

Studies on the Temperature Dependence of Extinction Oxygen Index Values for Cellulosic Fabrics. I. 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

The concept of extinguishability as a measure of textile flammability is reviewed. Definition and determination of extinction oxygen index enables a parameter to be defined from which the effects of ignition time and fabric structure may be removed. This so-called extinction oxygen index (EOI) and the derived value at zero ignition time $[\text{EOI}]_0$ more exactly define the burning/nonburning fabric boundary than does the more widely used limiting oxygen index (LOI). This first paper reports the determination of EOI and $[\text{EOI}]_0$ values for a series of cotton fabrics in the temperature range 20–200°C. The influence of the various fabric parameters of area density, air permeability, sample thickness, bulk density, and moisture content was investigated. The advantages of using the EOI rather than the LOI concept as a measure of textile flammability is indicated in the discussion of the results of this study with reference to previous work concerned with LOI data for cotton. In particular, the significance that environmental temperature has on EOI and related parameters reported here and previously reported LOI data is discussed in terms of various published models which define the burning/extinction threshold.

CONCEPT OF EXTINGUISHABILITY

The measurement of the burning behaviour of a textile fabric usually involves the quantification of parameters such as ease of ignition,^{1,2} linear,³ and mass⁴ burning rates, rates of energy evolution,^{5,6} and limiting oxygen concentration (LOI) for sustained burning.^{7,8} For a given fabric all these depend on the nature of the igniting source,^{2,9} the orientation of the fabric and location of ignition (top, bottom, edge, or face) and the environment conditions. With regard to the latter, not only are moisture^{10–12} and temperature^{10,13} important, but also whether still or forced-draught conditions prevail.¹⁴

Extinguishability or the ease with which an ignited fabric is extinguished is a much less studied concept in spite of its lower dependence on certain of the above factors, in particular the character of the igniting source and mode of ignition. Miller et al.¹⁵ initially considered the concept and measurement of extinguishability as a flammability criterion. By determining burning rate as a function of environment oxygen concentration, these workers were able to quote intrinsic oxygen index $(\text{OI})_0$ values, at extrapolated zero burning rates for cotton, wool, acrylic, modacrylic, and aramid for top ignition of vertically

*To whom correspondence should be addressed.

orientated fabrics and for bottom ignition of both vertically and 45° inclined samples. Intrinsic oxygen index values for extinction were consequently much lower than normal LOI values, for example, for top-ignited cotton a value of $(OI)_0 = 0.13$ compares with the normal LOI = 0.18.

Almost concurrent studies by Krasny and Francis¹⁶ attempted to rank a range of cotton and polyester-cotton blend fabrics of varying area densities in order of ease of extinguishability. In order to represent actual human response conditions, a simulated "beating hand" was used to extinguish burning fabrics. The time to extinguish burning for cotton fabrics depended on area density with pile structures further enhancing difficulty of extinguishment. The blend fabrics were more difficult to extinguish with less obvious area density dependence.

Subsequent work by Bhat et al.¹⁷ attempted to define extinguishability and, using the TRI flammability analyzer,¹⁸ measured linear and mass burning rates and heat fluxes as functions of oxygen concentration. With few exceptions, most fabrics exhibited a linear relation between the various burning parameters and oxygen concentration. Intrinsic oxygen index values, after the manner of Miller et al.,¹⁵ could be defined by extrapolation of both burning rates and heat fluxes. $(OI)_0$ values for a given fiber type, determined from linear burning rates, showed dependence on area density while those derived from mass burning rates and heat fluxes were less so dependent. However, it was concluded that the time to extinguish under specified conditions, decreased with increasing area density for a given fiber.

The effects of contact with cooler inert bodies on fabric extinguishability have been considered by these same workers,¹⁹ Miller et al.,²⁰ Zawistowski et al.,²¹ and Backer et al.²² These studies demonstrated that inert bodies enhance extinguishability by promoting heat loss, local oxygen concentration depletion, and changes in burning behavior. Thus fabrics in contact with the human body have a lower burn-injury potential than when free-hanging. This effect is less noticeable, however, for thermoplastic fiber-containing fabrics.

Spivak et al.^{23,24} extended former work by studying the effects of air flow on extinguishability and showed that enhanced velocity can decrease heat transfer from a burning garment to the wearer. Furthermore, burning rates may decrease and extinction occur above critical flow rates²³ in a manner which depends on fabric orientation.²⁴ Fairhall and Spivak²⁵ subsequently extended this work to embrace the effects of simulated slapping, thereby adding to the earlier work of Krasny and Francis¹⁶ by investigating a greater number of fiber types. While slapping data did not correlate with mannequin-contact extinction data, the former depended greatly on fiber type and test conditions but less so on fabric structure and area density. Reeves et al.,²⁶ however, measured the extinction of cotton and polyester-cotton blend fabrics in the presence of selected flame retardants supported on a semicircular frame. The extinction data determined appeared to have a linear correlation with limiting oxygen index (LOI).

In an attempt to more fully quantify the effect of fabric variables on extinguishability, Horrocks and Ugras²⁷ have extended the original concept of Miller et al.¹⁵ By measuring the persistence-of-burning times of a fabric as a function of oxygen concentration, extrapolation enables the extinction oxygen index (EOI) to be defined as the oxygen concentration at which zero burning

time is achieved. Persistence-of-burning times in this work using a standard oxygen index apparatus are similar to the self-quenching times determined by Stuetz et al.²⁸ These workers used a specially designed apparatus for determining critical oxygen conditions required for both burning and extinction of a selection of polymeric and textile materials. While Stuetz et al.²⁸ determined self-quenching times after 5-s application of an igniting source, Horrocks and Ugras²⁷ found that EOI values are dependent upon ignition conditions. Extrapolation of respective EOI values to zero igniter application time removes the influence of ignition and gives the parameter $[EOI]_0$, which linearly varies with area density and the logarithm of fabric air permeability for cotton, polyester, and nylon 6,6 fabrics.

For cotton, this concept was later extended to extinguishability at 100°C,²⁹ where similar relationships were noted.

The authors have recently initiated a systematic investigation of the temperature dependence of the extinguishability of cellulosic fabrics and the influence thereon of fabric parameters. This first paper is concerned with the behavior of cotton fabrics. Future papers will report studies of flame-retardant cotton fabrics.

EXPERIMENTAL

Five pure cotton plain woven fabrics of differing area densities were used. Three (A, B, and E) were laboratory prepared and bleached in an unrestrained manner. Two (C and D) were commercially prepared which included singeing and steam-can drying to give a smooth finish. All fabrics were thus freed of natural and adventitious impurities. Samples were cut to appropriate sizes prior to conditioning at a relative humidity of 65% at 20°C.

The area densities (M), thickness (t), and air permeability (A) of the samples, in single and multilayer forms, are collated in Table I. Air permeabilities were determined using a Shirley air permeability apparatus at an air pressure of 10 mm water gauge. Thickness measurements were made to BS2544: 1967 using a Shirley thickness tester.

All burning time measurements were carried out using a Stanton Redcroft FTA limiting oxygen index unit and general procedures described previously²⁷ with the following modifications. The type 2 chimney³⁰ (210 mm length, 95 mm diameter) used for experiments at 20°C was replaced by the Stanton Redcroft HFTA module at elevated temperatures (100, 150, and 200°C). This incorporated a type 1 chimney^{30,31} (450 mm length, 75 mm diameter) about which is wound a heater element. At the base of the chimney, a similarly programmed heater preheats the entering gas. By use of a probe thermocouple, both heater controls were adjustable to give a required chimney and sample temperature which varied by less than 2°C over the length of the vertical fabric faces. In accordance with the recommendation of Wharton,³² an aluminium annulus, of internal diameter 50 mm, was fitted to the open end of the type 1 chimney to prevent entrainment of oxygen from the air.

After introducing a mounted fabric sample into the heated chimney, at least 2 min were needed for thermal equilibration to be restored and reproducible burning times to be achieved. In practice, 3 min were allowed for equilibration prior to igniter application.

TABLE I
Physical Properties of Fabric Samples Used in Current Investigation

Fabric/no. layers	Description: weave; ends and picks (cm^{-1})	Conditioned area density M (gm^{-2})	Air permeability A ($\text{cm}^3 \text{s}^{-1} \text{cm}^{-2}$)	Thickness t (mm)
A 1	Plain, 25 × 25	147	22.2	0.49
2		294	10.8	0.99
3		441	7.2	1.50
4		588	5.5	1.95
5		735	4.6	2.52
B 1	Plain, 9.4 × 9	303	13.1	1.35
2		606	6.7	2.72
3		909	4.0	4.01
4		1212	2.9	5.51
5		1515	2.3	6.89
C 1	Plain, 35 × 29	130	21.0	0.32
2		260	10.0	0.53
3		390	6.5	0.85
4		520	5.0	1.10
5		650	3.5	1.40
D 1	Plain, 27 × 25	190	6.0	0.47
2		380	3.0	0.86
3		570	2.0	1.26
4		760	1.5	1.67
5		950	1.0	2.08
E 1	Plain, 26 × 26	153	22.7	0.51
2		307	11.6	1.01
3		460	6.3	1.49
4		614	5.3	1.90
5		767	4.2	2.54

All experiments were carried out under conditions of constant mass flow rate and premixed gases were introduced at linear velocities of 44 mm s^{-1} at 20°C (equivalent to 40 mm s^{-1} at 0°C ³⁰) into both chimneys. This corresponded to respective volumetric flow rates of 11.0 and $17.5 \text{ dm}^3 \text{ min}^{-1}$ for type 1 and 2 chimneys. After heating at 100°C , the actual gas velocity at the same mass flow rate was 55 mm s^{-1} ³¹ within the HFTA module.

The recording of persistence-of-burning times has been described previously²⁷ but an ignition flame length of 25 mm , more typical of the standard LOI ignition condition, was used.^{30,33} Comparison of results for cotton fabrics in this work with those reported elsewhere²⁷ show that this smaller flame has little effect on recorded persistence-of-burning times. In addition, using this smaller flame, it was necessary to follow the advancing flame front during igniter application in order to maintain igniter flame contact. Using this technique, derived EOI values were found to be linearly dependent upon ignition time unlike the nonlinear relationship observed earlier.²⁷

Persistence-of-burning times were recorded within the range 2 – 16 s for most fabrics and igniter application times of $2, 4, 6, 8,$ and 10 s were used.

RESULTS

Determination of $[EOI]_0$

The burning time for each sample/ignition time/oxygen concentration/temperature condition was determined as the average from at least three sets of experiments. Linear regression analysis was carried out on the burning time vs. % oxygen concentration data as previously described.^{27,29} This showed that, for each fabric at each ignition time and temperature, the relationship was linear with a high correlation, as has previously been observed.^{27,29} The computed intercept value was taken as the EOI value for each particular fabric and ignition time. Linear regression analysis of these EOI values vs. ignition time again showed high correlation and yielded the $[EOI]_0$ values collated in Table II; $[EOI]_0$ represents the extinction oxygen index at zero ignition time.

Effect of Area Density M on $[EOI]_0$

Collation of the area density M data of Table I with the determined $[EOI]_0$ values, Table II, shows that $[EOI]_0$ increases with area density. Previous work^{27,29} has indicated that $[EOI]_0$ shows a simple linear dependence on area

TABLE II
Values of $[EOI]_0$ Determined at Various Temperatures for Cotton Fabrics Detailed in Table I

Fabric/ no. layers	20°C		100°C		150°C		200°C	
	$[EOI]_0$	M_c^a	$[EOI]_0$	M_c^a	$[EOI]_0$	M_c^a	$[EOI]_0$	M_c^a
A 1	0.140	142	0.113	137	0.115	137	—	—
2	0.142	286	0.121	275	0.120	273	—	—
3	0.145	432	0.121	413	0.121	410	—	—
4	0.150	578	0.122	554	0.124	548	—	—
5	0.153	724	0.125	694	0.127	684	—	—
B 1	0.154	294	0.126	283	0.127	282	—	—
2	0.152	596	0.131	570	0.127	565	—	—
3	0.174	895	0.144	864	0.142	849	—	—
4	0.175	1200	0.154	1160	0.152	1143	—	—
5	0.183	1502	0.158	1462	0.154	1425	—	—
C 1	—	—	—	—	0.100	121	0.088	121
2	—	—	—	—	0.105	242	0.096	242
3	—	—	—	—	0.117	362	0.109	362
4	—	—	—	—	0.127	485	0.115	483
5	—	—	—	—	0.136	605	0.119	604
D 1	—	—	—	—	0.117	176	0.102	176
2	—	—	—	—	0.121	354	0.112	353
3	—	—	—	—	0.127	531	0.120	529
4	—	—	—	—	0.133	709	0.127	706
5	—	—	—	—	0.144	887	0.133	882
E 1	0.142	148	0.114	143	—	—	—	—
2	0.143	299	0.120	287	—	—	—	—
3	0.151	451	0.123	432	—	—	—	—
4	0.155	604	0.124	579	—	—	—	—
5	0.166	757	0.127	726	—	—	—	—

^a Corrected area densities M_c ($g\ m^{-2}$) at various temperatures.

TABLE III
 Regressional Analysis Coefficients for $[EOI]_0$ vs. Area Density Data

Fit	Temperature (°C)	E_0	$E_1/10^{-5}$	$E_2/10^{-9}$	Correlation coefficient
<u>Conditioned area density</u>					
Linear	20	0.135	3.28	—	0.938
	100	0.109	3.37	—	0.938
	150	0.106	3.55	—	0.926
	200	0.087	5.10	—	0.957
Quadratic	20	0.135	3.32	- 0.25	0.938
	100	0.112	1.88	8.85	0.945
	150	0.103	4.89	- 8.93	0.931
	200	0.081	8.34	- 31.01	0.971
<u>Moisture loss-corrected area density</u>					
Linear	20	0.135	3.30	—	0.938
	100	0.109	3.39	—	0.939
	150	0.107	3.77	—	0.923
	200	0.086	5.67	—	0.965
Quadratic	20	0.135	3.37	- 0.458	0.938
	100	0.112	2.12	8.41	0.945
	150	0.103	5.33	- 11.02	0.930
	200	0.082	7.91	- 23.06	0.970

density M . Linear regressional analysis of the results in Table II, for an equation of the form

$$[EOI]_0 = E_0 + E_1M \quad (1)$$

yields the 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 III. Although these correlations show a good fit, the data was also subjected to a curve-fitting routine with respect to the quadratic equation

$$[EOI]_0 = E_0 + E_1M + E_2M^2 \quad (2)$$

The values of the coefficients E_0 , E_1 , and E_2 are also given in Table III together with the respective correlation coefficients. These correlation coefficients are slightly higher than those for the linear regression. Intuitively, however, the linear fit appears the better choice since the intercepts at each temperature are comparable, within error for the two analyses and the values for the slope are more easily understood. The slopes E_1 represent the dependence of $[EOI]_0$ on the area density.

The intercept values E_0 represent the intrinsic extinction oxygen indices of cotton, independent of ignition and area density variables, at the temperatures investigated. These intrinsic values represent cellulose material properties where maximum access to oxygen is possible at each temperature. These are temperature-dependent, and thus the major temperature dependence of

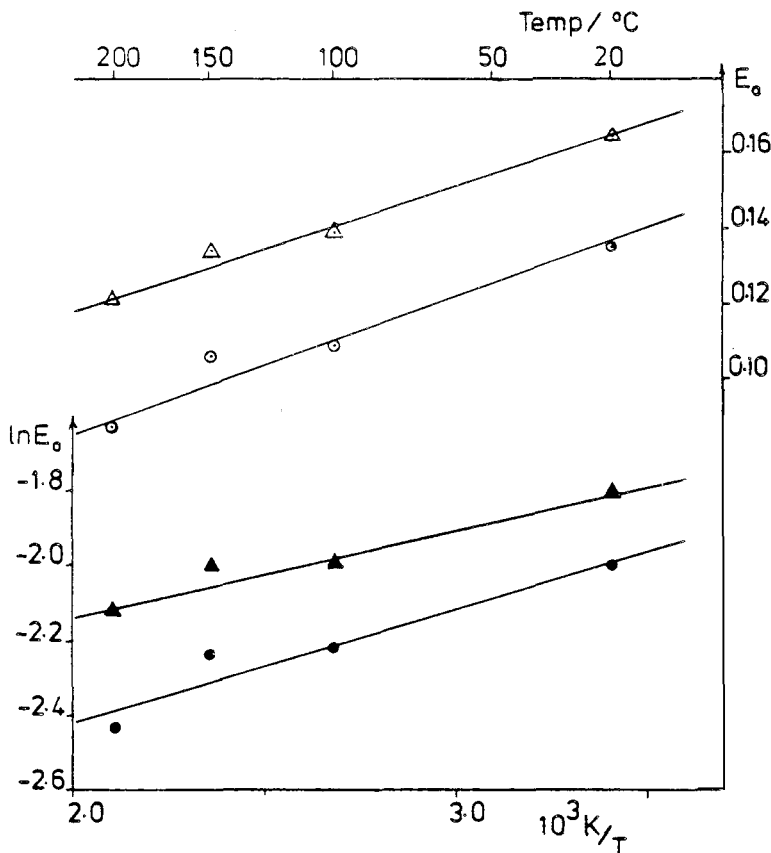


Fig. 1. Combined plots of $\ln E_0$ and E_0 vs. $1/T$ (k^{-1}) for cotton fabrics at zero area density [(●) $\ln E_0$; (○) E_0] and unit specific air permeability [(▲) $\ln E_0$; (△) E_0] conditions.

the $[EOI]_0$ /area density relationship arises from this intrinsic extinction term. A plot of $\ln E_0$ vs the reciprocal of the absolute temperature is given in Figure 1.

The area density dependent coefficients E_1 show temperature independence up to 150°C. At 200°C, an increase in E_1 is observed suggesting that increased area density is exerting a larger influence on $[EOI]_0$. It is noteworthy that experiments above 200°C were not carried out because of the tendency of the fabrics to char. This enhanced charring tendency may have contributed to the increased value of E_1 at 200°C.

Effect of Moisture

In previous studies which have considered oxygen index as a function of area density,¹⁰ no attempt to correct for the change in fabric mass caused by the dehydrating effect of the dry oxygen and nitrogen gases was made. Similarly, our earlier studies^{27,29} have considered $[EOI]_0$ as a function of conditioned area density. Moisture is known to influence oxygen index measurements.¹⁰⁻¹² Also the rates of change in area density through moisture desorption will vary with the magnitude of the area density M , the number of

layers in a sample, the environmental temperature, and the time of sample exposure to the gases in the chimney prior to igniter application. It was, therefore, decided to investigate the influence of moisture content on our results. The loss in mass through moisture desorption was determined gravimetrically following the exposure of mono- and multilayered fabric samples of fabrics B, C, and D to dry gas mixtures in the respective chimney-flow rate combination at each temperature over the range 20–200°C. The time of exposure was chosen to be 3 min, the typical sample equilibration time. It was found that the loss in moisture expressed as a fraction of the initial conditioned sample moisture content for a given number of layers, decreased smoothly as an increasing function of area density at 20, 100, and 150°C. At 200°C, all samples were fully dehydrated after the 3-min exposure time. From these results, it was possible to predict the moisture losses under each condition for fabrics A and E. The fabric area densities, M_c corrected for moisture loss during equilibration prior to igniter application, for all samples are listed in Table II.

Analysis of the data in accord with eqs. (1) and (2) yields the respective coefficients in the lower half of Table III. While hardly affecting the magnitudes of E_0 and E_1 , correction of M for moisture loss does make a slight improvement in the correlations of linear dependencies of $[EOI]_0$ on area density at the various temperatures, although within the error of the technique this effect is perhaps negligible.

TABLE IV
Bulk Density and Specific Volume Data for Cotton Fabric Samples Detailed in Table I

Fabric/no. layer	Bulk density (g/cm ³)	Specific volume S_0 (cm ³ /g)	A/S_0 (g cm ⁻² s ⁻¹)
A 1	0.300	3.333	6.661
2	0.297	3.367	3.208
3	0.294	3.401	2.117
4	0.302	3.311	1.661
5	0.292	3.425	1.343
B 1	0.224	4.464	2.935
2	0.223	4.484	1.494
3	0.227	4.405	0.908
4	0.220	4.545	0.638
5	0.220	4.545	0.506
C 1	0.406	2.463	8.526
2	0.491	2.037	4.909
3	0.459	2.179	2.983
4	0.473	2.114	2.365
5	0.464	2.155	1.624
D 1	0.404	2.475	2.424
2	0.442	2.262	1.326
3	0.452	2.212	0.904
4	0.455	2.198	0.682
5	0.457	2.188	0.457
E 1	0.301	3.322	6.833
2	0.304	3.298	3.527
3	0.309	3.236	1.947
4	0.323	3.095	1.712
5	0.302	3.309	1.269

Effect of Sample Thickness (t) on $[EOI]_0$

Before commenting upon the effect of sample thickness on $[EOI]_0$, it is perhaps pertinent to consider the variations in fabric bulk density (= area density/thickness) which exist between the various fabric samples. These are listed in Table IV. Fabrics A, B, and E, in both mono- and multilayer forms, have lower bulk densities than C and D. This probably relates to the laboratory method of preparation in an unrestrained condition of the former group compared with the commercial singeing and width-restrained preparation of the latter.

Figures 2 and 3 show the variation of $[EOI]_0$ with thickness under the various temperature conditions investigated. At 20°C a single smooth curve can be drawn to fit the experimental points obtained from the three laboratory prepared fabrics (A, B, and E) studied. The same is also true at 100°C and the curve is shifted considerably below that at 20°C. At 150°C, the data points indicate two regions of almost linear behavior while at 200°C the data, obtained only for fabrics C and D, correspond to a single, almost linear region which is similar in slope to the initial linear region of the 150°C data. The plots given in Figures 2 and 3 indicate that there is not a simple relationship between the $[EOI]_0$ values and the sample thickness. In fact, it could be argued that two different regions exist for the two respective sets of fabric at 150°C which may be determined by the differences in respective bulk densities

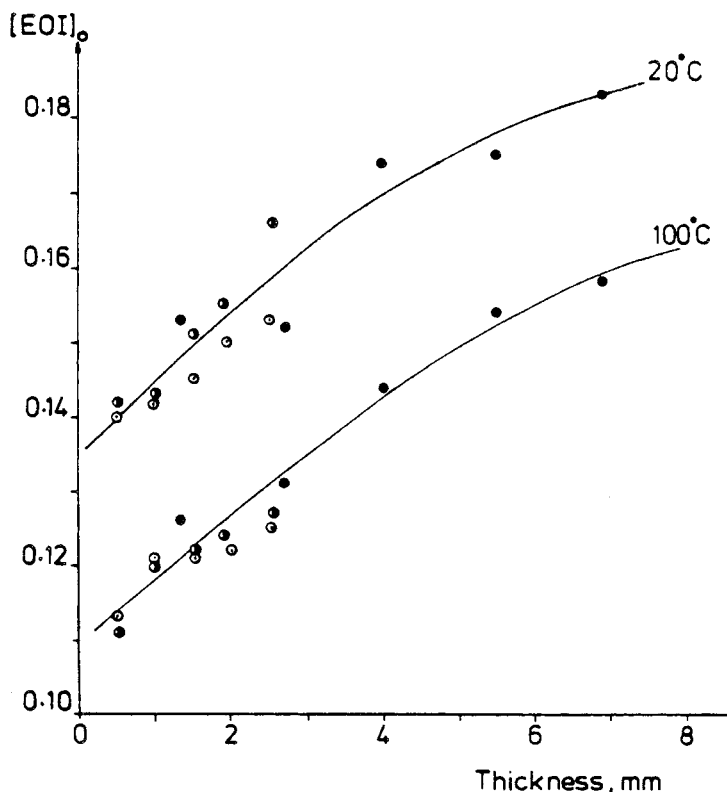


Fig. 2. The effect of thickness on $[EOI]_0$ at 20 and 100°C for cotton fabrics A (○), B (●), and E (◐).

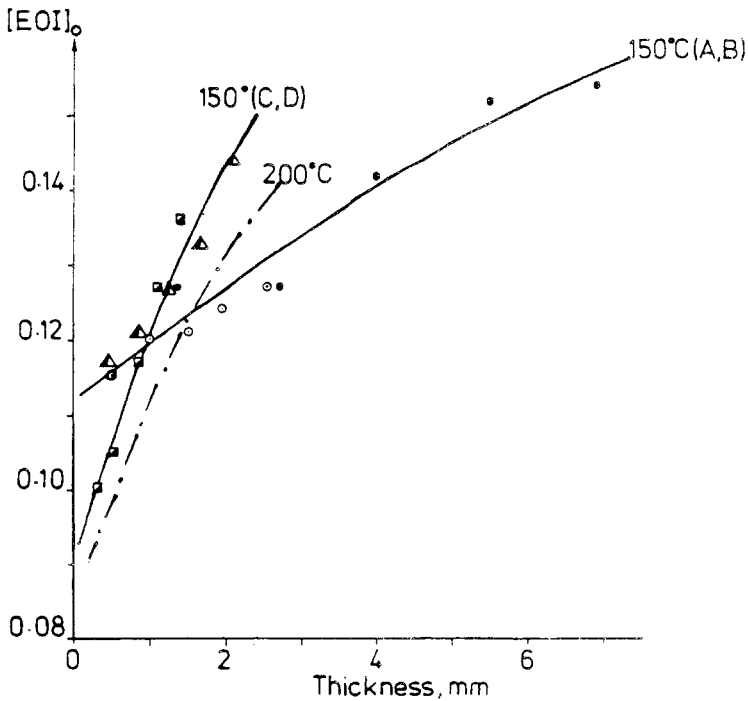


Fig. 3. The effect of thickness on $[EOI]_0$ at 150°C for cotton fabrics A (\circ), B (\bullet), C (\square), and D (\triangle) and at 200°C for fabrics C and D (---, data points omitted for clarity).

as shown in Table IV and previously commented upon. Since fabrics with a range of bulk densities have been investigated, attempts were made to ascertain if there is any correlation between the $[EOI]_0$ values and bulk density. No correlation was found. Recent work by Jeler and Cerić³⁴ showed a similar lack of correlation with the more conventional LOI.

Effect of Air Permeability (A) on $[EOI]_0$

Previously published data from fabrics A and B²⁹ show the plot of $[EOI]_0$ against $\log A$ is definitely curved for the temperatures 20 and 100°C. The current work provides additional new data at 150 and 200°C. The correlation for a linear fit is poor at 150°C but reasonable at 200°C. Neither situation is improved by attempting a quadratic fit unlike the previous data at 20 and 100°C.²⁹ Consequently, the air permeability was normalized with respect to sample thickness and area density by plotting $[EOI]_0$ against $\log A/S_v$, where S_v is the specific volume of the sample. For each fabric assembly, specific volume data are collated in Table IV, and Figure 4 shows the plot of $[EOI]_0$ vs. $\log A/S_v$ for cotton at 20, 100, and 200°C. For clarity the data at 150°C is omitted from Figure 4 but shows a similar trend. A simple linear regression for the data at all temperatures showed good coefficients as indicated in Table V. Note that the slope coefficient E_1 is temperature-independent. It was also found to be the case for $[EOI]_0$ vs. $\log A$.²⁹ The values of the various coefficients evaluated by a quadratic fit of the data are presented also in Table V. The correlation coefficients are improved at the two lower temperatures

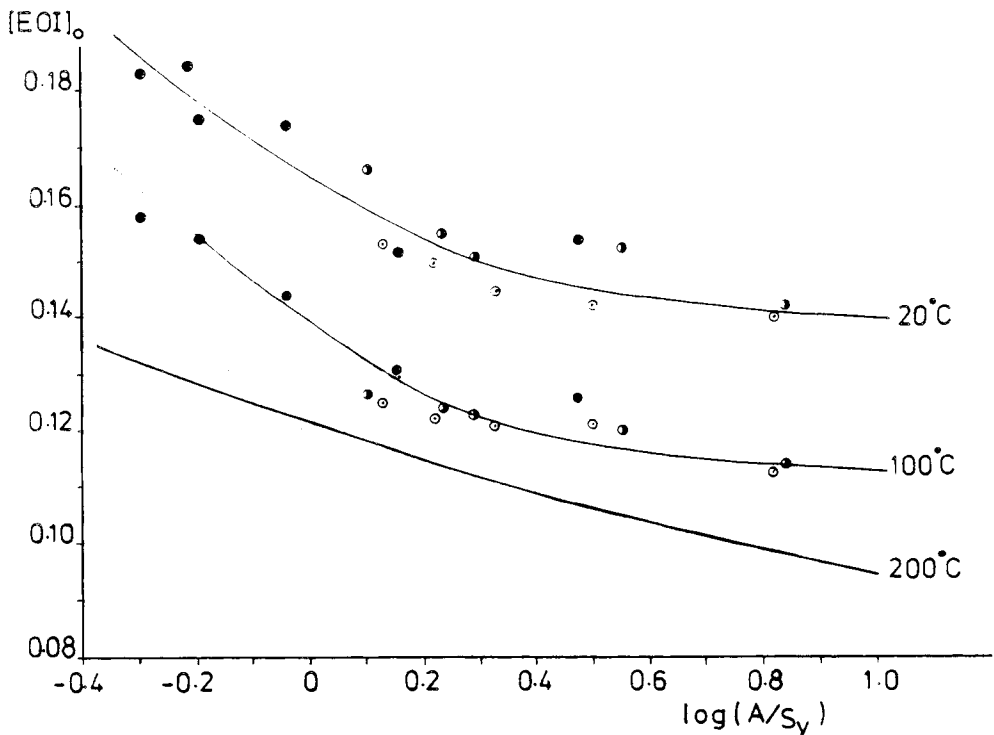


Fig. 4. The quadratic fits (Table V) for $[EOI]_0$ vs. $\log(A/S_v)$ for cotton fabrics at 20, 100, and 200°C; data points for fabrics A (○), B (●), and E (●) are present at 20 and 100°C only.

TABLE V
Coefficients for Linear and Quadratic Relationships between $[EOI]_0$ and $\log(A/S_v)$

Fit	Temperature (°C)	E_0	E_1	E_2	Correlation coefficient
Linear	20	0.165	-0.037	—	0.894
	100	0.139	-0.037	—	0.871
	150	0.134	-0.034	—	0.883
	200	0.121	-0.034	—	0.953
Quadratic	20	0.165	-0.057	0.034	0.947
	100	0.139	-0.067	0.048	0.956
	150	0.134	-0.038	0.007	0.885
	200	0.121	-0.032	0.004	0.954

studied but virtually unchanged at 150 and 200°C. The coefficients E_1 and E_2 show some indication of temperature dependence, E_2 becoming less significant at the higher temperatures. Interestingly, it is at the higher temperatures where a reasonable linear fit was obtained.

It is important to note that the intercept E_0 values are the same for both the linear regression and the quadratic fits. The authors consider that these are, therefore, sound values for E_0 , which represents the intrinsic extinction oxygen index of cotton fiber assemblies of unit-normalized air permeability,

independent of ignition, and hence bulk density variables, at the appropriate temperature. The values obtained are temperature-dependent and the van 't Hoff type plot of $\ln E_0$ vs. the reciprocal of the absolute temperature is reasonably linear as shown in Figure 1. It must be noted, however, that air permeabilities will change in magnitude at elevated temperatures because of reduced gas density and changes in fabric character. These latter will primarily be associated with moisture loss although above 150°C, slow char formation following hot gas exposure alone may have a measurable effect. Therefore, the E_0 and E_1 values above should be considered in the light of these provisions.

DISCUSSION

The validity of $[EOI]_0$ as a burning parameter independent of ignition conditions has been discussed previously^{27,29} and placed within the context of previously published extinction-related oxygen index values.^{15,17} Choice of a linear dependence of $[EOI]_0$ on cotton fabric area density not only gives rise to acceptable values of intrinsic extinction oxygen indices of 0.135, 0.109, 0.106, and 0.087 at 20, 100, 150, and 200°C, respectively, but also slopes which are temperature independent up to and including 150°C. Comparison with conventional LOI vs. area density data recorded at varying ambient temperatures shows considerable improvement of linear correlation for the EOI results. Hendrix et al.³⁵ and Miller and Meiser³⁶ both show evidence of linear dependence of LOI on area density for cotton fabrics, although with lower correlation coefficients (0.854 and 0.807,[†] respectively). Extrapolation of their data to zero area density yields "intrinsic" limiting oxygen index values of 0.175 and 0.171, respectively.

The correlations between $[EOI]_0$ and air permeability normalized with respect to area density and fabric thickness are considerable improvements over those previously reported^{27,29} and are far superior to those in which limiting oxygen index values are cited.³⁵ The intercepts 0.165, 0.139, 0.134, and 0.121 at 20, 100, 150, and 200°C, respectively, which represent $[EOI]_0$ values for fabrics of unit air permeability and unit specific volume, are more representative of highly condensed cellulose fibrous aggregates. These intrinsic extinction oxygen indices represent an opposite extreme of unlimited oxygen accessibility to completely separated fibers. Stuetz et al.²⁸ in their attempt to achieve a truly limiting or critical oxygen index parameter quote a value for cotton of 0.135 for a bottom ignited sample and 0.174 for a top ignited sample. The latter compares well with published LOI values, but they note that, on progressively reducing the oxygen concentration below 17.4%, measurement of self-quenching time (similar to persistence-of-burning times in this work) enables an oxygen concentration to be reached at which this time is zero. For cellulose and other polymers, this extinction condition coincides with the concentration required for sample burning following bottom ignition. Their value of 0.135 is identical to our zero area density of single fiber intrinsic extinction oxygen index at 20°C. Our bulk fiber intrinsic EOI value of 0.165 at 20°C, however, is still less than quoted LOI values.

[†] Estimate from literature data.

The effect of temperature on intrinsic EOI values reflects that observed for LOI values. If the extinction condition represents a limit above which exothermic combustion can occur albeit for an infinitesimally short time following ignition, then the temperature effect as shown by the van 't Hoff type of plots in Figure 1 is as expected. As pointed out by Stuetz et al.,²⁸ oxidative pyrolysis and flame propagation at the limiting oxygen index condition is influenced by the nature of the debris, such as char, and its affect on oxygen accessibility. Thus, because extinction oxygen index is perhaps less susceptible to such effects, it may be considered to be a more valid parameter. The van 't Hoff type of relationships seen in Figure 1 are significant because they would support this hypothesis. Attempts to find similar relationships between LOI and temperature have met with some success. DiPietro et al.³⁷ have shown that LOI decreases linearly with temperature for certain flame retarded cottons, polyester, and nylon up to 180°C. Hendrix et al.³⁸ have shown similar almost linear decreases in LOI for cotton, polyester, and cotton-polyester blends for temperatures in the range -50 to 250°C. More recently, Jeler and Ceric³⁴ have corroborated these observations for various cellulose-derived fabrics both alone and in blends which contain synthetic fibers.

Our intrinsic $[EOI]_0$ data, at both zero air permeability and $A/S_0 = 1$ conditions in Tables III and V, respectively, also shows that respective E_0 values decrease approximately linearly with increasing temperature.

Confusion exists with regard to the exact nature of the oxygen index vs. temperature function. Kanury³⁹ considered LOI for polymer melt pool flames to be a function of the geometry and dynamics of a diffusion flame fueled by polymer pyrolysis products. An analysis of the energy balance and oxygen requirements of this situation enabled the derivation of a relationship in which oxygen index depended on the reciprocals of both the heat of combustion, ΔH_c , and the ambient temperature. This study confirmed the earlier empirical dependence of LOI on $1/\Delta H_c$ first noted by Johnson⁴⁰ for a range of polymers. Johnson also analyzed the temperature dependence of oxygen index of polystyrene from results initially reported by DiPietro and Stepniczka⁴¹ and showed that for these samples LOI does not depend upon the reciprocal ambient temperature but varies as $T^{3/2}$. While Kanury rationalized his inverse temperature dependence on the effect of convection heat loss rate from the fire plume,³⁹ Johnson⁴⁰ considers that a negative $T^{3/2}$ dependence suggests that diffusion processes are more significant than the activation of pyrolysis in determining LOI. Tewarson and Pion,⁴² however, equate oxygen index with a mass burning rate function defined in terms of a steady state heat balance equation. To a first approximation, this treatment suggests that a simple LOI vs. temperature relationship exists at least for polystyrene.

If the LOI condition is equated with a simple chemical equilibrium model, then a van 't Hoff $\ln(\text{LOI})$ vs. $1/T$ relationship might be expected to hold. The LOI results of Hendrix et al.³⁸ and Jeler and Ceric³⁴ over the range 20–200°C are plotted as LOI vs. $1/T$ and $\ln(\text{LOI})$ vs. $1/T$ in Figure 5. The effect of area density on LOI is clearly seen in these plots, unlike those for EOI (as E_0) in Figure 1. Because the 115 g m⁻² cotton fabric of Hendrix et al.³⁸ is comparable in area density to that studied by Jeler and Ceric,³⁴ the combined data sets for both LOI and $\ln(\text{LOI})$ conditions in Figure 5 may be analysed. Similar linear correlations (0.94) exist for both conditions, and so no

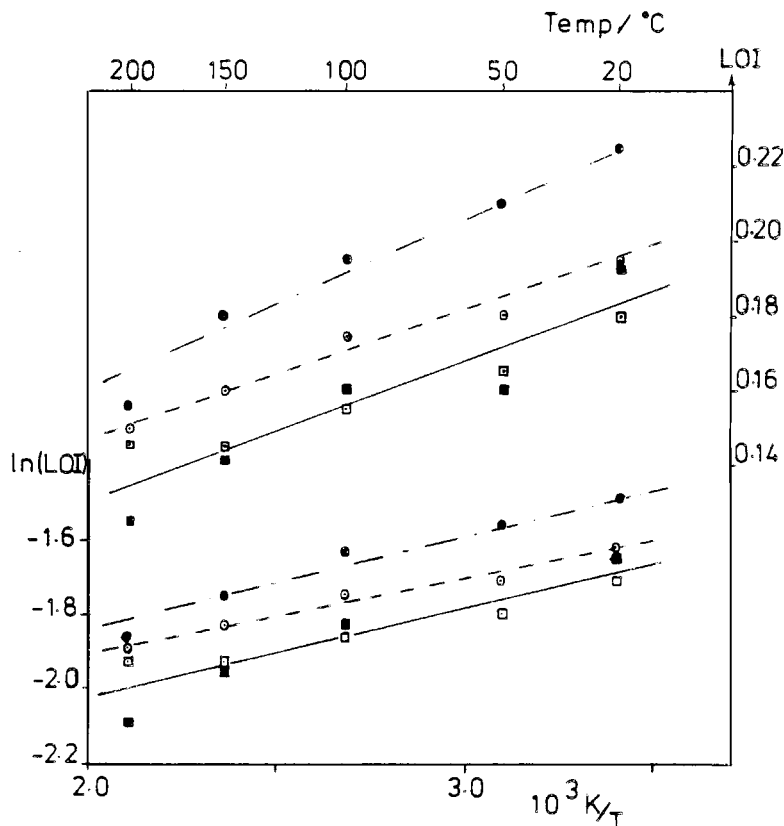


Fig. 5. Combined plots of $\ln(\text{LOI})$ and LOI vs. $1/T$ (K^{-1}) for various cotton fabrics; (\square) 115 g m^{-2} ; (\circ) 312 g m^{-2} ; (\bullet) 835 g m^{-2} (Hendrix et al.³⁸); (\blacksquare) $< 140 \text{ g m}^{-2}$ (Jeler and Ceric³⁴).

distinction may be made concerning their relative validity. Therefore, from these oxygen index measurements, whether the temperature dependence is determined by a steady-state heat balance,⁴² convective heat loss,³⁹ or thermodynamic equilibrium considerations cannot be decided.

Unfortunately, a similar indecision follows with regard to the cause of the temperature dependence of E_0 as is seen by superimposing E_0 vs. $1/T$ plots on the van 't Hoff type relationships in Figure 1. It is interesting to note, however, that if a power law relationship is considered of the type

$$E_0 = kT^\alpha$$

then analysis of $\ln E_0$ vs. $\ln T$ for $M = 0$ and $A/S_c = 1$ conditions gives $\alpha = -0.84$ and -0.62 , respectively. The former value is close to the $\alpha = -1$ condition predicted by Kanury. Similar analysis of Johnson's results, derived from original LOI values of DiPietro and Stepniczka,⁴¹ for neoprene, polystyrene, ABS, and polyester-styrene at temperatures of 100, 200, and 300°C

shows, however, that such a linear power law relationship does not hold. Furthermore, our E_0 values do not vary linearly with $T^{3/2}$. Consequently, it would seem that for cotton, diffusional processes are not as important as perhaps suggested by Johnson.

It is hoped that further work may clarify the cause of the observed reduction of extinction oxygen index with increasing temperature.

One of us (M. T.) wishes to thank Albright and Wilson Ltd. for financial support.

References

1. B. Miller, J. R. Martin, and C. H. Meiser, *J. Appl. Polym. Sci.*, **17**, 629 (1973).
2. B. Miller, J. R. Martin, and R. Turner, *Text. Res. J.*, **50**, 256 (1980).
3. D. L. Simms, *Text. Inst. Ind.*, **4**, 43 (1966).
4. B. Miller and C. H. Meiser, *Text. Chem. Colorist*, **3**, 118 (1971).
5. B. Miller, J. R. Martin, and C. H. Meiser, *Thermochim. Acta*, **20**, 253 (1977).
6. U. Einsele, W. Koch and H. Herlinger, *Melliland. Textilber.*, (Engl. Ed.), **13**(3), 190 (1984).
7. G. C. Tesoro and C. H. Meiser, *Text. Res. J.*, **40**, 430 (1970).
8. B. Miller and C. H. Meiser, *Text. Chem. Colorist*, **2**, 205, (1970).
9. C. D. Ward and S. M. Jaekel, *J. Text. Inst.*, **67**(9), 309 (1976).
10. J. F. Hendrix, G. L. Drake, and W. A. Reeves, *Text. Chem. Colorist*, **5**, 144 (1973).
11. J. F. Krasny and E. Braun, *Fire Mater.*, **6**(1), 38 (1982).
12. B. Miller, J. R. Martin, B. C. Goswami and C. H. Meiser, *Text. Res. J.*, **45**, 328 (1975).
13. J. DiPietro, H. Stepniczka, and R. C. Nametz, *Text. Res. J.*, **41**, 593 (1971).
14. D. G. Saurers, *J. Fire Flammability*, **7**, 181 (1976).
15. B. Miller, B. C. Goswami, and R. Turner, *Text. Res. J.*, **43**, 61 (1973).
16. J. F. Krasny and J. B. Francis, *Text. Chem. Colorist*, **6**, 135 (1974).
17. G. R. Bhat, I. Block, K. Yeh, and S. M. Spivak, *J. Consumer Product Flammability*, **3**, 155 (1976).
18. L. B. Miles, G. R. Bhat, R. L. Sun, K. Yeh, and S. M. Spivak, *J. Consumer Product Flammability*, **3**, 166 (1976).
19. L. B. Miles, G. R. Bhat, R. L. Sun, K. Yeh, and S. M. Spivak, *J. Consumer Product Flammability*, **5**, 135 (1978).
20. B. Miller, J. R. Martin, and C. H. Meiser, *Text. Res. J.*, **50**, 305 (1980).
21. E. A. Zawistowski, J. F. Krasny, E. Braun, R. Peacock, and N. Williams, National Bureau of Standards, NBSIR 77-1236, June 1977.
22. S. Backer, G. C. Tesoro, T. Y. Toong, and N. A. Moussa, *Textile Fabric Flammability*, MIT Press, Cambridge, Ma, 1976.
23. P. A. Potthoff, R. L. Sun, F. W. Derrick, and S. M. Spivak, *J. Consumer Product Flammability*, **6**, 261 (1979).
24. R. L. Sun and S. M. Spivak, *J. Consumer Product Flammability*, **8**, 35 (1981).
25. P. A. Fairhall and S. M. Spivak, *J. Fire Sci.*, **2**, 189 (1984).
26. W. A. Reeves, M. A. Hammons, and K. L. Koonce, *Am. Dyestuff Rep.*, **71**(1), 12 (1982).
27. A. R. Horrocks and M. Ugras, *Fire Mater.*, **7**(3), 111 (1983).
28. D. E. Stuetz, A. H. DiEdwardo, F. Zitomer, and B. P. Barnes, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 967 (1980).
29. A. R. Horrocks and M. Tunc., *J. Text. Inst.*, **77**, 119 (1986).
30. Standard Method of Test for Flammability of Plastics using the Oxygen Index Method, Test Method D2863-70, ASTM, Philadelphia (1970); revised 1974, 1976, and 1977.
31. J. P. Redfern, Stanton Redcroft (London) Technical Information Sheet No. 24, Stanton Redcroft Ltd., Copper Lane, London.
32. R. K. Wharton, *J. Fire Flammability*, **12**, 266 (1981).
33. Methods of Testing Plastics, BS2782: 1978, British Standards Institution, London.
34. S. Jeler and B. Ceric, *Textilveredlung*, **15**, 251 (1980).
35. J. E. Hendrix, G. L. Drake, and W. A. Reeves, *J. Fire Flammability*, **3**, 38 (1972).
36. B. Miller and C. H. Meiser, *Text. Chem. Colorist*, **2**, 205 (1970).

37. J. DiPietro, H. Barda, and H. Stepniczka, *Text. Chem. Colorist*, **3**, 40 (1971).
38. J. E. Hendrix, J. V. Beninate, G. L. Drake, and W. A. Reeves, *J. Fire Flammability*, **3**, 2 (1972).
39. A. M. Kanury, in *Proc. International Symposium on Fire Safety of Combustible Materials*, University of Edinburgh, October, 1975, 187.
40. P. R. Johnson, *J. Appl. Polym. Sci.*, **18**, 491 (1974).
41. J. DiPietro and H. Stepniczka, *J. Fire Flammability*, **2**, 36 (1971).
42. A. Tewarson and R. F. Pion, *Combustion Flame*, **26**, 85 (1976).

Received January 3, 1987

Accepted February 10, 1987