

## Flammability Characteristics of Cotton and Polyester Fibers

H. STEPNICZKA and J. DIPIETRO, *Michigan Chemical Corporation, Research and Development Laboratories, St. Louis, Michigan 48880*

### Synopsis

This study was undertaken to measure quantitatively the flammability characteristics of cotton and polyester fibers. The smoke density generated during the burning of these fabrics was also studied at various temperature conditions. A mathematical relationship was established between the results obtained in an oxygen-depleted atmosphere chamber and those obtained in a chamber in which there was constant replenishing of an oxygen and nitrogen atmosphere. Three commercially available flame-retardant treatments were utilized in this study. The effect of temperature as well as the influence of fabric weight on the flammability behavior and the smoke density of these fabrics were investigated. A novel instrument built according to ASTM standards was employed throughout this study; it was found to be versatile, convenient, and highly reproducible in the generation of the data. It was found that polyester fabrics generate far more smoke than cotton fabrics without the phenomenon of afterglow. It was found also that as the temperature increases, the smoke density of cotton fabrics increases as well, but in the case of polyester fabrics the opposite relationship was obtained.

### INTRODUCTION

Existing and pending federal as well as state legislation is presently concerned with the flammability of fabrics. There has been considerable activity both at the industrial and academic levels to develop effective techniques of imparting flame retardancy to fabrics. It was only recently, however, that the smoke generated by burning textiles has begun to receive some attention.<sup>1,2</sup> The issuance of Federal Air Regulation (25.853), which sets specific guidelines limiting the amount of smoke and toxic gases generated by burning fabrics, has prompted aircraft manufacturers to take these new criteria into consideration.<sup>3</sup>

The study reported here involves an investigation of several parameters which influence the flammability and smoke generation of some commercial fabrics.

### EXPERIMENTAL

#### Materials

The fabrics used in our study were: (a) 100% cotton sheeting (Type 128), 135 g/m<sup>2</sup> (4.3 oz/yd<sup>2</sup>); (b) 50:50 cotton-polyester blend, 120

g/m<sup>2</sup> (3.8 oz/yd<sup>2</sup>); (c) 35:65 cotton-polyester blend, 56 g/m<sup>2</sup> (1.8 oz/yd<sup>2</sup>); and (d) 100% polyester fabric, 80 g/m<sup>2</sup> (2.6 oz/yd<sup>2</sup>).

For the determination of the relationship between fabric weight and the amount of smoke generated by the burning fabrics, the following textiles were used: 100% polyester fabric, 44 g/m<sup>2</sup> (1.4 oz/yd<sup>2</sup>); and five 100% polyester doubleknits of varying structure, with the fabric weights of 312, 356, 380, 417, and 467 g/m<sup>2</sup>, respectively.

### Flame-Retardant Treatments

In addition to the untreated fabrics, three finishes were used in our study (see Tables I and II): (a) THPC/TMM/urea (tetrakis(hydroxymethyl)phosphoniumchloride/trimethylolmelamine/urea); (b) tris(2,3-dibromopropyl) phosphate (T23P); (c) dual treatment in sequence with THPC/TMM/urea plus T23P.

THPC polymerizes with the methylolmelamine to form an insoluble resin within the cotton fibers.<sup>4</sup> During the polymerization, hydrochloric acid is split out of the THPC molecule. Urea is employed in the formulation primarily to tie up this free acid that is formed during the curing operation to protect the cotton from acid tendering. Although the minimum amount of urea needed to prevent acid tendering is associated with the amount of THPC in the formulation, it is difficult to calculate the quantity needed because it reacts with THPC to become part of the polymer and decomposes during the high-temperature cure. Thus, the amount of urea necessary was established experimentally. More details on the chemistry of resin formulation of THPC with amines and amides have been given recently by Reeves and his co-workers at the Southern Regional Research Laboratory in New Orleans.<sup>5</sup>

When the THPC/TMM/urea finish was employed, either in single or double treatment, the finish was cured on the fabric at 300°F, then rinsed with deionized water, and dried. When applying the THPC/TMM/urea finish to 100% polyester, no aftercure rinse with deionized water was used because the finish would wash off. A double treatment of 100% polyester fabric did not prove feasible since after treatment and curing of a THPC/TMM/urea finish, the finish washed off when followed by an application of T23P either from an aqueous emulsion or in benzene. When a dual treatment was possible, the THPC/TMM/urea was applied first. The elemental analyses of the hetero atoms present in the flame-retardant compounds, Br, N, and P, on fabrics treated with 11.5% T23P, 13% THPC/TMM/urea, and the dual treatment, respectively, are reported as follows:

<i>Fabrics treated with 11.5% T23P:</i>	Br, 7.13%; P, 0.45%;
<i>Fabrics treated with 13% THPC/TMM/urea:</i>	N, 3.08%; P, 1.39%;
<i>Double-treated fabrics:</i>	Br, 6.39%; N, 2.89%; P, 1.66%.

The values given above are actual averages for all fabrics used in this study. There were no significant deviations from this average in any

TABLE I  
Flame-Retardant Treatments

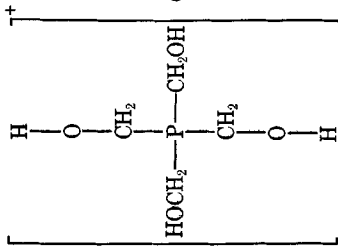
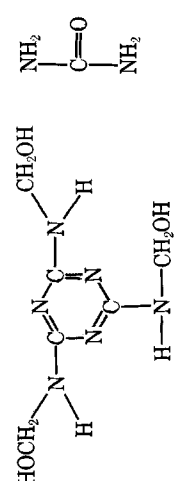
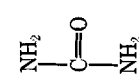
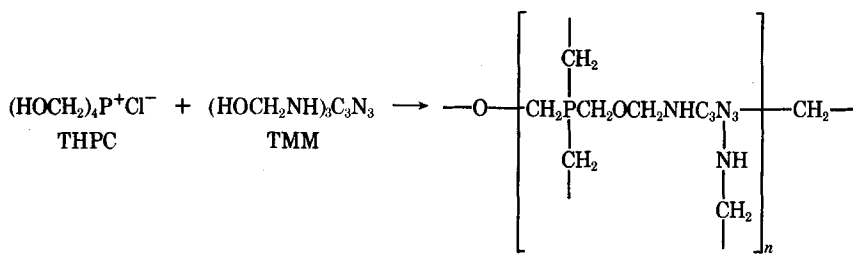
	Chemical structure
A. THPC/TMM/Urea tetraakis(hydroxymethyl)phosphonium chloride/ trimethylolmelamine/urea	$\left[ \begin{array}{c} \text{H} \\   \\ \text{O} - \text{CH}_2 \\   \\ \text{P} - \text{CH}_2\text{OH} \\   \\ \text{HOCH}_2 - \text{P} - \text{CH}_2 \\   \\ \text{CH}_2 - \text{O} - \text{H} \end{array} \right]^+ \text{Cl}^-$   
B. T23P tris(2,3-dibromopropyl) phosphate	$[\text{BrCH}_2 - \text{CHBr} - \text{CH}_2 - \text{O}]_3 \text{P} = \text{O}$
C. Double Treatment: THPC/TMM/urea plus T23P	

TABLE II  
Composition of the THPC/TMM/Urea Treatment

Compounds	Per cent by weight
Water	64.1
THPC (80% solids)	18.5
Trimethylmelamine (TMM)	8.5
Urea	8.8
Surfactant	0.1

Condensation of THPC with TMM



particular case. The lower P content of the fabrics treated only with T23P (0.45% versus 0.465% in theory) indicates the presence of some inherent volatile compounds present in the flame retardant.

### Oxygen Index Measurements

The oxygen indices of the various fabric specimens were determined using an instrument built according to specifications given in ASTM Method D-2863-70.<sup>6</sup> Figure 1 shows a photograph of the instrument which also includes the smoke densitometer assembly.

The gas-mixing chamber was modified to include heating elements. The temperature of these heating elements can be controlled by a variable transformer. The samples and the flowing gases were preheated to the desired temperatures by means of the heating element.

The textile specimens were 14.5 cm × 3.8 cm (5.75 in. × 1.5 in.) and were fastened in a vertical position by means of a U-shaped holder. The 100% polyester specimens had three cotton threads sewn lengthwise to prevent dripping during combustion. If the oxygen index was to be run at ambient temperature (25°C), the chamber was purged with the oxygen-nitrogen mixture for one minute at a rate of 300 cm<sup>3</sup>/sec. If determinations were to be made at elevated temperatures, the flow was continued for 30 min prior to ignition at this rate. Specimen temperature was measured by means of a Chromel-Alumel thermocouple placed in a position midway down the vertical length of the specimens. Ignition of all specimens was made with a propane-air torch with a sharp flame length of 1 in.

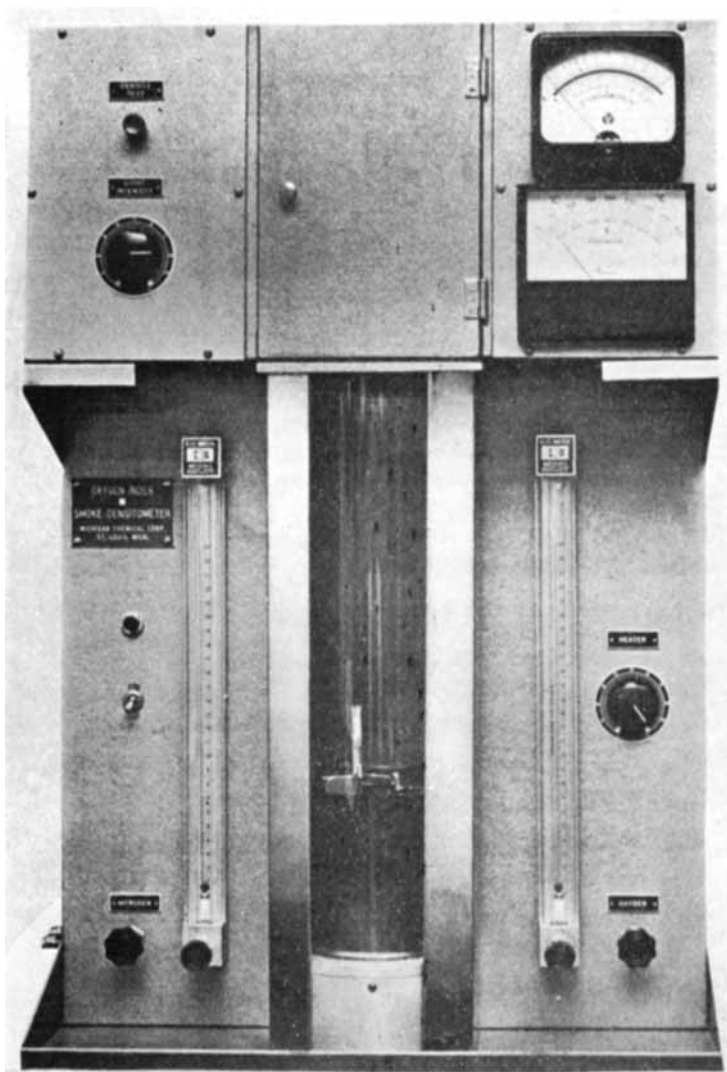


Fig. 1. Michigan Chemical Oxygen Index-Smoke Densitometer.

### Smoke Density Measurements

Two instruments were employed in this study: the Michigan Chemical Oxygen Index-Smoke Densitometer (see Fig. 1) and the Rohm & Haas XP2 Smoke Density Chamber (Fig. 2). Both instruments are described elsewhere.<sup>1,7-12</sup>

Using the attenuation of light by the smoke at any given time, the smoke's optical density was determined using a method developed by Gross, Loftus, and co-workers<sup>13</sup> which is based on Beer's law:

$$D = \log_{10} \cdot \frac{I_0}{I_t} \quad (1)$$

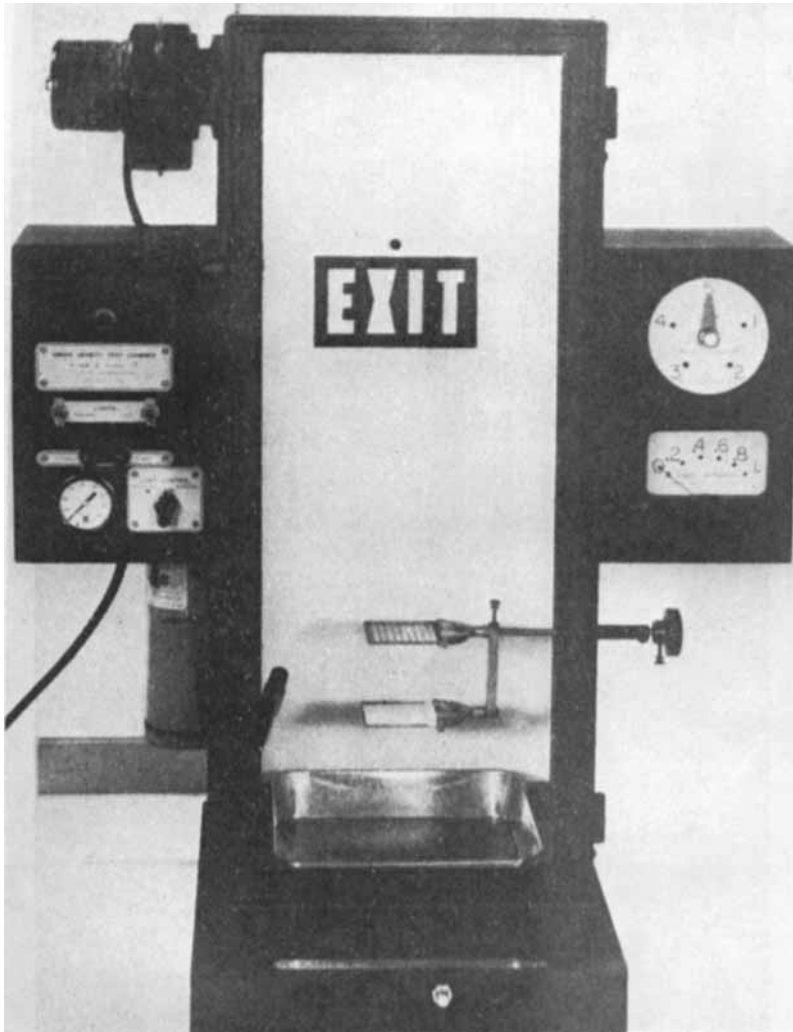


Fig. 2. XP2 Smoke Density Chamber.

where  $D$  is smoke density,  $I_0$  is the initial light intensity, and  $I_t$  is the intensity of light transmitted. Since optical density is directly proportional to the path traveled by the light, the value for any path length,  $D/l$ , can be readily obtained for the optical density per unit path.

When a nonmonochromatic light is used for the measurements and light is not absorbed by a homogeneous medium but by small light-scattering particles, the Beer-Lambert law does not strictly apply. It has been reported, however, that for purposes of measuring smoke densities, these small deviations from Beer's law can be neglected.<sup>14</sup>

For the MC unit, specimen dimensions, holder, purging technique

prior to ignition, and ignition period were the same as those used when making oxygen index determinations.

In the R & H chamber, textile specimens of the dimensions 5 cm × 5 cm (2 in. × 2 in.) were used, and the propane pressure of the burner was adjusted to 40 psi.

Prior to testing, the specimens were kept 40 hr in a desiccator over silica gel. In order to compare the results obtained with the two units, all data were calculated for a standard chamber of 1000 cm<sup>3</sup> (1 liter, 61.4 cu. in.), a light path length of 1 cm, and a specimen dimension of 5 cm × 5 cm (2 in. × 2 in.) under the assumption that all smoke generated was accumulated in the chamber.

The MC unit is constantly being purged by gases, thus no smoke accumulation occurs; therefore, the time differential parameter is measured by this method. In comparing smoke data when using only the MC unit, the gross amount of smoke generated by the burning specimen can be determined either by the Extended Simpson's Rule<sup>15</sup> or graphically.

If we wanted to determine the smoke which is accumulated in the chamber, we then have to integrate the curve over the time of smoke generation. Using the Improved Euler-Cauchy Method,<sup>16</sup> we derived a relationship between smoke and time as shown in Figure 3.

Using the equation shown in Figure 3, we then could determine the amount of smoke which would accumulate in a standard chamber.

Smoke densities were also determined with specimens heated to elevated temperatures, using the MC Oxygen Index-Smoke Densitometer. In order to compare all data obtained at various gas temperatures, the data were extrapolated to 25°C and reported as such.

Figure 4 shows the relationship between light-obscuration and elapsed burning time for the XP2 chamber. The smoke density is derived from the

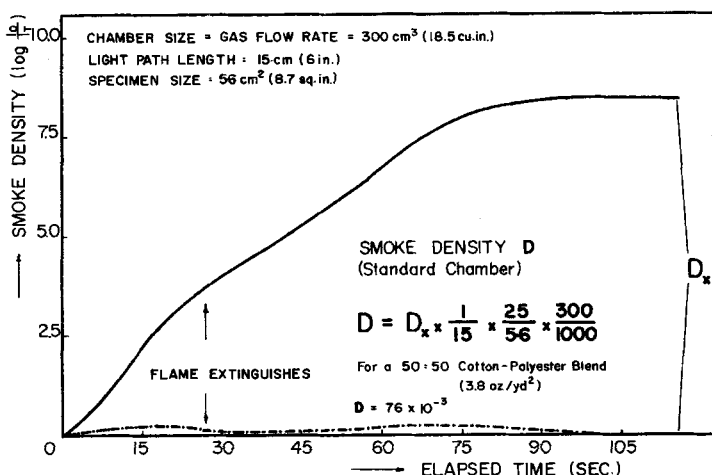


Fig. 3. Determination of the smoke using the MC smoke density chamber.

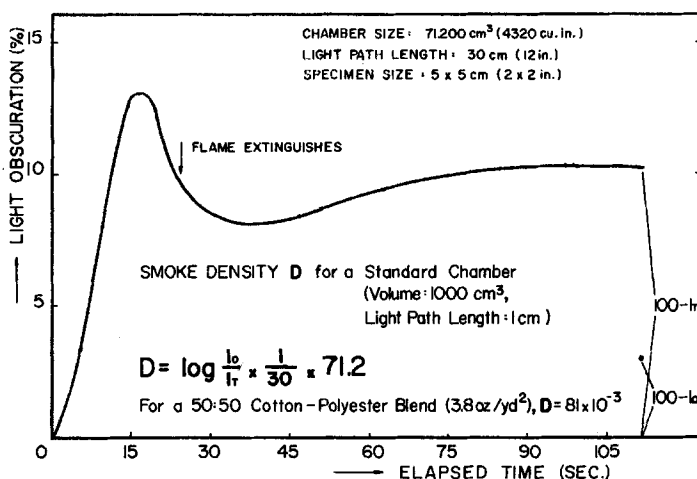


Fig. 4. Determination of the smoke using the XP2 smoke density chamber.

light obscuration data at the end of the combustion. In order to derive the value for  $I_0$ , a correction for smoke deposition on the windows of the smoke chamber during combustion had to be made. The initial peak of the light obscuration is caused by the initial accumulation of smoke (in the hot combustion gases) in the upper part of the chamber; after some time, an equal distribution of smoke will be found in the chamber. The smoke density for the standard chamber,  $D$ , can be calculated using the equation given in Figure 4.

It is known that conditioning affects the smoke generated by burning specimens.<sup>12</sup> This was another reason why the specimens were dried before their combustion.

## RESULTS AND DISCUSSION

### Oxygen Index Determinations

Thermoplastic fibers have not been considered very hazardous because, upon ignition, they usually would melt and carry away the flame from the combustion zone. When they are blended with nonmelting fibers, however, they do burn easily. Kruse termed this the "scaffolding effect," in which the nonmelting fiber under combustion forms a carbonaceous grid work which holds the synthetic melting fiber in place so that it can be consumed more readily.<sup>17,18</sup> He also found that in order to flame retard a fabric of a multiblenched composition, in which no component represents more than 85% of the total, both components have to be flame retarded.

The concept of a dual treatment for a blend of polyester/cotton material has been followed by several investigators. A one-bath application of THPC and T23P was an effective treatment to provide excellent fire retardancy to a 50:50 cotton/polyester sheeting.<sup>19</sup>



The effect of specific flame retardants on the flammability behavior of a 50:50 cotton/polyester blend was studied by applying treatments which were selectively absorbed by the components.<sup>20</sup> Diammonium phosphate was applied from an aqueous solution and was found to be absorbed selectively by cotton, while tris(2,3-dibromopropyl) phosphate was selectively applied to the polyester component from perchloroethylene. Further, the two treatments were applied in sequence. It was found that the oxygen index of the blend given a single treatment was significantly lower than that predicted from relationships previously established between oxygen index and per cent diammonium phosphate in 100% cotton and oxygen index and per cent tris(2,3-dibromopropyl) phosphate in 100% polyester. This negative effect was readily overcome in the blend by the addition of a small amount of DAP to the cotton component, along with the treatment for the polyester component. It was concluded that an effective flame-retardant treatment for polyester/cotton blends must include modification of the flammability of both components.

Figure 5, which was constructed from data given in Table III, shows how the oxygen index, as determined at room temperature, varies with the fabric composition. While Tesoro and co-workers<sup>20</sup> have shown that indices of cotton/polyester blends ranging in cotton content from 15% to 85% were slightly lower than either 100% cotton or 100% polyester, we did not find this behavior in our study. This difference has been attributed to the fact that we have used blends of varying fabric weight and structure rather than needle-punched felts of a constant weight as Tesoro and co-workers did in their study.

TABLE III  
Influence of Specimen Temperature on the Oxygen Indices  
of Various Flame-Retarded and Untreated Fabrics

Flame retardant	Temp., °C	Oxygen index of fabric			
		Cotton	50:50 Blend	35:65 Blend	Polyester
None	25	18.0	19.8	18.3	19.0
	95	16.5	17.5	17.0	18.0
	180	15.0	15.0	15.5	16.5
T23P, 11.5%	25	23.3	24.1	24.3	25.5
	95	21.8	22.7	22.3	24.0
	180	17.1	17.2	18.7	21.0
THPC/TMM/ Urea	25	27.5	23.6	21.9	22.4
	95	22.0	21.1	20.3	20.6
	180	20.5	18.4	17.1	17.7
T23P, 11.5% plus THPC/TMM/ Urea	25	36.1	29.5	28.9	—
	95	33.9	27.5	26.0	—
	180	20.7	18.9	19.6	—

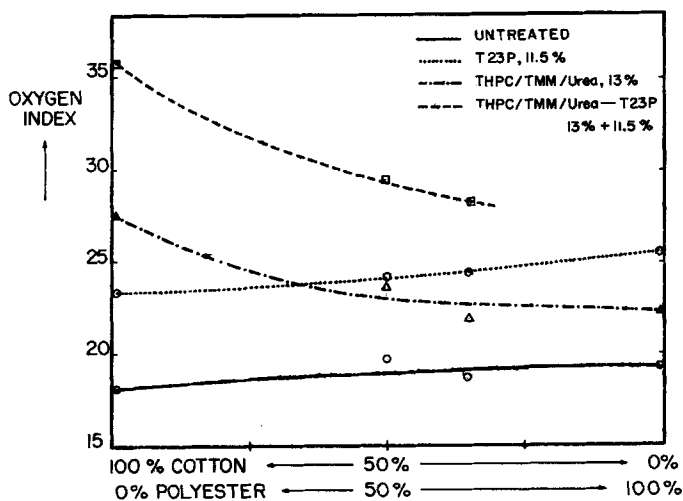


Fig. 5. Oxygen indices at room temperature.

THPC/TMM/urea treatments appear to be more effective on cotton than on 100% polyester. As the amount of polyester in the blend increases, the oxygen index of the fabric appears to decrease. This is true for the single THPC/TMM/urea treatment and for the dual treatment as well. These findings might indicate that this treatment works almost exclusively on cotton. Tris(2,3-dibromopropyl) phosphate (T23P), on the other hand, appears to be equally effective on single-component fabrics as well as blends.

When plotting the data for 95°C and 180°C, respectively, similar trends were observed to those seen in the measurement of indices at room temperature. However, we now begin to experience an overall drop in the indices for all fabrics.

In Figure 6, the oxygen index has been plotted against temperature so that the influence of the latter can be seen more clearly. For 100% cotton, the oxygen index is observed to decrease with temperature in all cases, indicating an increase in the fabric's flammability.

There is an almost straight-line relationship between oxygen index and temperature for cotton receiving no treatment. The reduction in the index is gradual over the temperature range studied and amounts to about three oxygen index units. With the THPC/TMM/urea treatment, a significantly rapid decrease in oxygen occurs between 25°C and 95°C; above this temperature, however, the index drops only gradually following a straight-line relationship with temperature. Weight loss determinations on the specimens and analytical data indicate that, at the lower temperatures, unreacted components of the applied finish are lost. The specimens lose approximately 2% of their weight between room temperature and 95°C. This means a 17% weight loss of the flame retardant. Elemental analyses have confirmed this observation. The nitrogen and phosphorus contents

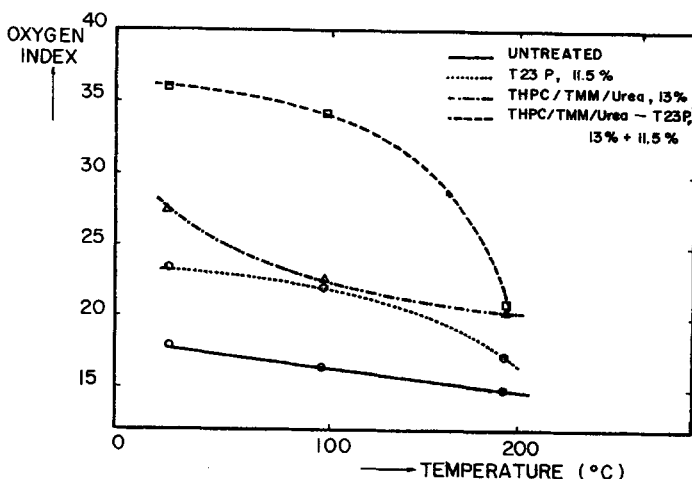


Fig. 6. Influence of temperature on oxygen indices (100% cotton fabric).

of the fabrics drop from 3.08% to 2.53% (nitrogen) and from 1.39% to 1.09% (phosphorus), respectively. Between 95°C and 180°C, however, little or no decomposition and/or volatilization of the finish occurs. This was found by weight and elemental determinations as well, and the minute decrease in the fabric's oxygen index has proved this point.

The oxygen indices of fabrics treated with T23P decrease slowly below 95°C and quite rapidly above this temperature. The most likely explanation for this behavior may be that volatilization and/or decomposition of the flame retardant mainly occurs only when the fabric is heated to 180°C for 30 min. At 95°C, no weight losses or changes in the specimens' bromine and phosphorus contents were found. Isothermal thermogravimetric analyses did not indicate any weight loss at this temperature. The low vapor pressure of T23P at 95°C,  $7.05 \times 10^{-6}$  atm, also rules out any substantial losses. At 180°C, however, a total weight loss of 1.2%, which is equivalent to an 11% loss of the flame retardant component, was determined. The fabrics' bromine and phosphorus levels decreased about 10% (Br: 6.37% from 7.13%; P: 0.42% from 0.45%). The flame retardant's vapor pressure at 180°C,  $2.39 \times 10^{-4}$  atm, alone is not sufficient to explain the total experimental weight losses. Thus, additional decomposition of the flame retardant in the hot oxygen-enriched atmosphere is also likely to have occurred.

A dramatic decrease in the oxygen index occurs with dual-treated cotton fabrics at temperatures above 95°C. Up to that temperature, the fabrics lost only about 1.2% of their weight. This is less than one would expect, since fabrics treated solely with THPC/TMM/urea exhibit a larger weight loss within this temperature range. Differences in the elemental analyses of nonheated fabrics and those preheated to 95°C are also negligible. A 30-min heating period at 180°C, however, causes considerable

weight losses and decreases in the Br, P, and N contents of the fabric. A total weight loss of 7.6% indicates the loss of about 38% of the flame retardants. Reductions in the bromine content by 49% and in the P content by 45% versus a nitrogen loss of 27% allows us to draw a tentative conclusion, that at these high temperatures the THPC/TMM/urea treatment almost "catalyzes" the decomposition of T23P.

Although the numerical changes in the oxygen indices were different for the blends and the 100% polyester fabrics, the trends found on untreated and flame-retarded cotton fabrics prevailed throughout this study.

Synergism in conferring flame resistance to textiles is a highly desirable phenomenon. Referring to Table IV, synergistic effects can be seen in the dual treatments used on the three fabrics at room temperature, but this apparently is lost at 180°C. This may be due to the interaction and decomposition of the treatments at elevated temperatures. In fact, in all cases, the oxygen index at 180°C is lower than would be expected from an additive effect of each treatment.

TABLE IV  
Oxygen Indices of Double-Treated Textiles.  
Actual Results vs. Expected Results\*

	Oxygen index		
	25°C	95°C	180°C
100% Cotton			
Actual	36.1	33.9	20.7
Expected	32.8	27.2	22.6
50:50 Cotton/Polyester Blend			
Actual	29.5	27.5	18.9
Expected	27.9	26.3	20.6
35:65 Cotton/Polyester Blend			
Actual	28.9	26.0	19.6
Expected	27.9	25.6	20.3

\* Additive results of the two single treatments. Flame retardants: T23P, 11.5%, plus THPC/TMM/Urea, 13%.

### Smoke Density Determinations

#### *Characteristics of the Combustion*

When the smoke generated by the burning textiles was determined in the MC Oxygen Index-Smoke Densitometer, the specimens were exposed to a "candle type" combustion at the oxygen indices. In Figure 7, the smoke density generated by the four untreated fabrics is plotted against the time of combustion.

It can be seen that, over the entire burning period, cotton generates relatively low amounts of smoke. On the other hand, 100% polyester

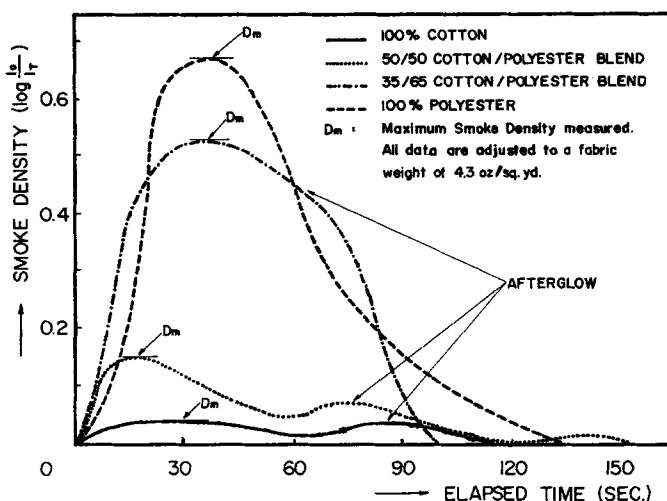


Fig. 7. Smoke density vs. burning time (Nontreated textiles, MC chamber).

generates a considerable amount of smoke rather quickly. The 50:50 polyester/cotton blend displays smoke generation characteristics more like those of cotton, while the 35:65 cotton/polyester blend generates almost the same amount of smoke as a 100% polyester fabric.

"Afterglow" plays a significant role in the combustion process of cotton and definitely contributes to the production of smoke. The first inflection in the curve occurs during the actual flaming of the cotton fabric, while the second inflection occurs during the "afterglow." The amount of smoke appears to be nearly as great in the later period as in the actual flaming period. The "afterglow" effect on smoke generation is far less accentuated in the case of burning cotton/polyester blends and loses its significance as the amount of polyester in the blend increases. Very little "afterglow" was visually noted on the 35:65 cotton/polyester blend, and the graph indicates that in this instance the afterglow contributes only a minor amount of smoke. In the case of 100% polyester, no inflection in the curve can be seen, and this corresponds with the visual observation of the burning fabric.

The effect of the afterglow, if its smoke were allowed to accumulate in the chamber rather than being carried away by the gas flow, could be seen in Figure 3. When the specimens are burned in the XP2 Smoke Density Chamber, the effect of an afterglow can also be detected for cotton and its blends. Figure 4 shows quite clearly that the afterglow of the textile contributes to the total amount of smoke.

#### *Influence of Fabric Weight on Smoke Density*

As shown in both Table V and Figure 8, there is a straight-line relationship between fabric weight and smoke density for fabrics having a thermo-

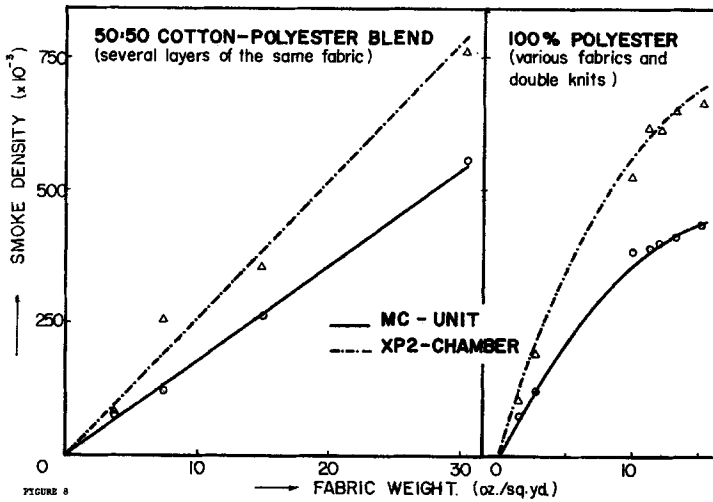


Fig. 8. Influence of fabric weight on smoke density (calculated for a standard chamber).

plastic component of 50% or less. This relationship was the same for both types of combustion. When droplets of molten polymer were formed during combustion, as in the case of a 35:65 cotton/polyester blend or of a 100% polyester fabric, reduced amounts of smoke were generated with an increasing fabric weight. Instead of a straight line, a parabolic curve was obtained.

TABLE V  
Influence of Fabric Weight on Smoke Density (Calculated for a Standard Chamber)

Fabric weight, oz/yd <sup>2</sup>	Oxygen index	Smoke density, $\times 10^{-3}$	
		MC smoke densitometer	XP-2 chamber
A. 50:50 Cotton/Polyester Blend, 120 g/(3.8 oz/yd <sup>2</sup> ) (several layers of same fabric)			
3.8	19.8	76	81
7.6	19.8	118	258
15.2	19.9	262	346
30.4	20.0	565	760
B. 100% Polyester Fabrics (various fabrics and doubleknits)			
1.4 <sup>a</sup>	19.0	75	103
2.6 <sup>a</sup>	19.0	121	191
10.0 <sup>b</sup>	19.2	390	522
11.4 <sup>b</sup>	19.3	393	617
12.2 <sup>b</sup>	19.4	406	610
13.4 <sup>b</sup>	19.3	417	647
15.0 <sup>b</sup>	19.5	447	661

<sup>a</sup> Polyester fabrics.

<sup>b</sup> Polyester doubleknits.

In the first case, the cotton tends to reinforce the fabric and to maintain the general fabric structure during combustion. Thus, the burning area of the fabric tends to remain constant, and the loose fabric structure permits the access of oxygen to the burning fabric. This is not so in the latter case. When polymer droplets are formed during combustion, they tend to char rather than to burn completely. The heavier the fabric, the larger the droplets tend to be, and therefore a proportionately larger amount of polymer is protected from the flames by the surrounding char. This char formation was observed to have taken place even in the XP2 chamber, where a large flame was continuously applied to the fabric specimen. If a certain percentage of the fabric does not burn, less smoke will be developed in relation to what one would expect by predicting smoke generation from the standpoint of fabric weight.

The fabric structure—at least in the case of fabrics that melt and form droplets during the combustion—does not appear to influence the amount of smoke generated. Although the polyester fabrics and doubleknits had quite different structures, the smoke density data of both fabrics could be plotted quite easily on the same curve. One would expect such behavior, for as the sample starts to burn, the original fabric structure is lost in the molten polymer.

Having found these relationships between fabric weight and smoke density, we were able to extrapolate all smoke data to a fabric weight of 134 g/m<sup>2</sup> (4.3 oz/yd<sup>2</sup>, weight of standard cotton sheeting). This was done for comparison purposes only.

The data obtained from melting fabrics are far less reproducible than those for fabrics which maintain their structure during the combustion process. While six parallel determinations in the MC chamber and ten in the XP2 chamber were sufficient to determine smoke densities for 100% cotton and 50:50 blends, almost twice as many determinations were needed to obtain meaningful average values for 35:65 blends and 100% polyester fabrics.

#### *Influence of Atmosphere on the Generation of Smoke by Burning Fabrics*

It is generally known and acknowledged that the atmosphere in which a specimen is being burned will influence the amount of smoke generated.<sup>5,7,13,21</sup> Studies on this subject have only dealt with non-flaming combustion, and the results obtained by some investigators are quite contradictory. In this study, the relationship between atmosphere and smoke density was determined under flaming combustion conditions using the Michigan Chemical Oxygen Index-Smoke Densitometer unit. The results are summarized in Table VI and Figure 9.

When the oxygen concentration in the environment is increased above the specimen's oxygen index level, an increase in the amount of smoke can be observed. After reaching a maximum, the smoke density decreases with the rising amount of oxygen in the atmosphere.

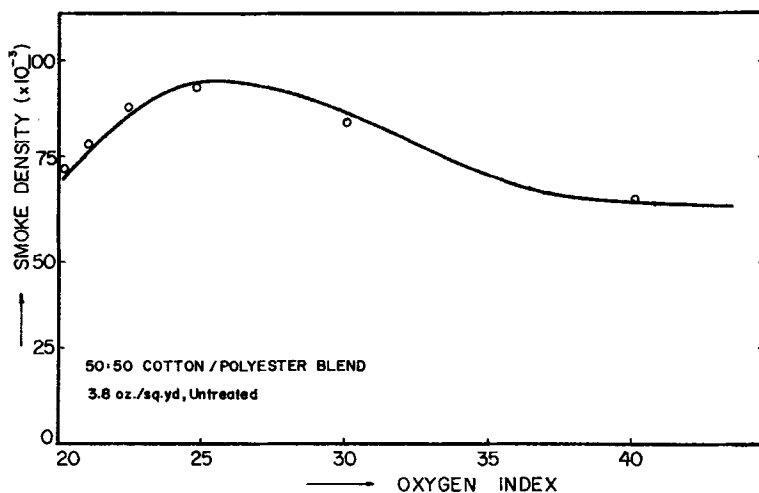


Fig. 9. Relationship between atmosphere and smoke.

*Influence of Fabric Composition and Flame Retardants on the Smoke Density*

Regardless of the type of combustion a fabric undergoes, an increase in the amount of polyester in the fabric leads to an increase in the amount of smoke which is generated. This trend can be found for treated and untreated materials as well.

TABLE VI  
Relationship Between Atmosphere and Smoke Density  
(calculated for a standard chamber)<sup>a</sup>

Oxygen index	Smoke density, $\times 10^{-3}$
20.0	76
21.0	78
22.5	89
25.0	92
30.0	81
40.0	63

<sup>a</sup> 50:50 Cotton/Polyester blend, 120 g/m<sup>2</sup> (3.8 oz/yd<sup>2</sup>)

While during a "candle type" combustion there is an almost linear relationship between the smoke generated and the polyester content of the fabric, this is not the case when a flame is continuously applied to the fabric. The polyester phase of the fabric with more than 50% polyester content will melt and form droplets which burn at the surface and have a tendency to form a char, which prevents the droplet from being entirely consumed by the flames. This behavior is accentuated when the fabrics are flame retarded. However, when a very hot flame is applied continuously to the fabric, the char formed on the droplet is not compact



TABLE VII  
Density of Smoke Generated by Several Untreated and Flame-Retarded Fabrics\*

Treatment	Chamber <sup>b</sup>	Smoke density, $\times 10^{-3}$			
		100% Cotton	50:50 Blend	35:65 Blend	100% Polyester
None	MC	9	86	165	195
	XP2	14	91	126	560
11.5% T23P	MC	13	95	168	307
	XP2	34	366	545	825
13% THPC/TMM/ Urea	MC	17	101	210	760
	XP2	217	600	770	1250
11.5% T23P plus 13% THPC/TMM/Urea	MC	47	134	265	
	XP2	259	985	1780	

\* Standard chamber, room temperature, data adjusted to a fabric weight of 135 g/m<sup>2</sup> (4.3 oz/yd<sup>2</sup>).

<sup>b</sup> MC: Michigan Chemical Oxygen Index-Smoke Densitometer unit; "candle-type" combustion at the fabric's oxygen index value. XP2: Rohm & Haas Smoke Density Chamber; a torch is always applied to the fabric, the combustion takes place in air (O.I. = 20.9).

enough to prevent some further decomposition and successive combustion, but even here some occlusion by char still occurs. Thus, higher smoke densities were found for fabrics containing greater portions of polyester in the XP2 chamber than in the MC smoke densitometer. When little or no char is formed during the combustion of a fabric, there is very little difference in the numerical data obtained between the two units, as can be seen in the case of 100% cotton fabrics.

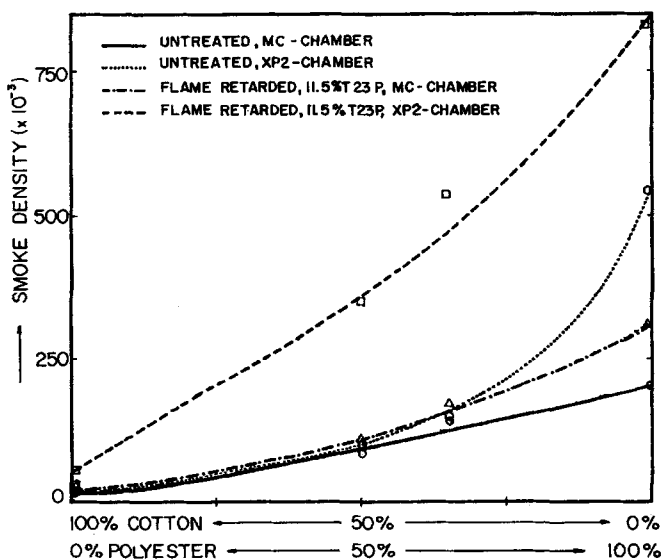


Fig. 10. Density of smoke generated by various fabrics (standard chamber, fabric weight 4.3 oz/yd<sup>2</sup>).

The results obtained for the smoke densities of untreated and flame-retarded fabrics are shown in Table VII, while Figure 10 graphically presents some of the data.

A comparison of the two flame-retardant treatments, T23P and THPC/TMM/urea, after adjustment of the additive level of the latter to 11.5%, clearly indicates that T23P causes smaller increases in smoke density. Due to the large additive level of 24.5%, the dual treatment generates significantly more smoke. But it also causes a higher amount of smoke than would be expected when one compares the effects of the two single treatments by themselves.

When the textiles are ignited in air rather than in a gaseous mixture set at their oxygen index value, the flame-retarded ones will extinguish either immediately after removal of the ignition source or before the entire specimen is consumed by the flames. The amount of smoke generated by the nonflame-retarded samples is more than that generated by the treated textiles. Table VIII presents resulting data.

TABLE VIII  
Amount of Smoke Generated by Flame-Retarded and Untreated Textiles at Several Oxygen Index Levels<sup>a</sup>

Textile	Flame retardant	Oxygen index	Smoke density, $\times 10^{-3}$		
			At the O.I. level	In air (O.I. = 20.9)	At O.I. = 27.0
Cotton	—	18.0	9	8	7
Cotton	11.5% T23P, 13%	23.3	13	6	10
Cotton	THPC/TMM/	27.5	17	— <sup>c</sup>	15
Cotton	Urea dual treatment	36.1	47	— <sup>c</sup>	— <sup>c</sup>
50:50 Cotton/Polyester Blend	—	19.8	86	82	70
50:50 Cotton/Polyester Blend	11.5% T23P, 13%	24.1	95	14 <sup>b</sup>	83
50:50 Cotton/Polyester Blend	THPC/TMM	23.6	101	27 <sup>b</sup>	90
50:50 Cotton/Polyester Blend	Urea dual treatment	29.5	307	— <sup>c</sup>	48 <sup>b</sup>
35:65 Cotton/Polyester Blend	—	18.3	165	143	121
35:65 Cotton/Polyester Blend	11.5% T23P, 13%	24.3	168	37 <sup>b</sup>	150
35:65 Cotton/Polyester Blend	THPC/TMM/	21.9	210	180 <sup>b</sup>	186
35:65 Cotton/Polyester Blend	Urea dual treatment	28.9	265	— <sup>c</sup>	110 <sup>b</sup>
Polyester	—	19.0	195	182	172
Polyester	11.5% T23P, 13%	25.5	307	28 <sup>b</sup>	310
Polyester	THPC/TMM/ Urea	22.4	760	205 <sup>b</sup>	710

<sup>a</sup> Standard chamber, room temperature, data adjusted to a fabric weight of 134 g/m<sup>2</sup> (4.3 oz/yd<sup>2</sup>).

<sup>b</sup> Flames extinguish before the entire specimen is burned.

<sup>c</sup> Flames extinguish immediately after the torch is removed.

The textile specimens were also ignited in an atmosphere containing 27% oxygen. This oxygen level was chosen because several investigations have shown that specimens which will not burn at this oxygen level can be considered self-extinguishing.<sup>20,22</sup> The flame-retarded textiles with an oxygen index lower than 27.0 (generally those with relatively low add-on levels of flame retardants) will generate more smoke than untreated textiles when burned in such an atmosphere. Highly flame-retarded fabrics, however, will extinguish even at this oxygen level and then generate less smoke than the untreated ones or even no measurable amount of smoke if they extinguish immediately after removal of the torch.

#### *Influence of Temperature on Smoke Density*

As we can see in Figure 11, the specimen temperature before ignition plays a significant role in regards to the question of smoke by the burning fabric. By comparing the smoke which developed during the burning of an untreated 50:50 cotton/polyester blend at various higher temperatures (95°C and 180°C), we see that greater amounts of smoke are produced at the elevated temperatures than at room temperature. The burning characteristics at the two elevated temperatures, however, are nearly the same. "Afterglow" still plays a role in smoke development at elevated temperatures, but its effect is overshadowed by the large amount of smoke which is produced rather quickly under these conditions.

The data concerning the influence of temperature on the density of smoke generation by burning fabrics are summarized in Table IX. We can observe a very interesting phenomenon: While the density of the smoke coming from burning cotton or blends with polyester tends to increase with rising temperature, the opposite is found to be true for the 100% polyester fabric. At elevated temperatures, a distinct maximum in smoke generation occurs with the 35:65 cotton/polyester blend. As we previously mentioned, polyester fabrics melt and generate charring

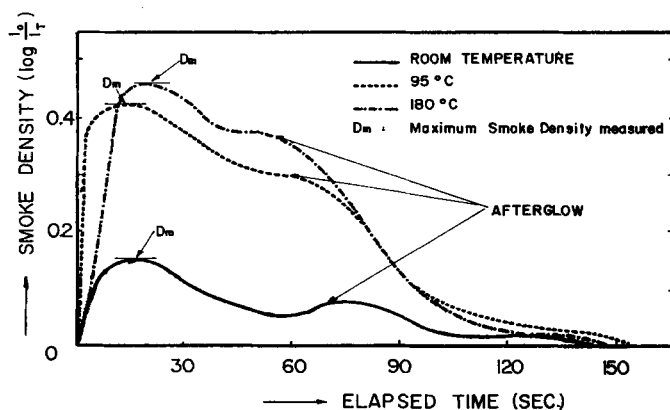


Fig. 11. Smoke density vs. burning time (untreated 50:50 cotton/polyester blend, 3.8 oz/yd; MC chamber; various temperatures).

droplets which do not burn completely. In the blends, however, the "scaffolding" effect of cotton prevents the formation of most of these droplets, thus allowing the polyester to be entirely consumed by the flames. This may be the reason why polyester-containing blends exhibit a maximum in smoke density. These two apparent countereffects render the interpretation of the maximum smoke density for their respective blends at elevated temperatures somewhat more difficult.

TABLE IX  
Influence of Temperature on Smoke Density<sup>a</sup>

Temp., °C	Smoke density, $\times 10^{-3}$			
	100% Cotton	50:50 Blend	35:65 Blend	100% Polyester
No Treatment				
25	9	86	165	195
95	22	266	268	102
180	33	285	285	91
11.5% T23P				
25	13	95	168	307
95	135	525	835	242
180	61	308	457	131
13% THPC/TMM/Urea				
25	17	101	260	1160
95	30	294	305	1035
180	42	467	600	995
11.5% T23P plus 13% THPC/TMM/Urea				
25	47	133	256	—
95	60	440	640	—
180	64	396	775	—

<sup>a</sup> Generated by various flame-retarded and untreated textile samples burning at their oxygen index values in the MC Oxygen Index-Smoke Densitometer. All data are computed for a standard chamber; the data are adjusted to a fabric weight of 135 g/m<sup>2</sup> (4.3 oz/yd<sup>2</sup>) (weight of standard cotton sheeting).

In an attempt to clarify the effect that temperature has on the development of smoke, the smoke density produced by burning the 50:50 cotton/polyester blend and the 100% polyester fabric (with and without treatments) has been plotted versus temperature, as shown in Figure 12.

For the untreated blend, it appears that smoke increases rapidly with rising temperatures up to about 100°C and then levels off. The fabric, which was treated with THPC/TMM/urea, generates more smoke than the untreated one, especially at 180°C. An interesting phenomenon can be observed with the T23P-treated fabric. A rather steep increase in smoke density occurs between room temperature and 95°C, but less smoke is generated at 180°C than at 95°C. Volatilization and/or decomposition of the flame retardant, as discussed earlier, undoubtedly contrib-

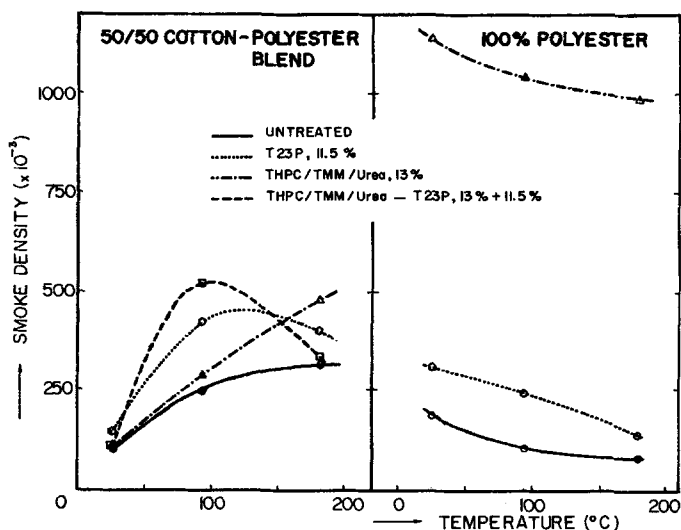


Fig. 12. Influence of temperature on smoke density (standard chamber; data adjusted to a fabric weight of 4.3 oz/yd<sup>2</sup>).

utes somewhat to this effect. However, it cannot entirely explain the magnitude of this effect. It is probable that an ester exchange has taken place between the phosphate group of T23P and the acetoxy group of the polyester substrate. Qualitative IR studies support this assumption. This "maximum type" curve was also found in the cotton and 35:65 blend when treated with T23P. The double-treated fabric exhibits features similar to those of the fabric with T23P as a flame retardant. However, it should be noted that at 180°C the double-treated fabric generates less smoke than each of the single-treated fabrics. Here again, the reduction in smoke generation can be explained in part by losses of the flame retardant at these temperatures. However, the magnitude of smoke reduction cannot be explained entirely by a weight-loss of the additives. Thus, one might speculate that an interaction of the two treatments has taken place at these elevated temperatures.

Untreated 100% polyester fabrics will generate less smoke at elevated temperatures than they do if ignited at room temperature. When they are treated with tris(2,3-dibromopropyl) phosphate, we find that the same characteristic trend holds. This would indicate that the substrate has a dominating influence on the behavior of the flame-retarded fabric, at least with regard to smoke densities, at elevated temperatures.

## CONCLUSIONS

When textiles are heated prior to their ignition, their oxygen indices decrease, indicating an increase in the specimens' flammability. This was found to be true for cotton, polyester, and their blends, in both the untreated and the flame-retarded condition. The energy that is supplied

externally to the burning system is likely to alter the thermodynamics and/or chemistry of combustion. This, in turn, may cause the increased flammability of the textiles at elevated temperatures.

When flame retardants are applied to the fabrics, additional factors, such as volatilization and/or decomposition of the additives or even interaction of the flame retardants with either each other or the substrate, may become important parameters. These factors will also contribute to the textiles' accelerated loss of flame retardancy after a preignition period.

The THPC/TMM/urea treatment appears to specifically flame retard cotton fibers. Tris(dibromopropyl) phosphate, on the other hand, seems to be equally effective on cotton, polyester, and on blends of the two. This has been well documented in measurements of several specimens at ambient as well as at elevated temperatures.

A synergistic effect of the two flame-retardant treatments could be observed on double-treated cotton and cotton/polyester blends. While this effect prevails at room temperature and at 95°C, it apparently is lost at 180°C. Losses of the flame retardants and eventually additional interactions of the treatments at elevated temperatures may account for some loss in flame retardancy. The type of substrate does not appear to influence the synergistic effects of the additives.

The type of combustion a fabric undergoes will influence the amount of smoke generated. While numerical data are not identical for the same material under different combustion conditions, the overall trends in smoke generation appear to be the same.

The phenomenon of afterglow definitely contributes to the total smoke generated by cotton and its blend with polyester. With increasing amounts of polyester in the fabric, the afterglow effect loses its importance.

There appears to be a direct relationship between fabric weight and the smoke generated during the burning of the fabric, especially if the structure of the fabric is maintained during its combustion because of the "scaffolding" effect of the cotton material. However, if the fabric melts, as in the case of polyester fabrics and doubleknits, we find a nonlinear relationship. The molten polymer appears not to burn completely because of a char formation developing on the molten polymer droplets.

The atmosphere in which combustion is taking place seems to influence the smoke generation, but it does not play as significant a role as has been previously assumed by some other investigators. It has been found that polyesters generate far more smoke than cotton fabrics, without the phenomenon of afterglow. When the fabrics are ignited in air rather than in a controlled O<sub>2</sub>/N<sub>2</sub> gaseous mixture, most flame-retarded specimens will extinguish immediately after ignition. Thus they generate far less smoke than untreated fabrics, which burn until they are entirely consumed by the flames.

Preignition temperature also has an effect on the smoke generated by the burning fabric. While untreated as well as treated polyester

fabrics generate less smoke after a preheating period, the opposite was found to be true in the case of cotton. Since the flame-retarded systems exhibit the same trends, it is suggested that the substrate must play a greater role insofar as smoke generation is concerned than the flame retardant itself.

Cotton/polyester blends generate more smoke at elevated temperatures than the individual component fabrics under the same experimental conditions. The "scaffolding effect" of cotton in the blends probably is the reason for this behavior.

The smoke density-temperature relationship of fabrics treated with some of the flame retardants studied here exhibits a maximum, followed by a subsequent decrease in smoke development. Volatilization and/or decomposition of the flame retardants, as well as a possible interaction of the additives with either each other or the substrates, probably contribute to the decrease of smoke generation at temperatures higher than 95°C.

The authors would like to express their gratitude to Professors Drs. Reegen and Frisch of the University of Detroit for permission to use their Rohm & Haas XP2 Smoke Density Chamber. They also thank Mr. R. F. Lindemann of Michigan Chemical and Professor T. Bailey of Alma College for their advice, and Miss C. Sutfin for performing some of the experimental work, and especially Michigan Chemical for allowing this study to be carried out in its research laboratories.

### References

1. J. DiPietro, H. Barda, and H. Stepniczka, *Text. Chem. Colorist*, **3** (2), 40, 48 (1971).
2. M. J. Koroskys, *Amer. Dyestuff Rep.*, **58**, 15 (March 1969).
3. Federal Aviation Administration, Fed. Air Reg. FAR-25.853, June 1968.
4. W. A. Reeves and J. D. Guthrie, *Dyer*, **111**, 567 (1954).
5. W. A. Reeves, D. J. Daigle, D. J. Donaldson, and G. L. Drake, Jr., *Text. Chem. Color.*, **2** (16), 30/283 (1970).
6. American Society for Testing and Materials, *1970 Annual Book of ASTM Standards*, D-2863-70, Philadelphia, 1970, pp. 719-722.
7. American Society for Testing and Materials, *1970 Annual Book of ASTM Standards*, D-2843-70, Philadelphia, 1970, pp. 704-712.
8. Anon., *NFPA Qrtly.*, **57** (3), 276 (1964).
9. J. DiPietro and H. Stepniczka, Soc. Plast. Eng., 28th Ann. Tech. Conf., Tech. Pap., 463 (1970).
10. J. DiPietro and H. Stepniczka, *J. Fire Flammability*, **2**, 36 (1971).
11. J. DiPietro and H. Stepniczka, *SPE J.*, **27**, 23 (1971).
12. F. J. Raring and A. J. Bartosic, *Evaluation of the XP2 Smoke Density Chamber*, American Society for Testing and Materials, ASTM STP 422, Philadelphia, 1967, pp. 106-124.
13. D. Gross, J. J. Loftus, and A. F. Robertson, *A Method of Measuring Smoke from Burning Materials*, American Society for Testing and Materials, Philadelphia, ASTM-STP 422, 1967, pp. 166-191.
14. W. W. Foster, *Brit. J. Appl. Phys.*, **10**, 416 (1959).
15. M. Abramowitz and J. Stegun, *Handbook of Mathematical Functions*, NBS Applied Mathematics Series, Washington, D.C., 1965, p. 886.
16. E. Kreyszig, *Advanced Engineering Mathematics*, Wiley, New York, 1963, p. 94.
17. W. Kruse, *gdi Occas. Publ.* 45, G. D. Inst. for Ec. and Soc. Std., Rüsçhlikon-Zürich, Switzerland, 1969, pp. 137-161.

18. W. Kruse, *Melliand Textilber.*, **50** (4), 460 (1969).
19. Anon., *Amer. Dyestuff Repr.*, **57**, 323 (1968).
20. G. C. Tesoro and C. H. Meiser, Jr., *Text. Res. J.*, **40**, 430 (1970).
21. K. Bürgi, International Study Conference Plastics and the Consumer, G. D. Inst. for Ec. and Soc. Studies, Rüschlikon-Zürich, Switzerland, Nov. 1970.
22. C. P. Fenimore and F. J. Martin, *Mod. Plast.*, **44** (3), 141, 142, 146, 148, 192 (1966).

Received April 5, 1971