig. 2. The limiting oxygen index values for cotton samples treated with nitrogen-containing agents as a function of percentage nitrogen content by weight. Methylolated derivatives of melamine: (⊙,⊡) Tesoro and Meiser[8]; (△) Willard and Wondra,[13] urea-formaldehyde; (×) this study.

Similarly, the increase in flame-retarding properties resulting from the addition of phosphorous to a nitrogen-containing fabric can be evaluated by subtracting the predicted increase in flame retardation due to nitrogen, LOI_N, from the actual oxygen index, $LOI_{P,N}$, of the phosphorous and nitrogen-containing fabric, to give $LOI_{(P,N-N)}$. The combined results of this analysis are shown in Table I.

For each nominal percentage nitrogen content, a plot of the increase in oxygen index attributable to the phosphorous component of the finish, $LOI_{(P,N-N)}$, vs. the amount of phosphorous present is shown in Figure 3. This plot suggests that, at each nominal nitrogen level, there is an optimum phosphorous content above which little further increase in limiting oxygen index occurs. It is interesting to note that this optimum phosphorous level reduces with increasing nitrogen concentration. The results in Figure 3 suggest that above a certain phosphorous level, the addition of nitrogen is antagonistic. This is especially shown in Table I by observing the decrease in the magnitudes of $LOI_{(P,N-P)}$, which represents the change in oxygen index arising from the nitrogen component, as the phosphorous level increases. For $P > 6\%$, $LOI_{(P,N-P)}$ becomes negative.

An alternative means of assessing the nature of the nitrogen-phosphorous interaction may be made by calculating the oxygen index values for additive interaction, $LOI_{(P+N)}$, using eqs. (1) and (2). Values of $LOI_{(P+N)}$ are listed in Table I and may be compared with the experimentally determined

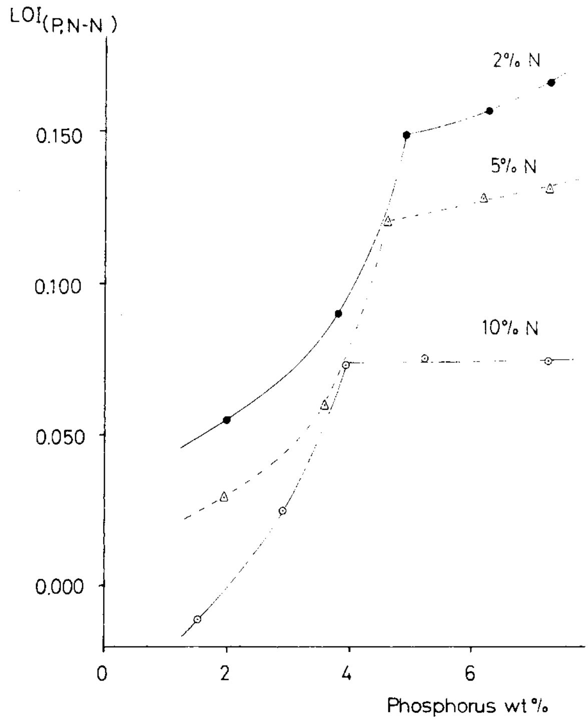

Fig. 3. The increase in oxygen index, $LOI_{(P,N-N)}$, caused by the phosphorous component of a NaH_2PO_4-urea-formaldehyde finish applied to cotton as a function of increasing phosphorous percentages at nominal applied levels of nitrogen of 2, 5, and 10% by weight.

values, $LOI_{P,N}$. For all samples, $LOI_{(P+N)}$ is greater than $LOI_{P,N}$ and so nitrogen–phosphorous interaction is less than additive, let alone synergistic. Divergence between the two sets of values increases at high phosphorous levels where the effect of nitrogen is one of antagonism. These results therefore support previous observations[8,10,11] that synergism is dependent upon the chemical character of the nitrogen present in a given flame-retardant formulation.

Mechanisms of nitrogen–phosphorous interaction on cellulose has been reviewed by Weil.[11] Of particular note is the work of Hendrix et al.,[2,10] which provides evidence that nitrogen synergism is a consequence of its ability to enhance the phosphorylating tendency of the phosphorous moiety probably via initial P—N bond formation. Not only does this reduce levoglucosan formation but also consolidates char. Later work by Pandya and Bhagurat[16] suggested that nitrogen in phosphoramide retardants acts as a nucleophile in promoting P=N bond formation, which then enables facile phosphorylation of cellulose. This study demonstrated the superior flame-retarding and char-promoting effect of secondary nitrogen relative to tertiary nitrogen present in the phosphoramide. The enhanced activity of secondary nitrogen was noted by Weil[11] in his analysis of the works of Tesoro et al.[7,8] and Willtard and Wondra.[13] Weil pointed out in the later study that bis(methoxymethyl)uron, which lacks secondary nitrogen, ceases to be nonsynergistic and, indeed, nonadditive at the higher phosphorous (2% P) levels used. In addition, the presence of a triazone resin with its basic tertiary nitrogen shows no increase in flame retardant activity at 1% P and antagonism at 2% P. These resins were applied with the commercial phosphonamide flame retardant, Pyrovatex CP.

In this work, using the ratio urea:formaldehyde = 1:1.6, which is a typical cellulosic textile formulation, it is likely that the cured resin will have a low secondary nitrogen content and so not show any synergistic tendency. In fact, based on Weil's hypothesis, the observed antagonism of the urea–formaldehyde nitrogen should relate to its high tertiary nitrogen content.

The recent study by Inagaki et al.[15] noted that the mode of application to cotton of nitrogen-containing vinyl polymers with either H_3PO_4 or NaH_2PO_4 determines whether or not nitrogen–phosphorous synergism is observed. Analysis of their results for NaH_2PO_4 in the presence of polymers of either *N,N*-dimethylacrylamide or *N*-methylolacrylamide shows that, in fact, nitrogen present antagonized the action of the phosphorous in its ability to increase the oxygen index of flame-retarded samples. A similar antagonism may be observed from the results for phosphorylated cotton treated with the latter polymer. In their samples, both secondary and tertiary nitrogens were present in the amide groups, which, however, might not be expected to behave quite as would free amine groups, although Reeves et al.[9] showed that amines and amides function in a similar manner with regard to their flame-retardant behavior.

Working with polyester/cotton blends, however, Holme and Patel[17] demonstrated that urea–formaldehyde plus diammonium phosphate (DAP) exhibits nitrogen–phosphorous synergism, which decreases with increasing cotton content; phosphorous present is considered to operate in both condensed and vapor phases in this system. No synergism was observed for a DMDHEU–DAP treatment in which the phosphorous was prevented from volatilizing and retarding the polyester flame. More recent work by Bajaj et al.,[18] however, using DAP to phosphorylate the cotton component of polyester/cotton blends, showed that synergism was observed if the urea–formaldehyde resin was present but not if other methylol resin treatments such as DMDHEU were present. These observations could be explained in terms of relative degrees of methylolation of the applied resins as well as their ability to fix phosphorous in the condensed phase.

CONCLUSIONS

The limiting oxygen index of cotton fabrics impregnated with increasing concentrations of sodium dihydrogen orthophosphate and urea–formaldehyde, both alone and together, shows linear increase with percentage phosphorous and nitrogen contents when present individually. When both elements are present, the linear increase in LOI with their combined concentrations was less than that expected for an additive nitrogen–phosphorous interaction. Above a critical phosphorous concentration of about 6%, the presence of nitrogen causes an antagonistic flame-retardant effect. This effect is discussed in terms of the observation by Weil, that tertiary nitrogen present in a retardant prevents possible synergism with the phosphorous entity.

References

1. R. M. Perkins, G. L. Drake, and W. A. Reeves, *J. Appl. Polym. Sci.,* **10**, 1041 (1966).
2. J. E. Hendrix, T. K. Anderson, T. J. Clayton, E. S. Olson, and R. H. Barker, *J. Fire Flammability,* **1**, 170 (1970).
3. B. J. Eisenberg and E. D. Weil, *J. Am. Assoc. Text. Chem. Col.,* **6**, 257 (1974).
4. R. H. Barker and J. E. Hendrix, in *Flame Retardancy of Polymeric Materials*, W. C. Kuryla and A. V. Papa, Eds., Dekker, New York, 1979, p. 39.
5. R. W. Little, *Flameproofing Textile Fabrics*, Reinhold, New York, 1947.
6. G. C. Tesoro, *Textilveredlung,* **2**, 435 (1967).
7. G. C. Tesoro, S. B. Sello, and J. J. Willard, *Text. Res. J.,* **38**, 245 (1968).
8. G. C. Tesoro and C. H. Meiser, *Text. Res. J.,* **40**, 430 (1970).
9. W. A. Reeves, R. M. Perkins, B. Piccolo, and G. L. Drake, *Text. Res. J.,* **40**, 223 (1970).
10. J. E. Hendrix, G. L. Drake, and R. H. Barker, *J. Appl. Polym. Sci.,* **16**, 41, 257 (1972).
11. E. D. Weil, in Ref. 4, p. 185.
12. Test Method D2863 - 77, American Society for Testing and Materials, Philadelphia, 1977.
13. J. J. Willard and R. E. Wondra, *Text. Res. J.,* **40**, 203 (1970).
14. W. E. Franklin and S. P. Rowland, *Text. Res. J.,* **49**, 170 (1979).
15. N. Inagaki, T. Toyoshima, and K. Katsuura, *J. Fire Retardant Chem.,* **8**, 51 (1981).
16. H. B. Pandya and M. M. Bhagurat, *Text. Res. J.,* **50**, 5 (1981).
17. I. Holme and S. R. Patel, *J. Soc. Dyers Col.,* **96**, 224 (1980).
18. P. Bajaj, S. Chakrapani, and N. K. Jha, *Text. Res. J.,* **54**, 619 (1984).

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