Studies on the Temperature Dependence of Extinction Oxygen Index Values for Cellulosic Fabrics: III. Comparison with Limiting Oxygen Index for Commercial Flame-Retarded Cotton

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Synopsis

Limiting oxygen index values of single and multilayer Proban CC- and Pyrovatex CP-flame retardant finished cotton fabrics having a variety of area densities were determined as a function of igniter application time and temperatures up to 200°C. Except for the lightweight (140 g m^{-3}) Proban CC-treated fabrics, LOI, like comparable extinction oxygen index (EOI) values, increased as ignition times were increased from 2 to 10 s. Extrapolation to zero ignition time enabled $[LOI]_0$ values to be determined at each temperature, which, for a given flame retardant, increased linearly with area density of mono- and multilayered fabric combinations. Comparison with earlier extinction oxygen index results showed that this $[LOI]_0$ vs. area density dependence had significantly lower correlation than that for $[EOI]_0$. These poor former correlations further substantiated the claims that the EOI concept offers a more effective means of quantifying textile fabric flammability. Analysis of the linear relationships enabled intrinsic limiting oxygen index, L_0, and area density-dependent, L_1, terms to be determined. Like conventional LOI values, L_0 values also reduce significantly at elevated temperatures.

INTRODUCTION

Previously reported work[1,2] has attempted to quantify the burning behavior of both unretarded and flame-retarded cotton fabrics in terms of the extinction oxygen index (EOI) concept.[3] It has been demonstrated that analysis of EOI results enables the respective contributions that fiber and fabric structures make to the overall fabric burning (or extinction) behavior to be quantitatively resolved. Comparison with earlier published works based on the use of limiting oxygen index (LOI)[4-7] for quantifying fabric burning properties suggested that the application of the EOI concept is more effective as a means of assessing textile flammability.[1-3]

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In Part II[2] of this series of publications, analysis of the effect of temperature on the EOI values of commercially available Proban CC- (Albright and Wilson Ltd., U.K.) and Pyrovatex CP- (Ciba Geigy, U.K.) treated cotton fabrics was undertaken. This paper considers the effect of temperature on the limiting oxygen index values of these same fabrics.

EXPERIMENTAL AND RESULTS

Two lightweight (130 and 140 g m^{-2}) and one heavyweight (190 g m^{-2}) Proban CC-treated and one lightweight (137 g m^{-2}) and heavyweight (202 g m^{-2}) Pyrovatex CP-treated commercial flame retarded, plain woven cotton fabrics were used as described in Part II of this series.[2]

The experimental procedure used to determine the LOI values of each fabric at 20, 100, and 200°C was an extension of that previously described[1,2] for finding persistence-of-burning times at ignition times of 2, 4, 6, 8, and 10 s. Once burning times, after removal of the butane flame igniting source, were greater than 30 s, not only did the samples burn almost completely, but the oxygen concentrations were very close to the limiting oxygen index condition as described in ASTM D2863-77. Thus LOI values could be easily found at each ignition application or ignition time during the previously reported EOI experiments[1,2] by recording the minimal oxygen concentration required for complete fabric combustion.

Each fabric was tested at a given temperature and ignition time as single and multilayer forms. The averaged results of at least three separate experiments for each single layer fabric are shown in Table I, where it is seen that, at each temperature, LOI increases with ignition time.

For each fabric, temperature, ignition condition, the typical effect of multilayering is shown for the 10 s ignition time condition for each temperature in Table II.

TABLE I
Effect of Ignition Time on LOI of Flame-Retarded Cotton Fabrics at 20, 100, and 200°C

Flame retardant	P (%)	N (%)	Temp (°C)	Area density (g m^{-2})	LOI at ignition times				
					2 s	4 s	6 s	8 s	10 s
Proban	3.26	3.23	20	140	0.319	0.313	0.315	0.317	0.319
	2.70	2.63	100	130	0.258	0.269	0.272	0.277	0.281
			200		0.201	0.209	0.217	0.216	0.221
	2.91	2.83	20	190	0.335	0.337	0.335	0.343	0.341
			100		0.286	0.285	0.284	0.279	0.280
			200		0.200	0.200	0.211	0.213	0.222
Pyrovatex	1.95	2.09	20	137	0.290	0.291	0.293	0.296	0.299
			100		0.250	0.251	0.255	0.257	0.262
			200		0.209	0.211	0.215	0.221	0.226
	1.84	1.78	20	202	0.289	0.295	0.299	0.299	0.300
			100		0.261	0.269	0.275	0.277	0.280
			200		0.212	0.219	0.224	0.231	0.236

TABLE II
Effect of Multilayering on the LOI of Flame-Retarded Cotton Fabrics (Subjected to a 10 s Ignition Time) at Room Temperatures

Area density ($g\ m^{-2}$)	LOI at 20°C	LOI at 100°C	LOI at 200°C
Proban CC			
140	0.319		
280	0.328		
419	0.353		
559	0.366		
699	0.391		
130		0.281	0.221
260		0.286	0.217
390		0.292	0.226
520		0.301	0.248
650		0.307	0.262
190	0.341	0.280	0.222
379	0.350	0.305	0.227
569	0.369	0.315	0.231
758	0.380	0.313	0.231
948	0.382	0.317	0.244
Pyrovatex CP			
137	0.299	0.262	0.226
274	0.300	0.264	0.230
411	0.319	0.283	0.240
548	0.350	0.303	0.245
686	0.362	0.307	0.248
202	0.300	0.280	0.236
403	0.315	0.281	0.241
605	0.337	0.299	0.250
806	0.361	0.311	0.261
1008	0.376	0.320	0.266

DISCUSSION

Effect of Ignition Time

Table I shows that the LOI for single layer fabrics at a given temperature, except for 140 and 190 gm^{-2} Proban CC-treated cotton at 20 and 100°C, respectively, increases with ignition time. Except for these two fabric/temperature conditions, this behavior is typical also of the multilayered samples. Similar behavior was reported in Part II[2] for EOI values, although the converse relationship was observed for unretarded cotton fabrics.[1] The former effect was considered to be a consequence of dense char-forming character of the flame retardants present; it is probable that the same cause inhibits ignition and so gives rise to the observed LOI vs. ignition time effect.

As discussed by Horrocks et al.,[8] previous workers[9] have shown that LOI values may or may not vary with ignition time, depending on the polymer type when testing bulk samples. With textile materials, because of their rapid burning rates with respect to bulk polymer samples, ignition times considerably less than 60 s are required for LOI determination. Jeler and Ceric,[10] for example, cite 5 s as a reasonable value, although the possibility of ignition

TABLE III
$[LOI]_0$ Values for Proban CC- and Pyrovatex CP-Treated Cotton Fabrics at 20, 100, and 200°C

Flame retardant	Area density ($g\ m^{-2}$)	$[LOI]_0$ at 20°C	100°C	200°C
Proban CC	140	0.316		
	279	0.333		
	419	0.357		
	559	0.360		
	699	0.395		
	130	—	0.255	0.199
	260	—	0.260	0.191
	390	—	0.264	0.201
	520	—	0.272	0.214
	650	—	0.283	0.224
	190	0.333	0.283	0.192
	379	0.338	0.271	0.195
	569	0.352	0.285	0.199
	758	0.369	0.273	0.204
	948	0.379	0.278	0.208
Pyrovatex CP	137	0.287	0.246	0.203
	274	0.297	0.245	0.197
	411	0.302	0.265	0.203
	548	0.333	0.270	0.208
	686	0.357	0.294	0.226
	202	0.289	0.259	0.206
	403	0.302	0.264	0.212
	606	0.325	0.271	0.222
	806	0.341	0.272	0.220
	1008	0.355	0.289	0.229

time dependence was not discussed. Recent work in our laboratories on polyester–cotton-blended fabrics[11] has shown that LOI values are in fact independent of ignition time over the range 2–16 s.

The observed dependence in Table I enables extrapolation of LOI values for a given fabric to give $[LOI]_0$, the value at zero ignition time. Except for the 140 $g\ m^{-2}$ fabric, with all fabrics, as both mono- and multilayers, at each temperature, straight lines with high correlation were obtained following linear regression analysis (correlation coefficients > 0.90). $[LOI]_0$ values are listed in Table III. Values for the 140 m^{-2} Proban CC-finished fabrics which did not show the observed LOI vs. ignition dependence are averages of those at each ignition time in both mono- and multilayer forms.

Effect of Area Density

Inspection of the zero ignition time limiting oxygen index values in Table III suggests that, for a given fabric/temperature, $[LOI]_0$ increases with area density in a manner similar to that previously reported for extinction oxygen index.[1-3] Figures 1 and 2, respectively, show the plots of $[LOI]_0$ vs. uncorrected[1] area density, M for Proban CC- and Pyrovatex CP-treated fabrics. The apparent trends in Figures 1 and 2 are not as well defined as those for extinction oxygen index–area density relationships for the same fabrics.[2]

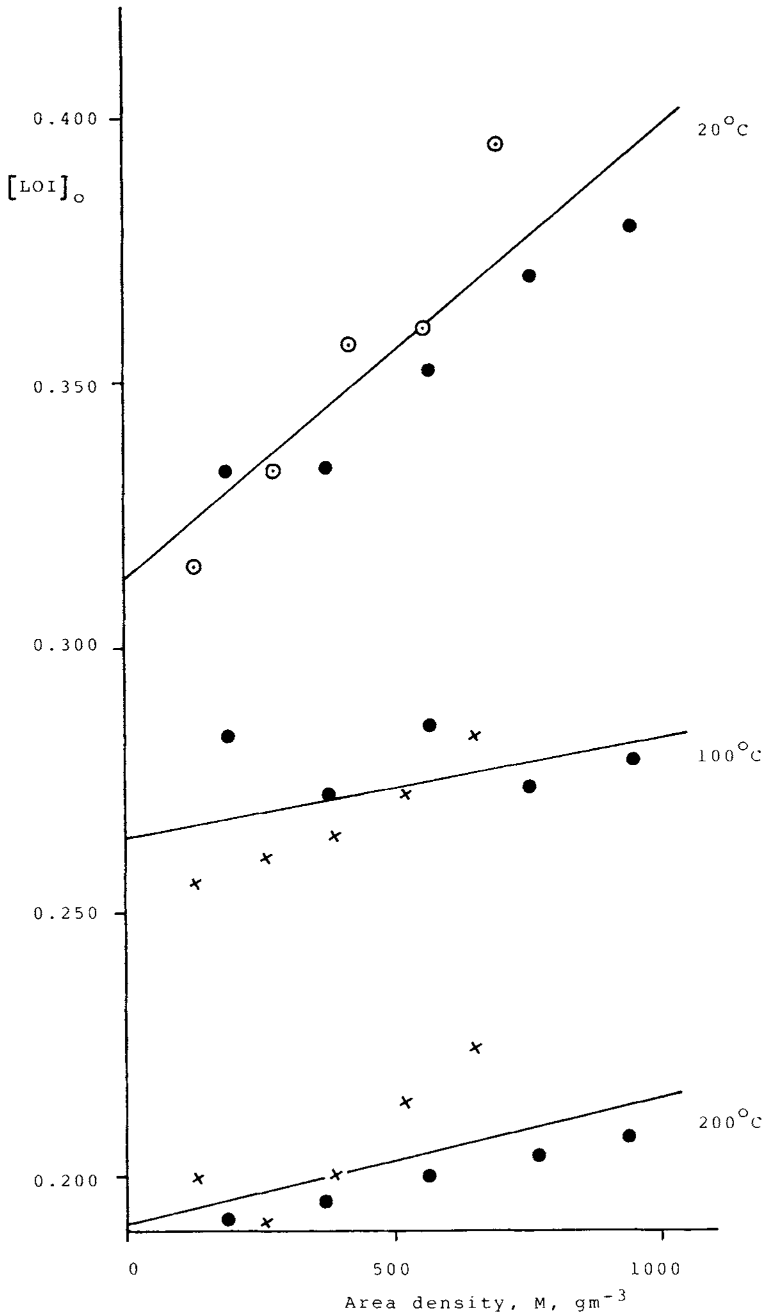

Fig. 1. Plots of limiting oxygen index at zero ignition time, $[LOI]_0$, vs. area density M of mono- and multilayered Proban CC-treated cotton fabrics at 20, 100, and 200°C; single layer fabric area densities are designated (⊙) for 140, (×) for 130, and (●) for 190 g m^{-2}.

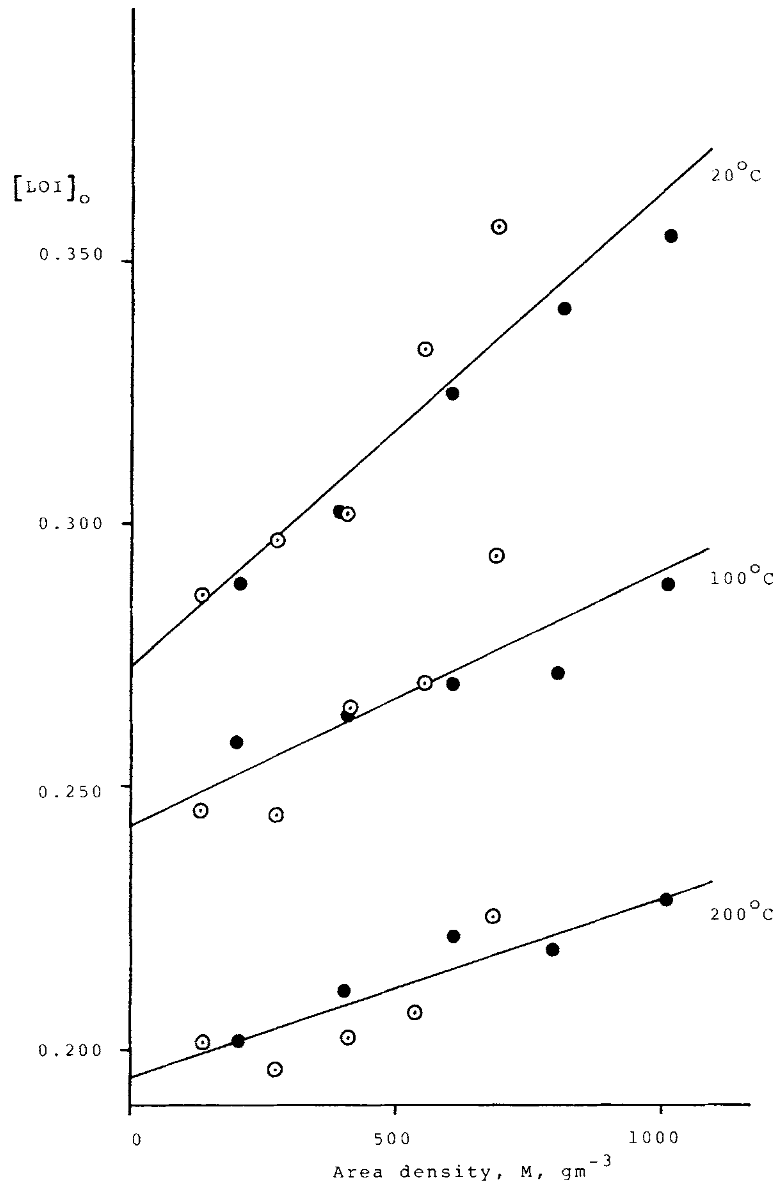

Fig. 2. Plots of limiting oxygen index at zero ignition time, $[LOI]_0$, vs. area density M of mono- and multilayered Pyrovatex CP- treated cotton fabrics at 20, 100, and 200°C; single layer fabric area densities are designated (⊙) for 137 and (●) for 202 g m^{-2}.

Linear regression gives the analysis in Table IV in terms of the equation $[LOI] = L_0 + L_1M$ and correlation coefficients are little improved by use of a polynomial curve-fitting procedure.[11]

In spite of the low correlations, especially for Proban CC-treated fabrics at 100 and 200°C, however, intercept L_0 values may still be representative of free-fiber burning behavior of the respective flame-retarded fabrics. For each retardant, they follow the similar LOI vs. temperature trends cited by

TABLE IV
Linear Regressional Analyses of $[LOI]_0$ vs. Area Density for Flame-Retarded Cotton Fibers

Flame retardant	Temperature (°C)	L_0	L_1 $\times 10^5$	Correlation coefficient
Proban CC	20	0.312	8.18	0.890
	100	0.264	1.79	0.426
	200	0.191	2.38	0.602
Pyrovatex CP	20	0.273	9.02	0.933
	100	0.243	4.90	0.854
	200	0.195	3.45	0.870

Hendrix et al.[12] and Stepniczka and DiPietro[13] for phosphonium salt condensate-retarded cotton.

Slopes L_1 in Table IV signify the area density dependence of LOI, while, at 20°C, L_1 values are similar for both retarded fabrics, raising the environmental temperature reduces these by differing degrees. For Proban CC-treated fabrics a fourfold drop occurs on heating to 100°C with little change above this value, thus showing that LOI becomes considerably less area density-dependent at high temperatures. On the other hand, Pyrovatex CP-finished fabrics, show a more progressive and gradual decrease in L_1 as temperature increases. Comparison of these results with similar data[2] for extinction oxygen index dependence on area density shows the converse to hold with regard to the E_1 term.

The observed poor relationship between LOI and M above, relative to those seen for EOI and M,[1-3] supports all previous published results whose generally poor correlations have been demonstrated for cotton[4-6] as well as a variety of other fiber-containing fabrics such as polyester,[5,6] polyamide,[5,6] acrylic,[6] wool,[6] and various blends.[6,7] Horrocks et al.[8] have fully reviewed this problem and note that, where sufficient data exists, correlation coefficients of 0.80–0.85[4,5] are observed for the LOI of cotton with respect to area density where fabrics exist in a variety of structures. Only if fabric structure is maintained constant are higher correlations seen; for example, Hendrix et al.[14] quote a coefficient of 0.979 for a series of cotton ducks having area densities within the range 500–900 g m^{-2}. No similar quantitative data exists to the authors' knowledge with regard to flame retarded cotton, although Mladenovic[14] noted that increasing area density (85–180 g m^{-2}) enhanced the LOI of Pyravatex CP-treated fabrics at 20°C.

Effect of Environmental Temperature

Close inspection of the L_0 values in Table IV as a function of increasing temperature shows that both flame-retarded intrinsic free-fiber LOI values rapidly fall below 0.21 as temperatures approach 200°C. Thus both flame-retardant treatments provide fiber characteristics which will enable their combustion to take place in air at elevated temperatures. Stepniczka and DiPietro[13] show that cotton treated with a phosphonium salt-urea condensate similar to Proban CC has an LOI of 0.275 at 25°C and 0.205 at 180°C. Although the lower concentration of flame retardant (13% ≡ 1.38% P, 3.08%N) used will explain the lower LOI values compared to those reported here, this earlier work suggests that burning in air of this fabric (135 g m^{-2}) will occur at about 180°C. This condition, often referred to as the temperature index,[15] may be estimated, from recently reported[16] work, to be 200°C for Proban-finished 325 g m^{-2} cotton. Unpublished work in our laboratory shows the temperature index to be 215°C for 192 g m^{-2} Proban CC-treated and 220°C for 200 g m^{-2} Pyrovatex CP-treated cottons having similar levels of application to those reported in Table I.

It is important to emphasize, therefore, that adequate flame retardancy can be expected to be retained at high temperature only if the area density of a fabric is maximized for a given end use.

CONCLUSION

The limiting oxygen index values of Proban CC- and, in particular, Pyrovatex-CP flame retardant-finished fabrics as mono- and multilayer samples generally increase with increasing ignition application time up to 10 s at 20, 100, and 200°C. This enables the limiting oxygen index at zero ignition time $[LOI]_0$ to be determined by extrapolation.

However, for a given flame retardant studied at a defined temperature, $[LOI]_0$ increases linearly with area density of layered fabrics. The correlation of this trend is significantly less than that seen for $[EOI]_0$ vs. area density for the same fabrics tested at ambient and elevated temperatures.[2] These results, therefore, add further weight to the consideration[1,2] that extinction oxygen index is a better parameter for defining textile fabric flammability than is the conventional LOI.

Behavior at elevated temperature shows, in agreement with other workers,[12,13] that LOI and its derivative L_0 values of flame-retarded cotton rapidly reduce so that fabrics will eventually burn in air. The effects of area density may be predicted and enable fabrics of high area density to better retain their flame retarding character.

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