

The Inhibition of Spontaneous Ignition by Flame-Retarding Cotton Fabrics

M. A. KHATTAB, *Department of Materials Science, Institute of Graduate Studies and Research, University of Alexandria, P.O. Box 832, Alexandria, Egypt*, D. PRICE, * *Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT, United Kingdom* and A. R. HORROCKS, *Department of Textile Studies, Bolton Institute of Higher Education, Bolton, BL3 5AB, United Kingdom*

Synopsis

The spontaneous ignition behavior of flame-retarded cotton cellulose has been investigated using differential thermal analysis (DTA). One durable, phosphonium salt-urea-ammonia polycondensate (Proban CC), and one nondurable, ammonium polyphosphate (Amgard TR) commercially flame-retardant-treated fabrics have been studied. The information obtained is compared to that previously reported for untreated cotton cellulose. The onset of spontaneous ignition, temperature T_i , was determined as a function of $[O_2]$ in the flowing O_2/N_2 atmosphere to which samples were exposed in the DTA furnace, whose temperature was raised at a known linear heating rate. The activation energy E_p for the rate-determining pyrolysis reaction was calculated. In the case of the Amgard TR fabric, E_p increased from 145 kJ mol^{-1} at 21% O_2 to 261 kJ mol^{-1} at 50% O_2 , whereas that for the Proban fabric increased from 230 to 400 kJ mol^{-1} .

A plot of $1/T_i$ vs. $\ln [O_2]$ shows two linear regions that intersect at about 40% O_2 , which is just above the limiting oxygen index values for these two flame-retarded samples. This intersection is interpreted as indicating that the combustion mechanism of these flame-retarded fabrics changes as $[O_2]$ passes through this 40% level. Below this value, significant amounts of char remained after the DTA experiment, suggesting that volatiles only were ignited, whereas above this value, both volatiles and char were burnt away. This is supported by evidence from the DTA traces. The difference in slopes of the two regions of the $1/T_i$ vs. $[O_2]$ plots is used to obtain a value for E_{ox} , the activation energy for gaseous oxidation. Values for E_{ox} of 270 and 536 kJ mol^{-1} were obtained for the Amgard TR and Proban CC fabrics, respectively. These are considerably higher than is the value of 215 kJ mol^{-1} previously reported for untreated cotton. Thus, one of the ways in which these flame retardants reduce the ease of combustion of the cotton is by increasing the activation energy for the oxidation of the evolved organic species.

INTRODUCTION

Spontaneous ignition is defined as the generation of flaming combustion resulting from placing a material in contact with a heated substance in the absence of any piloted flame. Spontaneous ignition of cellulose is similar to other ignition phenomena in that it occurs when a suitable combination of fuel, oxygen, and heat is available. Since the fuel concentration is not easily determined, a number of other parameters related to the ignition character of cellulosic materials have been studied.¹⁻³ Two of the important parameters are the "time to ignition" and the "ignition temperatures in a given environment."

* To whom correspondence should be addressed.

Most often, ignition temperatures have been determined using heating methods that include direct radiant heat,^{4,5} heated air,^{6,7} and piloted flames.⁸

One of the difficulties encountered in these studies is to define heating rate accurately, and another is the determination of the effect of oxygen concentration on the initial pyrolysis mechanism and its kinetics. Herein we report the use of differential thermal analysis (DTA) for kinetic investigation of the ignition behavior of flame-retarded cotton fabrics. Our previous work showed that DTA could be used to determine, with good accuracy, the temperature T_i at which onset of spontaneous ignition occurs.^{9,10} Values for the apparent activation energy of pyrolysis, E_p , and the activation energy of oxidation, E_{ox} , at different oxygen concentrations have also been determined and compared with the previously obtained results for untreated cotton fabric.¹¹

EXPERIMENTAL

Experiments were conducted on samples of a heavyweight cotton fabric treated with the durable flame-retardant Proban CC, which is a tetrakis (hydroxy methyl) phosphonium chloride (TMPC) condensate with urea (Albright & Wilson) or the nondurable flame-retardant ammonium polyphosphate (Amgard TR, Albright & Wilson). The 193 g/m² cotton fabric was commercially prepared and bleached; flame retardants were applied by standard pad-dry-ammonia-cure (Proban CC) or pad-dry (Amgard TR) methods. Details of the area density and the phosphorus and nitrogen contents of the various fabrics are given in Table I. The spontaneous igniting behavior of untreated and flame-retarded fabrics was recorded using DTA over a range of flowing oxygen concentrations according to our previously reported procedure.¹¹

Differential thermal analysis curves were recorded using a Stanton Redcroft 671B thermal analyzer over an ambient to 500°C temperature range. The methods of determining the ignition temperature, T_i , residual char, and subsequent derivation of kinetic parameters have been described previously.¹¹

RESULTS AND DISCUSSION

Tables II and III show the spontaneous ignition temperature, T_i , values obtained from 10 mg samples of cotton fabric treated with Amgard TR and Proban, respectively, in flowing atmospheres of varying oxygen concentration

TABLE I
Area Density, Phosphorus and Nitrogen Contents, and Limiting Oxygen Index (LOI) Values of the Unretarded and Flame-retarded Cotton Fabrics

	Cotton	Proban CC	Amgard TR
Area density (g/m ²)	193.0	192.0 ^a	213.5
Phosphorus (%)	—	2.91	2.19
Nitrogen (%)	—	2.83	2.92
LOI (single layer, 20°C)	0.185	0.320	0.369

^a Note the apparent weight reduction is a consequence of cellulose loss during processing.

TABLE II
Influence of Oxygen Volume Concentration on Ignition
Temperature T_i ($^{\circ}\text{C}$) for Amgard TR-Treated Cotton

H_R ($^{\circ}\text{C}/\text{min}$) \backslash O_2 (%)	10	21	30	40	50	60
5	271	263	261	266	261	256
10	278	273	276	271	266	261
15	283	281	278	276	271	266
20	290	285	271	278	273	271

(10–60 vol %). Each sample was subjected to various heating rates, H_R , within the range $5\text{--}20^{\circ}\text{C min}^{-1}$ and oxygen volume concentration at a constant flow rate of $150\text{ cm}^3\text{ min}^{-1}$. These may be compared with those reported by Horrocks et al.¹¹ for untreated cotton determined under similar conditions. It can be seen that, in general, at each heating rate, T_i decreases as the oxygen concentration increases, as previously noted.^{9–11} Plots of the reciprocal of T_i (in Kelvin) vs. $\ln[\text{O}_2]$ in Figure 1 show two different linear regions, as previously reported for untreated cotton fabrics.¹¹ These intersect at about 40% oxygen volume concentration $[\text{O}_2]_{T_i}$ for both treated fabrics compared with at 20% oxygen concentrations previously observed in the case of untreated fabrics.¹¹ Table IV shows the influence of oxygen volume concentration on the percentage residual char after ignition obtained from the untreated and flame-retarded fabrics. Of particular interest and as reported previously for untreated cotton¹¹ is the sudden decrease in the char residue that occurs at an oxygen concentration similar to that at the intersection of the two linear regions of the $10^3\text{ K}/T_i$ vs. $\ln[\text{O}_2]$ plots shown in Figure 1.

These $[\text{O}_2]_{T_i}$ values are close to the oxygen concentrations corresponding to published limiting oxygen index (LOI) values for these fabrics¹² and measured here (see Table I). It is known that the LOI values of materials are defined as the oxygen concentration required to sustain flaming combustion, i.e., below that condition no flaming ignition and sustained burning will occur. Thus, it can be concluded that at this specific oxygen concentration both the volatiles and char products are oxidized. Thus, at and above $[\text{O}_2]_{T_i}$, complete ignition

TABLE III
Influence of Oxygen Volume Concentration on Ignition Temperature
 T_i ($^{\circ}\text{C}$) for Proban-Treated Cotton

H_R ($^{\circ}\text{C}/\text{min}$) \backslash O_2 (%)	10	21	30	40	50	60
5	290	295	290	293	290	—
10	305	300	297	297	295	293
15	302	307	302	300	297	295
20	307	310	305	302	300	295

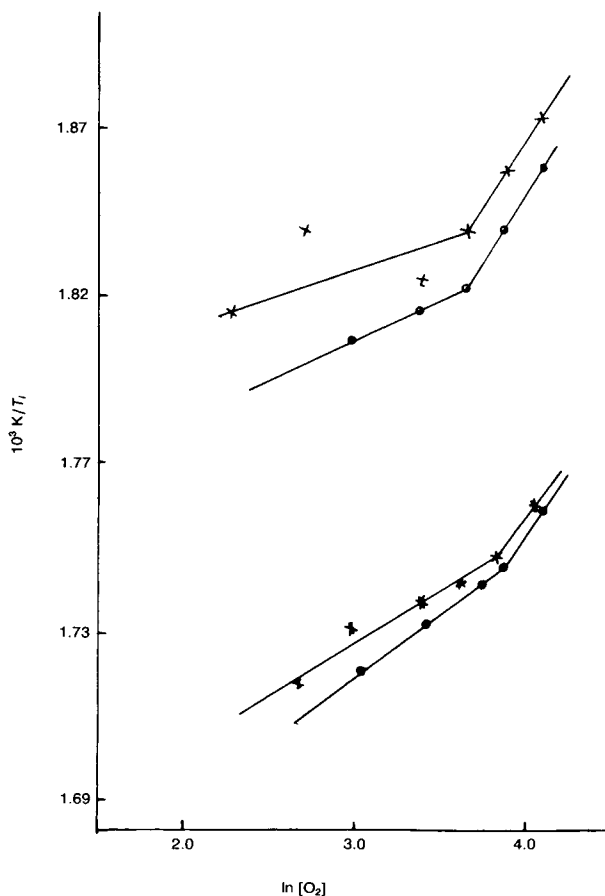


Fig. 1. Plots of $(10^3 \text{ K})/T_i$ vs. $\ln[\text{O}_2]$ at various heating rates for Amgard TR-treated [(x) $15^\circ\text{C min}^{-1}$; (o) $20^\circ\text{C min}^{-1}$] and Proban-treated [(*) $15^\circ\text{C min}^{-1}$; (●) $20^\circ\text{C min}^{-1}$] cotton fabrics; T_i is in K.

of the fabric occurs, whereas, below, the dominant mechanism is the oxidation of the volatiles only and residual char formation.

Figure 2 shows the DTA curves obtained for untreated cotton at two different flowing oxygen concentrations of 10% and 21%. When the oxygen concentration was 10%, an endotherm was observed at 300°C that may be attributed to the evolution of pyrolysis products. The first exotherm, with a maximum at 350°C , is associated with the oxidation of volatile products and the oxidation of the less stable components of the char.¹³ The second exotherm that occurs at higher temperature, with a maximum at 450°C , is attributed to the carbon burn-off following the oxidation of the more stable char.¹⁴ When the oxygen concentration is increased to 21%, the low-temperature endotherm is overshadowed by the exotherm that is of greater intensity and at lower temperature than at 10% oxygen and no high temperature exotherm corresponding to the char oxidation was observed. It is believed that, at this higher oxygen concentration, the hydroperoxide, formed during the initial interaction between oxygen and cellulose, could contribute to the bond scission, thus producing more flammable volatiles.¹⁵

TABLE IV
Influence of Oxygen Volume Concentration on the Percentage Residual Char from Proban-Treated, Amgard TR-Treated, and Untreated (Ref. 11) Cotton

O ₂ (%)	Char residue (%)		
	Proban CC	Amgard TR	Untreated ¹¹
5	42.2	28.1	18.2
10	42.0	27.5	15.0
15	35.4	28.0	19.9
21	36.0	28.0	4.5
30	30.1	22.1	2.2
40	17.9	18.0	2.8
45	—	—	1.1
50	17.3	18.3	< 1
60	17.3	17.9	< 1

The ratio between the oxidant and the flammable gases now becomes sufficient for flaming combustion to occur, and, hence, oxidation of the accompanying small amount of char formed takes place during the main exotherm. Thus, the disappearance of the high-temperature exotherm and the increased intensity of the main exotherm observed under 21% oxygen may be explained. The absence of a high-temperature exotherm confirms that above $[O_2]_T$, complete combustion occurs.

The presence of the phosphorus- and nitrogen-containing flame retardants, Proban CC and Amgard TR, has a significant effect on the pyrolysis of cotton, as can be seen from the DTA thermograms obtained for Amgard and Proban-

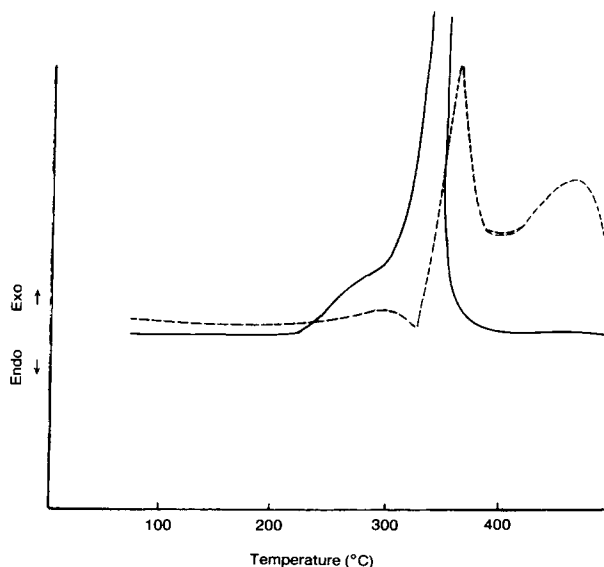


Fig. 2. DTA profiles for untreated cotton fabric; recorded with heating rate of $15^{\circ}\text{C min}^{-1}$ and either 10% (----) or 21% (—) oxygen vol% concentration.

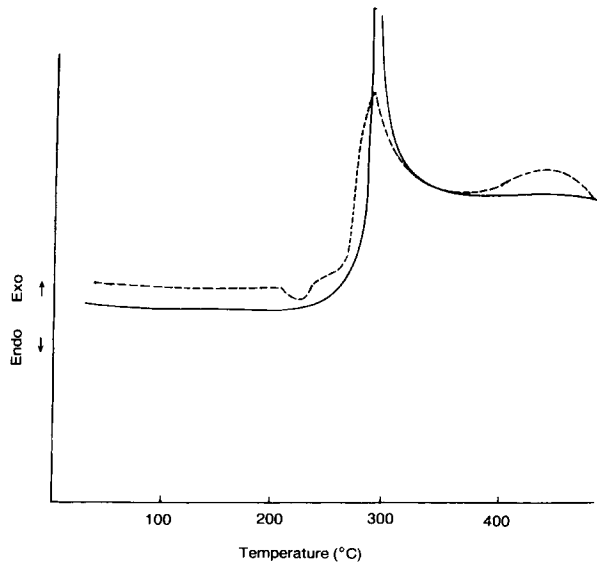


Fig. 3. DTA profiles, obtained at 21% oxygen vol% concentration and $15^{\circ}\text{C min}^{-1}$ heating rate, for Amgard TR- (---) and Proban CC- (—) treated cotton fabrics.

treated cotton shown in Figures 3 and 4, respectively, for the 21% and 50% oxygen conditions. The DTA curve for cotton treated with Amgard TR shows the appearance of a new low-temperature endotherm at about 200°C arising from the dehydration of the cotton. This endotherm was not observed in the case of either untreated or Proban-treated cotton. This indicates the greater dehydrating ability of the Amgard TR flame retardant compared with that of

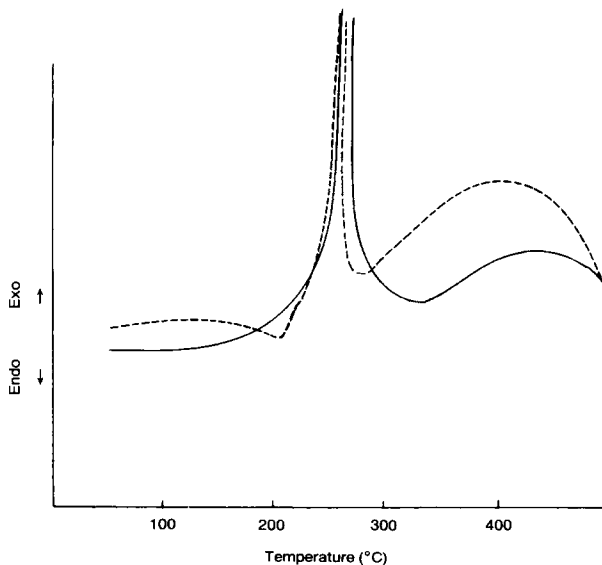


Fig. 4. DTA profiles, obtained at 50% oxygen concentration and $15^{\circ}\text{C min}^{-1}$ heating rate, for Amgard TR- (---) and Proban CC- (—) treated cotton fabrics.

Proban CC, as noted previously.¹² With both retardants, the large oxidation exotherm is still observed, although it occurs at much lower temperatures (280 and 290°C, respectively, for Amgard and Proban CC at 21% O₂), and each is more reduced in magnitude than is that of the untreated cotton sample. These temperatures reflect those for the evolution of flammable gases such as CO¹² as a consequence of the condensed-phase flame-retardant activities.

Of particular interest is the amount of char residue obtained from the two treated fabrics; Table IV indicates that, at oxygen concentrations below 40%, much larger amounts of char are formed in the case of Proban CC-treated samples than for Amgard TR-treated samples. Amgard TR's dehydrating activity probably arises as a consequence of the release of polyphosphoric acid, which promotes carbonaceous char formation. Proban CC is known to act as a dehydrating agent in a similar manner, but at the same time has a consolidation effect on the char formulation via possible P—N bond formation.¹⁶ As a consequence, char from the Proban CC-finished fabric is produced in a greater amount and is more stable than is char formed from Amgard TR-treated fabrics. The char oxidative exotherm, shown in Figure 4 at 400°C under 50% oxygen, suggests that Proban CC char is less exothermic and possibly less easy to oxidize, thus reflecting this enhanced char stability.

Our previously discussed steady-state kinetic model, developed for untreated cotton cellulose,¹¹ shows that

$$\ln\left(\frac{H_R}{T_i^2}\right) = -\frac{E_p}{R}\left(-\frac{1}{T_i}\right) + \ln A_p - \ln\left(\frac{E_p - E_{ox}}{R}\right) \quad (1)$$

where H_R is the heating rate, E_p and E_{ox} are the respective activation energies of pyrolysis and product oxidation, and A_p is the apparent Arrhenius A -factor for pyrolysis. Application of this to the T_i results in Tables II and III for the phosphorus-nitrogen-containing cotton fabrics enables a value of the apparent activation energy, E_p , for pyrolysis to be found. Figures 5 and 6 show the "best-fit" plots of $-\ln(H_R/T_i^2)$ vs. $(10^3 \text{ K})/T_i$ at different oxygen concentrations over the range 10%–60% for Amgard TR- and Proban CC-treated fabrics, respectively. Table V lists the apparent values, E_p (kJ/mol) at each oxygen concentration derived from the respective slopes of the linear plots in Figures 5 and 6. Figure 7 shows the plots of E_p values vs. the oxygen concentration derived for untreated¹¹ and Amgard TR- and Proban CC-treated fabrics. Both the treated fabrics show a stepped increase in the apparent values of E_p in the 30%–40% oxygen concentration range. This contrasts with the superimposed untreated fabric values¹¹ for which E_p increases gradually with increasing oxygen concentration and no stepped behavior is observed. Above about 40% oxygen, E_p of the two treated fabrics becomes effectively constant. This, together with the observation of the two linear regions below and above 40% oxygen in Figure 1, suggests a change in the rate-determining mechanism as the oxygen concentration is increased, i.e., the discontinuities in the plots indicates that two different mechanisms occur above and below about $[O_2]_{T_i}$, as previously suggested for untreated cotton.¹¹

With regard to the influence of oxygen concentrations on T_i , eq. (3) in Refs. 10 and 11 shows that plotting $-(1/T_i)$ vs. $\ln[O_2]$ should be linear with a slope

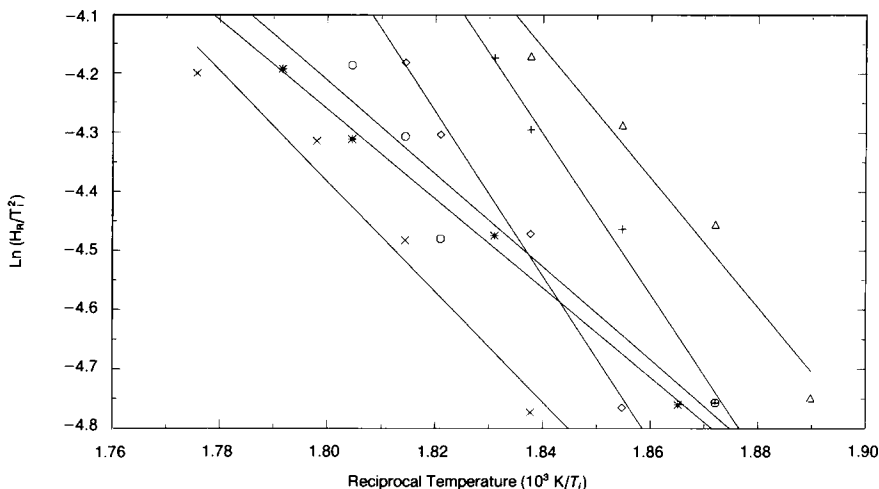


Fig. 5. Plots of $\ln H_R/T_i^2$ vs. $(10^3 \text{ K})/T_i$ obtained for Amgard TR-treated cotton fabric in various vol% concentrations of oxygen, viz. (x) 10%; (*) 21%; (O) 30%; (◇) 40%; (+) 50%; (△) 60%; T_i in K.

equal to $-[mR/(E_{ox} - E_p)]$. Taking the minimum and the maximum E_p values and estimating the slope of the two regions, values of the molar oxygen concentration “ m ” required for the oxidation of the volatiles and the activation energy for the oxidation E_{ox} can be calculated assuming that m and E_{ox} are independent of oxygen concentration. Table VI shows the E_{ox} (kJ/mol) and m values for the untreated¹¹ and the two treated fabrics. The value of m can be taken as a measure of the extent of the release of volatile oxidizable species during the pyrolysis of the appropriate fabrics. It is clear from the values given in Table VI that untreated cotton yielded more volatile oxidizable species than

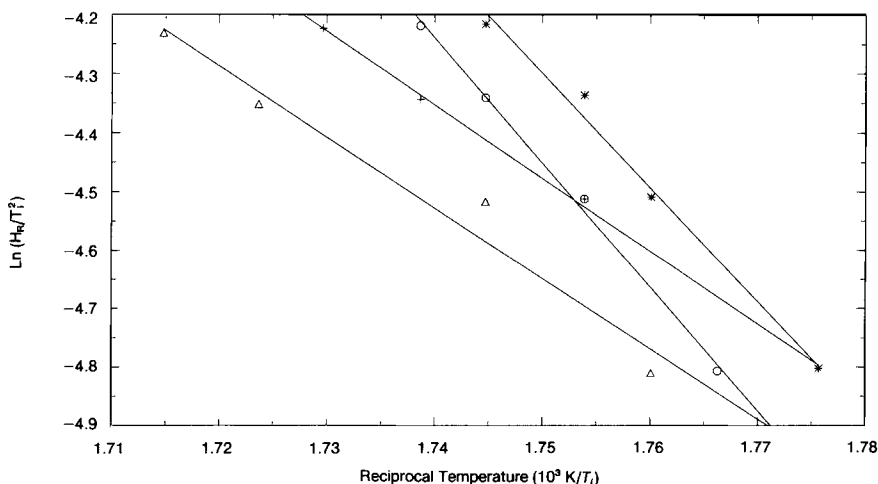


Fig. 6. Plots of $\ln H_R/T_i^2$ vs. $(10^3 \text{ K})/T_i$ obtained for Proban CC-treated cotton fabric in various vol% concentrations of oxygen, viz.: (△) 21%; (◇) 30%; (O) 40%; (*) 50%; T_i in K.

TABLE V
Apparent Activation Energies of Pyrolysis, E_p (in kJ mol^{-1}) at Different Oxygen Concentrations

O_2 (%)	E_p (Amgard TR)	Correlation coefficient	E_p (Proban CC)	Correlation coefficient	E_p (Ref. 11; untreated)
10	178	.981	—	—	127
15	—	—	—	—	130
21	145	.998	230	.982	154
30	150	.958	239	1.000	167
40	266	.994	404	1.000	—
45	—	—	—	—	173
50	261	.994	400	.994	—
60	—	—	—	—	168

did either of the flame-retarded fabrics. This confirms earlier work on Amgard TR-treated cotton¹² that showed that this ammonium polyphosphate treatment affects the decomposition of the cotton so that water constitutes the major decomposition product.

There is a moderate difference between the E_{ox} values for untreated and the Amgard-treated fabric. This suggests some similarity in the mechanism of and nature of the volatile product evolved during the pyrolysis and combustion of these two fabrics. The much higher E_{ox} value obtained for the Proban CC-finished fabric, however, possibly indicates a change in the character of the oxidizable volatiles produced from these samples. Thus, Proban CC treatment

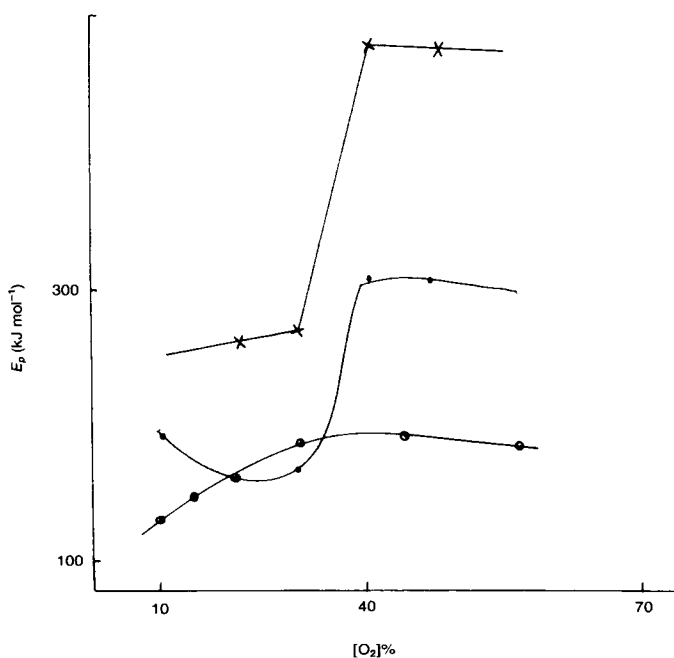


Fig. 7. Plot of E_p vs. oxygen vol% concentration for (○) untreated, (●) Amgard TR- and (X) Proban CC-treated cotton fabrics (the untreated data from Ref. 11).

TABLE VI
 Activation Energy of Oxidation E_{ox} (kJ mol^{-1}) and Oxygen
 Molar Concentration (m) for Fabrics Used

Fabric	E_{ox}	m
Amgard TR	270	0.0004
Proban	536	0.011
Untreated (Ref. 11)	215	0.28

perhaps results in a much greater modification of the volatiles evolved during combustion than does the Amgard TR finish. Again, this conclusion has been supported by earlier work using evolved gas analytical techniques under air conditions.¹² Since above $[\text{O}_2]_T$, complete char oxidation also occurs, the greater value of E_{ox} for Proban CC- than for Amgard TR-treated fabrics probably reflects, in addition, the enhanced char stability of the former as discussed above.

One of us (M.K.) wishes to thank the British Council for the award of a visiting fellowship and the University of Salford and the Bolton Institute of Higher Education for facilities to enable this work to be carried out.

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Received March 20, 1990

Accepted April 23, 1990