Studies on the Temperature Dependence of Extinction Oxygen Index Values for Cellulosic Fabrics. II. Commercial Quality Flame-Retarded Cotton

A. R. HORROCKS, *Department of Textile Studies, Bolton Institute of Higher Education, Deane Road, Bolton BL3 5AB, United Kingdom,* and D. PRICE* and M. TUNC, *Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, United Kingdom*

Synopsis

Extinction oxygen index (EOI) and the derived value at zero ignition time $[EOI]_0$ have been determined for a series of commercial quality flame-retarded cotton fabrics in the temperature range 20 to 200°C. The flame retardants used were Proban-CC (Albright and Wilson Ltd.) and Pyrovatex-CP (Ciba-Geigy). For all the flame-retarded cotton fabrics studied, EOI and $[EOI]_0$ decreased with increase in temperature. The influence of conditioned area density M at a given temperature can be predicted via the linear relationship

$$[EOI]_0 = E_0 + E_1 M$$

Substitution of moisture corrected area density data had negligible influence on the calculated values of E_0 and E_1. The dependence of $[EOI]_0$ on area density, E_1, has a negative temperature dependence. The similarly temperature dependent term E_0 is the "intrinsic oxygen-index," which is independent of ignition and area density variables. For a given flame retardant this represents the fabric properties where maximum access of oxygen is possible. In all cases studied, $E_0 \gg E_1$ and so the temperature dependence of $[EOI]_0$ is largely determined by E_0. Values obtained for the fractional increase in E_0, with respect to its value at 20°C, with increasing temperature indicate that the temperature sensitivity of the burning behavior of cotton is greater than that of Proban-CC-treated cotton, which itself is greater than that of Pyrovatex CP-treated cotton. It is inferred that effective flame-retardants should not only function under ambient conditions but also reduce the temperature sensitivity of the inherent fibre-burning behavior at elevated temperatures.

INTRODUCTION

The ability to quantify the affect of a flame-retardant species in the presence of a polymeric substrate was recognized by Fenimore and Martin in their original application of limiting oxygen index (LOI) techniques to polymeric solids.[1] Subsequent work by Willard and Wondra[2] led to the observation that, for several phosphorus-containing flame retardants applied to cotton, LOI increased linearly with phosphorus concentration. The flame retardants applied were *N*-methyloldicyandiamide, *N*-hydroxymethyl dimethyl phosphonopropionamide (Pyrovatex CP, Ciba-Geigy) applied with trimethylol melamine (TMM), tetrakis(hydroxy methyl)phosphonium chloride (THPC), and hydroxide (THPOH) condensates with urea and TMM and

*To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 37, 1051–1061 (1989)
 CCC 0021-8995/89/041051-11$04.00

tris(aziridinyl)phosphine oxide (APO). All except APO caused LOI to increase linearly with applied phosphorus content up to 2 % phosphorus. Arney and Kuryla[3] subsequently studied the flame-retardant efficiencies of a variety of phosphites, phosphonates, and phosphates on cotton and showed that, in many cases, after an initial rapid rise, LOI may approach asymptotic values at $P > 2\%$. However, whether linear or nonlinear relationships hold, oxygen index techniques have become well established as a means of investigating flame-retardant effectiveness on textile materials; Horrocks, Price, and Tunc[4] have recently reviewed the extensive literature within this area.

While it has been noted using standard LOI techniques[5] that the effectiveness of a flame retardant may be supplemented by increased fabric area density, no attempt has been made to resolve the burning behavior of flame-retardant fabrics into component fiber, fabric, and retardant contributions.

Part I[6] of this series describes the use of the extinction oxygen index (EOI) technique,[7,8] at temperatures in the range 20–200°C to quantify the contributions which fiber and fabric variables make to the burning characteristics of cotton fabrics. This second paper extends the current systematic application of the concept of EOI[9] to the behavior of selected durable flame-retarded cotton fabrics of commercial quality.

EXPERIMENTAL

Two lightweight and one heavyweight Proban-treated and one lightweight and heavyweight Pyrovatex CP-treated commercial flame retarded, plain woven cotton fabrics as shown in Table I were selected for investigation.

Previously reported work for pure cotton[6] and interim results[9] for fabrics A_1 and B at 20°C suggested that there is no simple relationship between the determined EOI values and fabric thickness and air permeability. These conclusions, coupled with the observations of significant increases in air permeability and the reductions in thickness of fabrics which occur during application of both flame-retardant systems, led to the decision not to consider these parameters for commercial fabrics of varied process histories. Consequently, in Table I, the only fabric parameter of major importance is the area density. However, because of the need to consider the effect of moisture during EOI determinations,[6] the respective moisture contents at 20°C and 65% relative humidity are also given.

All three Proban-treated cottons were commercially produced according to Albright and Wilson Ltd. standard procedure.[10] This involved initial padding with the Proban NX THPC-urea condensate,* drying, ammonia curing, and final oxidation to give a durable, effective finish. The Pyrovatex CP-treated fabrics essentially comprised *N*-hydroxymethyl dimethylphosphonopropionamide applied with a melamine-containing resin precondensate and phosphoric acid catalyst. The padded finish was dried and cured followed by sodium hydrogen carbonate washing off to remove free acid catalyst residues.

*Note: Proban 210 was the original THPC–urea finish produced until 1981. This was superseded by Proban NX in which THPC was replaced by its sulfate analogue. More recently (1983) this has been superseded by Proban CC, which is a return to a THPC–urea formulation. Fabrics in this work were finished with Proban NX.

TABLE I
Properties of Plain, Woven Fabrics Studied

Fabric code	No. of ends (cm^{-1})	Linear density warp (tex)	Cover factor warp	No. of picks (cm^{-1})	Linear density weft (tex)	Cover factor weft	Total cover factor	Area density M ($g\ m^{-2}$)	Moisture content[a] (%)	Phosphorus (%)	Nitrogen (%)
Proban-finished cotton											
A_1	32	25.7	16.2	29	22.5	13.8	39.4	140	7.38	3.26	3.23
A_2	33	29.7	13.0	29	19.3	12.8	30.7	130	7.38	2.70	2.63
B	24	35.3	14.3	22	60.0	17.0	31.3	190	7.93	2.91	2.83
Pyrovatex-finished cotton											
C	29	35.9	17.4	26	24.7	12.9	30.3	137	6.83	1.95	2.09
D	26	50.0	18.4	21	48.7	14.6	33.0	202	7.26	1.84	1.78

[a] At 20°C, 65% relative humidity.

All fabrics were produced to a standard commensurate with the requirements for a "flame-proof" fabric as defined in the British Standard BS 3120:1959. Samples were analyzed for applied concentrations of nitrogen and phosphorus within the laboratories of Albright and Wilson Ltd., Oldbury, U.K., and these are listed in Table I.

Preparation of samples and the determination of persistence-of-burning times for mono- and multilayered samples at 20, 100, and 200°C were carried out as described previously for cotton.[6] For a given sample exposed to a given temperature and igniter application time at least three burning times were recorded at each oxygen concentration.

RESULTS

Derivation of Extinction Oxygen Index

Previous studies for pure cotton[6-8] demonstrate that, for a given fabric, temperature and igniter application time combination, persistence-of-burning time increases linearly with oxygen concentration until the LOI sustained burning condition is realized.[11] For the flame-retarded fabrics used in this work, as previously reported[9] for 20°C, such a simple relationship does not hold. Figure 1 shows the experimental results for fabric C, finished with Pyrovatex CP, and exposed as a single layer at 20°C to igniter application times between 2 and 10 s. These results are similar to those for all other fabrics and reported[9] previously for fabric B. Two differences in trend are immediately apparent between the burning behavior of flame-retarded and unretarded cotton fabrics.[6] The curve shapes are nonlinear and resemble the

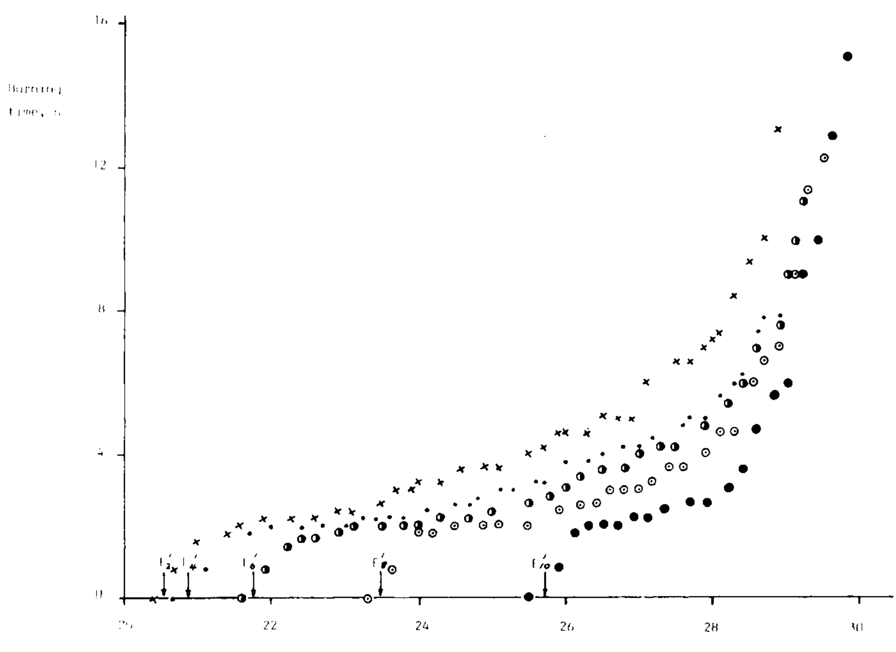

Fig. 1. Burning times of single layers of Pyrovatex CP–flame-retarded cotton fabrics (137 g m^{-2}) vs. oxygen concentration following various ignition times at 20°C: (×) 2; (·) 4; (◑) 6; (⊙) 8; (●) 10.

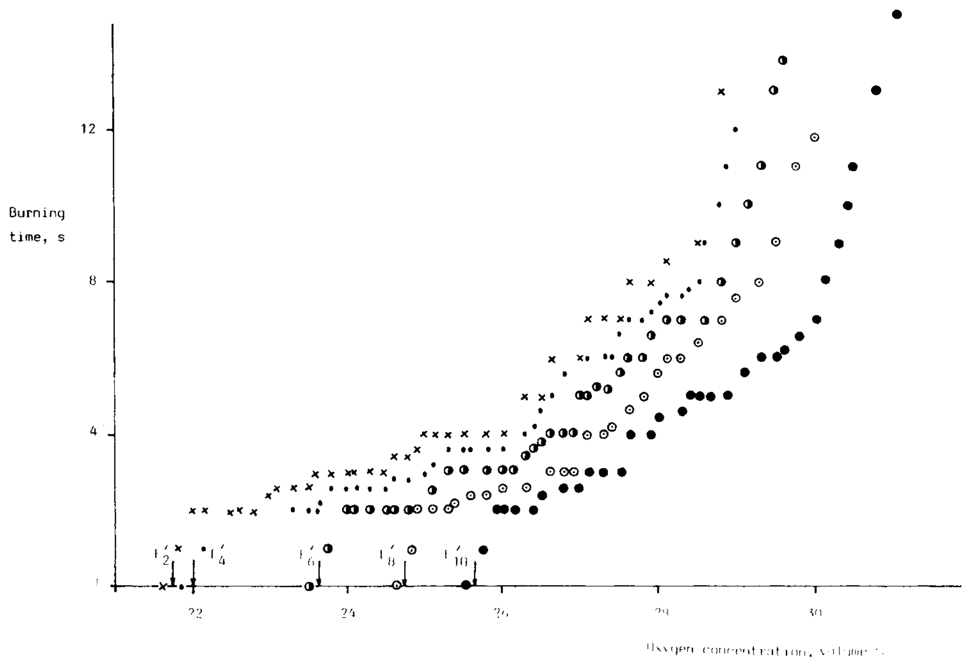

Fig. 2. Burning times of five-layered samples of Proban NX–flame-retarded cotton fabrics (5×130 g m^{-2}) vs. oxygen concentration following various ignition times at 100°C: (×) 2; (·) 4; (◑) 6; (⊙) 8; (●) 10.

similarly determined self-quenching time vs. oxygen concentration curves recorded for a number of polymers by Stuetz et al.[12]; while our curves asymptote to the minimum, reproducibly observable persistence-of-burning time of about 1–2 s, those of the latter do so to zero time. Secondly, at a given oxygen concentration, burning times for pure cotton increase with increasing ignition time, for the current flame-retarded fabrics the converse is true. This is probably associated with the formation of dense char during flame application to the flame-retarded fabrics, which, at longer times, extends beyond the impinging flame. The char prevents the flame being in permanent contact with uncharred fabric during its application.

The behavior shown in Figure 1 at 20°C was observed also for all mono- and multilayered fabrics studied at 100 and 200°C. The examples for layered Proban samples A_2 and B shown in Figures 2 and 3 at these respective temperatures are typical. The effect of increasing temperature is to enhance also the sensitivity of burning time to changes in oxygen concentration especially as the latter approaches the LOI condition.

It is evident that simple extrapolation of the curves in Figures 1–3 to zero burning time and hence the derivation of the respective extinction oxygen index values is not straightforward. Four attempts were made to satisfactorily determine the oxygen concentration at which the burning time is zero, i.e., the EOI condition, for each mono- and multilayered sample:

(i) use of a polynomial curve fitting procedure,
(ii) linear regressional analysis of the initial approximately linear region of each persistence-of-burning time vs. oxygen concentration curve,

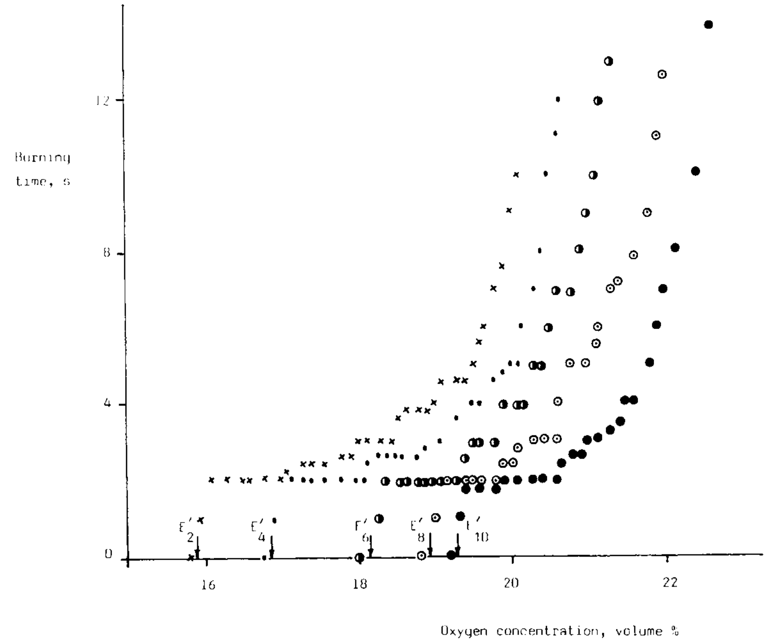

Fig. 3. Burning times of two-layered samples of Proban NX–flame-retarded cotton fabrics (2×190 g m^{-2}) vs. oxygen concentration following various ignition times at 200°C: (×) 2; (·) 4; (◑) 6; (⊙) 8; (●) 10.

(iii) linear regressional analysis of the most linear region of each experimental curve,

(iv) averaging the oxygen concentration for which a minimum burning time has been observed and that at which a zero time is apparent.

Using method (i), no commonly applicable polynomial fit was possible and the asymptoting tendency prevented a realistic assessment of EOI. Methods (ii) and (iii), while enabling extrapolations to be made, gave EOI values outside the limits of oxygen concentration used by method (iv). Consequently, method (iv) was deemed to be the best and was supported by previous experience with melt-dripping polyester and nylon 6.6 fabrics.[7,9] In Figures 1–3, each respective EOI value determined by method (iv) is signified as E_t', where t is the appropriate igniter application time. Table II lists the EOI values, expressed as decimal fractions, for each mono- and multilayered sample of Proban-treated fabric B at each temperature. These results are typical of those for all fabrics studied and show that, as the ignition time increases, E_t' also increases. Furthermore, for the same sample at constant t, an increase in environment temperature reduces E_t'.

Analysis of each set of E_t' vs. t results shows that a high degree of linear correlation (correlation coefficients > 0.94) exists for all fabrics and temperatures, thereby enabling extrapolation to $t = 0$. Values of EOI at $t = 0$, designated $[EOI]_0^{6-9}$ are listed for all mono- and multilayered fabrics at each temperature in Table III.

TABLE II
EOI Values Determined as E_t' (See Text) for the Proban-Treated Fabric B

Ignition time (s)	20°C	100°C	200°C
	Single layer: area density 190 g m^{-2}		
2	0.233	0.215	0.157
4	0.239	0.230	0.169
6	0.242	0.259	0.177
8	0.260	0.262	0.189
10	0.268	0.269	0.193
	Two layers: area density 380 g m^{-2}		
2	0.248	0.219	0.159
4	0.254	0.241	0.169
6	0.256	0.245	0.182
8	0.257	0.259	0.189
10	0.261	0.287	0.193
	Three layers: area density 570 g m^{-2}		
2	0.259	0.227	0.169
4	0.263	0.235	0.178
6	0.268	0.256	0.187
8	0.273	0.277	0.189
10	0.277	0.280	0.194
	Four layers: area density 760 g m^{-2}		
2	0.282	0.231	0.171
4	0.285	0.236	0.179
6	0.291	0.247	0.185
8	0.295	0.256	0.193
10	0.298	0.261	0.196
	Five layers: area density 950 g m^{-2}		
2	0.292	0.237	0.179
4	0.295	0.241	0.187
6	0.300	0.247	0.194
8	0.305	0.255	0.197
10	0.316	0.263	0.204

Effect of Area Density

The data collated in Table III show that $[\mathrm{EOI}]_0$ increases with area density. Previous work has indicated that $[\mathrm{EOI}]_0$ shows a simple linear dependence on area density. Assuming such a linear relationship to be of the form

$$[\mathrm{EOI}]_0 = E_0 + E_1 M \quad (1)$$

where M is the conditioned area density, then linear regressional analysis yields values for the slope E_1 and intercept E_0 at the temperatures investigated. The values obtained together with the respective correlation coefficients are presented in Table IV for the Proban-treated fabrics and Table V for the Pyrovatex-treated samples. Although these values show a good fit, the data was also subjected to a curve-fitting routine with respect to the quadratic equation

$$[\mathrm{EOI}]_0 = E_0 + E_1 M + E_2 M^2 \quad (2)$$

The values of the E_0, E_1, and E_2 together with the appropriate correlation

TABLE III
Conditioned Area Densities M, Moisture Corrected Area Densities M_c, and Values of $[EOI]_0$ Determined for Mono- and Multilayered Flame-Retarded Fabrics at 20, 100, and 200°C

		20°C		100°C		200°C	
Number layers	M (g m^{-2})	$[EOI]_0$	M_c (g m^{-2})	$[EOI]_0$	M_c (g m^{-2})	$[EOI]_0$	M_c (g m^{-2})
Fabric A_1							
1	140	0.206	134				
2	280	0.214	270				
3	419	0.242	409				
4	559	0.256	547				
5	699	0.264	688				
Fabric A_2							
1	130			0.171	120	0.144	120
2	260			0.177	242	0.161	241
3	390			0.186	363	0.162	361
4	520			0.190	484	0.168	482
5	650			0.208	608	0.176	602
Fabric B							
1	190	0.221	183	0.205	175	0.149	175
2	380	0.249	371	0.204	353	0.151	350
3	569	0.253	560	0.210	532	0.164	524
4	758	0.277	746	0.222	713	0.165	698
5	948	0.284	936	0.229	897	0.174	873
Fabric C							
1	137	0.186	132	0.184	128	0.154	128
2	274	0.194	266	0.186	257	0.146	255
3	411	0.241	402	0.185	385	0.170	383
4	548	0.259	538	0.186	517	0.182	511
5	685	0.274	674	0.197	647	0.183	638
Fabric D							
1	202	0.219	196	0.179	188	0.159	187
2	403	0.238	394	0.189	378	0.168	374
3	605	0.251	595	0.198	570	0.174	561
4	806	0.265	795	0.210	764	0.181	747
5	1008	0.282	996	0.220	960	0.182	935

coefficients are also presented in Tables IV and V. These correlation coefficients are only slightly higher than those for the linear regression. Intuitively, the linear fit appears the better choice since the intercepts at each temperature are comparable, within error, for the analyses and the values for the slope are more easily understood.

The slope E_1 represents the dependence of $[EOI]_0$ on area density, and it can be seen that the values obtained for E_1 decrease with increasing temperature. However, since $E_1 \ll E_0$, the influence of E_1 on the temperature dependence of $[EOI]_0$ will be small compared to that of E_0.

The intercept values E_0 are the intrinsic extinction oxygen indices of the flame-retarded cotton fabrics, independent of ignition and area density variables, at the temperatures investigated. Such values represent the fabric properties where maximum access of oxygen is possible. They are temperature-dependent. Thus the major temperature dependence of the $[EOI]_0$/area density relationship arises from this intrinsic extinction term.

TABLE IV
Regressional Analysis Coefficients for $[EOI]_0$ vs. Area Density Data for Proban-Treated Fabrics

Fit	Temperature (°C)	E_0[a]	$E_1/10^{-5}$	$E_2/10^{-8}$	Correlation coefficient
		Conditioned area density			
Linear	20	0.199	9.65		0.961
	100	0.172	5.95		0.820
	200	0.145	3.40		0.840
Quadratic	20	0.189	15.11	−5.18	0.969
	100	0.177	3.47	2.38	0.825
	200	0.137	7.51	−3.94	0.872
		Moisture-less corrected area density			
Linear	20	0.200	9.72		0.961
	100	0.172	6.28		0.821
	200	0.145	3.70		0.840
Quadratic	20	0.189	15.26	−5.38	0.970
	100	0.177	3.87	2.45	0.824
	200	0.137	8.12	−4.61	0.874

[a] Error less than ±0.001.

TABLE V
Regressional Analysis Coefficients for $[EOI]_0$ vs. Area Density for Pyrovatex-Treated Fabrics

Fit	Temperature (°C)	E_0[a]	$E_1/10^{-5}$	$E_2/10^{-8}$	Correlation coefficient
		Conditioned area density			
Linear	20	0.187	10.71		0.911
	100	0.171	4.35		0.930
	200	0.150	4.01		0.844
Quadratic	20	0.161	22.92	−11.02	0.945
	100	0.182	−0.89	4.73	0.967
	200	0.137	9.87	−5.29	0.895
		Moisture-less corrected area density			
Linear	20	0.187	10.78		0.911
	100	0.172	4.57		0.930
	200	0.150	4.33		0.846
Quadratic	20	0.161	23.13	−11.32	0.945
	100	0.182	0.74	5.04	0.967
	200	0.137	10.61	−6.10	0.896

[a] Error less than ±0.013.

Effect of Moisture

The problem concerning the need to correct fabric area densities from the conditioned values in Table I to allow for dehydration during burning time determination was considered previously for cotton fabrics.[6] While moisture loss did significantly reduce mono- and multilayer fabric area densities, allowance for this did not significantly change the analyses and derived conclusions. In Table III, based on the moisture contents given in Table I, moisture-corrected area densities M_c are shown and were derived as previously described.[6] Tables IV and V also present values of the various slopes and intercepts (E_0, E_1, and E_2), together with the appropriate correlation coefficients, obtained by regressional analysis for linear and quadratic fits to the $[EOI]_0$ and M_c data of Table III. Inspection of the two tables shows that substitution of the moistureless corrected area density values produced negligible changes in the slope, intercept, and correlation coefficient values calculated.

DISCUSSION

In contrast to the untreated cotton fabric, the limiting oxygen index is not generally a simple linear function of temperature for flame-retardant-treated cotton fabrics. The deviation may be positive or negative and can vary unpredictably with each flame retarded fabric.[13] Figures 1–3 illustrate the burning behavior observed for various layered samples of flame retarded fabrics at 20, 100, and 200°C and for various igniter application times. Similar dependences are observed in each figure, and this is typical of all the current experiments. Increase in the igniter application time results in the plots over a similar range of burning time shifting towards higher oxygen concentration. For a given fabric ignition condition, the oxygen concentration necessary to achieve a specified burning time decreases as the temperature increases. Also, for a given fabric temperature condition, as the igniter application time is increased, the oxygen concentration required to achieve a given burning time increases.

All the flame-retardant-treated fabrics studied responded in a very similar manner to environmental temperature changes. Thus the $[EOI]_0$ and E_0 parameters represent the most reliable measures of extinguishability both of which decrease with increase of temperature. Using this extinction concept, the influence of both area density and temperature can be predicted for a given flame-retardant-treated cotton fabric, preferably via the linear relationship of eq. (1). As seen in Tables IV and V, the slopes E_1 determined for this linear relationship show a general decrease with temperature increase. However, in the case of the Pyrovatex-treated fabric, the value of E_1 hardly changes in going from 100 to 200°C while in the Proban case the decrease in the value of E_1 between the two temperatures is two-thirds of that between 20 and 100°C. Thus the dependence of extinguishability on area density becomes less as the temperature increases. It might, therefore, be concluded that the flame-retarded cotton fabrics investigated have extinguishabilities which become less dependent on fabric structure variables as the environmental temperature is increased. This observation could have significance when attempting to design fabrics which must offer protection to underlying materials when subjected to high heat fluxes.

It is interesting to compare the values of the intrinsic extinction oxygen indices E_0 determined in the current work, Tables IV and V, with those for untreated cotton in Table III of Part 1. The relevant data are collated in Table VI.

The E_0 is at least 50% higher for the flame-retarded fabrics under all temperature conditions. The difference between the untreated and flame-retardant-treated values is a measure of extinguishability or flame-retarding character imparted by the flame-retardant treatment at each temperature. It is interesting to observe that the phosphonium-retardant Proban gives a higher E_0 at 20°C than does the phosphonate-retardant Pyrovatex. This

TABLE VI
Values, Determined at Various Temperatures, of E_0 and the Fractional Decrease in E_0 with Respect to the Value at 20°C

Temperature	Untreated		Proban		Pyrovatex	
(°C)	E_0	$\Delta E^a/E_0^{20}$	E_0	$\Delta E^a/E_0^{20}$	E_0	$\Delta E^a/E_0^{20}$
20	0.135		0.199		0.187	
100	0.106	0.215	0.172	0.136	0.171	0.086
200	0.087	0.356	0.145	0.271	0.150	0.198

$^a\Delta E = E_0^{20} - E_T^{\text{Temp}}$.

partly reflects the higher phosphorus and nitrogen concentrations for Proban given in Table I. At higher temperatures the E_0 values become equivalent. This suggests that, with respect to the mass of phosphorus and nitrogen applied, Pyrovatex is the more efficient retardant. Such an observation has been made previously by Hofmann and Loss.[14] The values obtained for the fractional decrease in E_0 with increasing temperature indicate that the temperature sensitivity of the burning behavior of cotton is greater than that of Proban-treated cotton, which itself is greater than that of Pyrovatex-treated cotton. Thus we infer that an effective flame retardant should not only function at ambient conditions but also reduce the temperature sensitivity of the inherent fiber burning behavior at elevated temperatures. Both the current flame retardants are effective in this respect. The implications of these observations with regards to LOI will be discussed in Part III.

The authors wish to thank Whitecroft plc for donating the Proban-treated samples and Ciba-Geigy Ltd. for the Pyrovatex-treated fabrics. One of us (M. T.) wishes to thank Albright and Wilson Ltd. and the Textile Institute for financial assistance.

References

1. C. P. Fenimore and F. J. Martin, *Mod. Plast.*, **44**, 141 (1966).
2. J. J. Willard and R. E. Wondra, *Text. Res. J.*, **40**, 203 (1970).
3. W. C. Arney and W. C. Kuryla, *J. Fire Flamm.*, **3**, 183 (1972).
4. A. R. Horrocks, D. Price, and M. Tunc, *Textile Progress*, to appear.
5. S. Mladenovic, *Tekstil*, **34**, 309 (1985).
6. A. R. Horrocks, D. Price, and M. Tunc, *J. Appl. Polym. Sci.*, **34**, 1901 (1987).
7. A. R. Horrocks and M. Ugras, *Fire Mater.*, **7**, 111 (1983).
8. A. R. Horrocks and M. Tunc, *J. Text. Inst.*, **77**, 119 (1986).
9. D. Price, A. R. Horrocks, and M. Tunc, in *Fundamental Aspects of Polymer Flammability*, London, G. Cox and G. Stevens, Eds., IOP Short Meeting Series No. 4, Institute of Physics, Bristol, 1987, p. 165.
10. M. Tunc, M.Sc. thesis, University of Salford, 1984.
11. ASTM D2863-1977.
12. D. E. Stuetz, A. H. DiEdwardo, F. Zitomer, and B. P. Barnes, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 967, 987 (1980).
13. J. E. Hendrix, J. V. Beninate, G. L. Drake, Jr., and W. A. Reeves, *Fire and Flammability*, C. J. Hilado, Ed., Technomic, Westport, CT, 1974, Vol. 4, p. 129.
14. P. Hofmann and R. Loss, *Textilver.*, **8**, 310 (1973).

Received January 5, 1988
Accepted February 24, 1988