Pyrolysis and Combustion of Polyester.   I. Thermochemistry of Poly(1,4-cyclohexylene Dimethylene Terephthalate) Treated With Selected Phosphorus- and Halogen-Containing Flame Retardants*

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Synopsis

A series of poly(1,4-cyclohexylene dimethylene terephthalate) (PCHDT) fabrics treated with selected phosphorus- and halogen-containing flame retardants has been studied by static oxygen bomb calorimetry. The amount of heat evolved when these fabrics are burned in the open atmosphere has been determined indirectly using calculations based on Hess' law of summation. This heat evolution when corrected for contributions due to burning of the flame retardant appeared to correlate with the efficiency of the flame retardant treatment and was interpretable in terms of mechanisms of flame retardant action. Also, this technique has been applied to blends containing polyester.

INTRODUCTION

Calorimetry has been a useful tool in the study of the combustion of polymeric materials. Oxygen bomb techniques have been used successfully to study the thermochemistry of treated cotton cellulose.[1] In this study, the amount of heat evolved by fabrics burning in the open atmosphere was determined indirectly using calculations based on Hess' law of heat summation and assuming complete combustion of all volatilized materials. This heat evolution was found to correlate inversely with the efficiency of the flame retardant treatment and was interpretable in terms of mechanisms of flame retardant action. The thermochemistry of this

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The figure shows:

$$(\Delta H_c^{\circ\prime})_{POLYMER} = \Delta + R(\Delta H_c^{\circ\prime})_{CHAR}$$

$$\Delta = (\Delta H_{PYR}^{\circ\prime})_{POLYMER} - (AMT.\ OF\ FLAMMABLE\ GAS)\ (\Delta H_c^{\circ\prime})_{GASES}$$

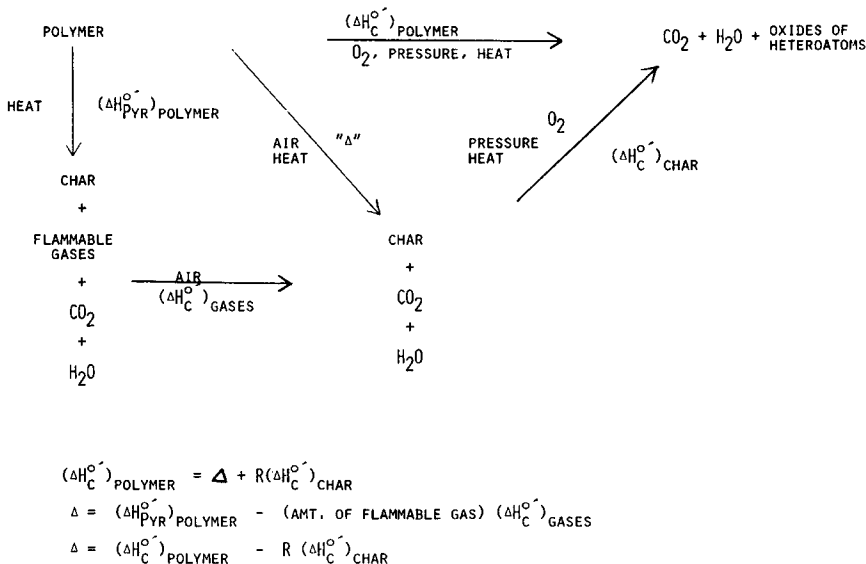$$\Delta = (\Delta H_c^{\circ\prime})_{POLYMER} - R\ (\Delta H_c^{\circ\prime})_{CHAR}$$

Fig. 1. Thermochemistry of the oxygen bomb technique.

method is given in Figure 1, where $(\Delta H_c^{\circ\prime})$ polymer $=$ total standard specific heat of combustion of the polymer; $(\Delta H_{pyr}^{\circ\prime})$ polymer $=$ standard specific heat of pyrolysis of the polymer; $(\Delta H_c^{\circ\prime})$ gases $=$ standard specific heat of combustion of the flammable gases; $(\Delta H_c^{\circ\prime})$ char $=$ standard specific heat of combustion of the polymer char; $\Delta =$ heat liberated per gram in normal atmospheric burning of the polymer; and $R =$ weight fraction of the treated polymer converted into char.

The process of fabric flammability is basically cyclic. In the initial stages, heat is supplied to the nonvolatile polymer substrate initiating an endothermic degradation reaction which is generally conceded to be predominantly pyrolytic in nature. There seems to be little evidence of significant oxidative processes occurring in the condensed phase.[2] The products of this polymer pyrolysis diffuse to the surface of the fabric and are released into the atmosphere immediately above the fabric. It is at this point that these flammable gaseous products begin to mix with the oxygen of the air so that combustion can take place. This is an exothermic process, of course, and the heat thus liberated can be returned in part to the fabric surface to continue the polymer pyrolysis, assuring a continuous supply of fuel for further flame propagation. This leads to the conclusion that the heat flux at the surface of the condensed phase is one of the most critical factors in determining whether a material will exhibit self-extinguishing characteristics. Unfortunately, this is not an easy quantity to measure unambiguously. However, the heat flux should be related to the total heat liberated during the burning of a fabric, and it would be logical to expect that good flame retardants should lower the amount of heat liberated during the combustion of the treated fabric.

Accordingly, the method of Yeh and Barker[1] seemed to offer a means for the determination of the liberated heat.   This method is not dependent on the nature of the polymer and should provide a means to correlate the efficiency of a flame retardant with its ability to reduce the heat evolution during the combustion of a given quantity of polymer.   An attempt has therefore been made to apply this technique to polyester.   Pure poly-(ethylene terephthalate) (PET) fabric under normal atmospheric conditions was found to melt in the igniting flame.   This resulted in dripping of the flaming polymer.   Collection of the molten material resulted in quenching which did not allow for complete air combustion of the PET fabric.   Also, a large volume of black smoke was liberated that was not easily collected for combustion.

EXPERIMENTAL

Chemicals.   All chemicals and solvents were reagent-grade commercial samples.

Fabrics.   The fabrics, PCHDT (greige) and a series of cotton/polyester blends, were obtained from Testfabrics, Inc.

Fabric Treatment: The PCHDT fabric was scoured in perchloro-ethylene to remove all residual spinning oils.   The triphenyl phosphate was applied using acetone as the solvent, and the tris(2,3-dibromopropyl) phosphate was applied using perchloroethylene as the solvent.   After being dried, the fabric pickup was determined gravimetrically, and the per cent phosphorus was then calculated from the molecular weight of the compounds.

Open Air Combustion.   Fabrics were cut into 2- $\times$ 6-in. strips and weighed.   The cotton/polyester blend fabrics were mounted 45° to the horizontal on a pin frame and burned.   A paper match was used to ignite each sample at the bottom edge.   Attempts to use this technique for PCHDT fabrics were unsuccessful due to their tendency toward excessive melting and shrinking.   These samples, therefore, were burned in the vertical position being held at the top.   The melt and drip were collected in a glass dish.   Those samples which were self-extinguishing under these conditions were reignited until the entire length of the sample had been charred.

Heats of Combustion.   All heats of combustion were determined using a Series 1200 Parr automatic oxygen bomb calorimeter and following the standard ASTM procedure (ASTM D 2382-65).

RESULTS AND DISCUSSION

A study of the heats of combustion of several widely used textile fabrics (Table I) has shown that while PET, which has a melting point of 260°C, could not be studied using this method, a related polyester, poly(1,4-cyclo-hexylene dimethylene terephthalate) (PCHDT), could be studied.   The

TABLE I
Heats of Combustion of Fabrics

Fabric	$-(\Delta H_c{}^{o\prime})_F$, cal/g	R	$-(\Delta H_c{}^{o\prime})_C$, cal/g	$-\Delta$, cal/g
Combed cotton	4013	0.015	7900	3890
Acetate	4400	0.299 ± 0.001	5031	2896
Viscose	3841	0.015	—	—
Arnel	4493	0.525 ± 0.002	4699	2025
Acrilan	7319	0.623 ± 0.032	7347	2740
PCHDT-Kodel II	6878	0.268 ± 0.034	6735	5073
PET-Dacron type 54	5474	—	—	—
PET-Dacron type 54/cotton (65/35)	4976	0.279 ± 0.042	6143	3265
Nylon 66	7439	—	—	—
Nomex	6462	—	—	—

PCHDT has a higher melting point (290°C), which allows the fabric integrity to be maintained long enough for ignition to be achieved. Since tris(2,3-dibromopropyl) phosphate (TBPP) has been used as a flame retardant on polyester,[3,4] it was studied along with triphenyl phosphate (TPP) to contrast the efficiency of two phosphates as flame retardants one of which contained halogen.

The results from these studies are given in Table II and are presented graphically in Figure 2. The calorimetric heats of combustion of PCHDT fabric treated with TBPP decreased linearly with increasing amounts of TBPP owing to its lower heat of combustion (1841 cal/g). However, with TPP the heats of combustion of treated fabric remain essentially the same since the $\Delta H_c{}^{o\prime}$ of TPP is 6799 cal/g, which is almost the same as that of PCHDT (6878 cal/g). The conditions used in determining these heats of combustion are such that total combustion of all the organic material is achieved.

The situation is much different when the combustions are carried out under atmospheric conditions. Thus, samples of these treated fabrics were burned in the open air, and the chars, including the melt and drip, were collected and weighed. The fractions of residue remaining from the

TABLE II
Thermochemical Data for PCHDT Fabric Treated with TPP and TBPP

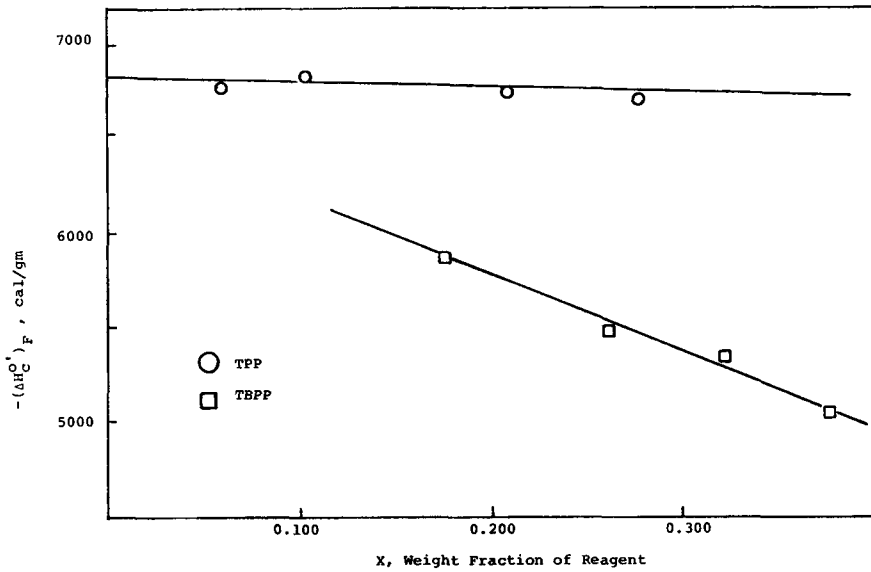| Reagent	X	%P	$-(\Delta H_c{}^{o\prime})_F$	R	$-(\Delta H_c{}^{o\prime})_C$	$-\Delta$
TPP	0.0579	0.6	6803	0.3387	6908	4463
	0.1019	1.05	6869	0.3835	6981	4192
	0.2084	2.14	6772	0.4146	6970	3882
	0.2777	2.85	6829	0.4292	7044	3805
TBPP	0.1751	0.77	5902	0.3154	6676	3796
	0.2615	1.15	5506	0.3703	6228	3200
	0.3221	1.42	5346	0.4225	5804	2894
	0.3776	1.66	5080	0.5230	5685	2106

Fig. 2. Heats of combustion of treated fabrics.

variously treated fabrics are shown in Figure 3.   In keeping with the
proposals concerning the nature and mechanisms of the flame retardant
process, the good flame retardant should give greatly increasing char
residues as the amount of phosphorus incorporated in the fabric is in-
creased.   With TPP, the R values increase only slightly as the phosphorus
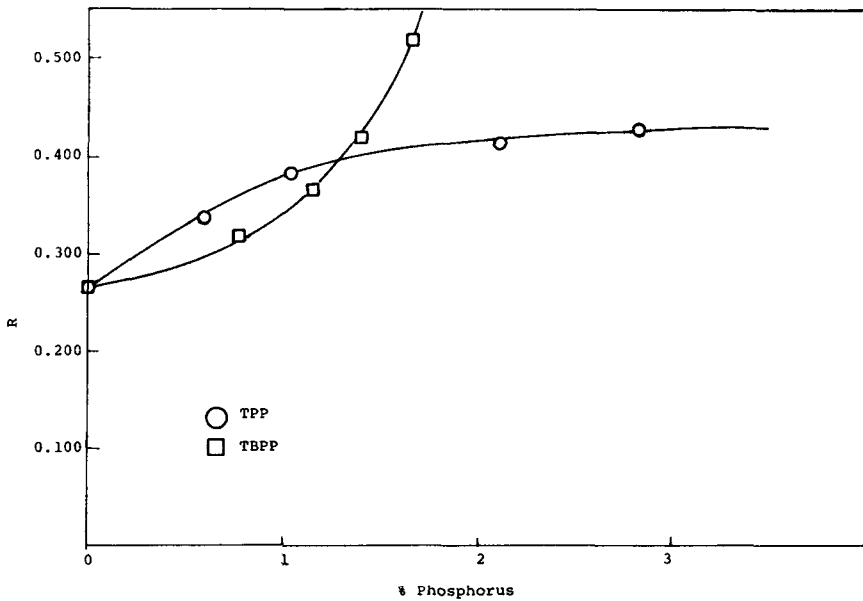

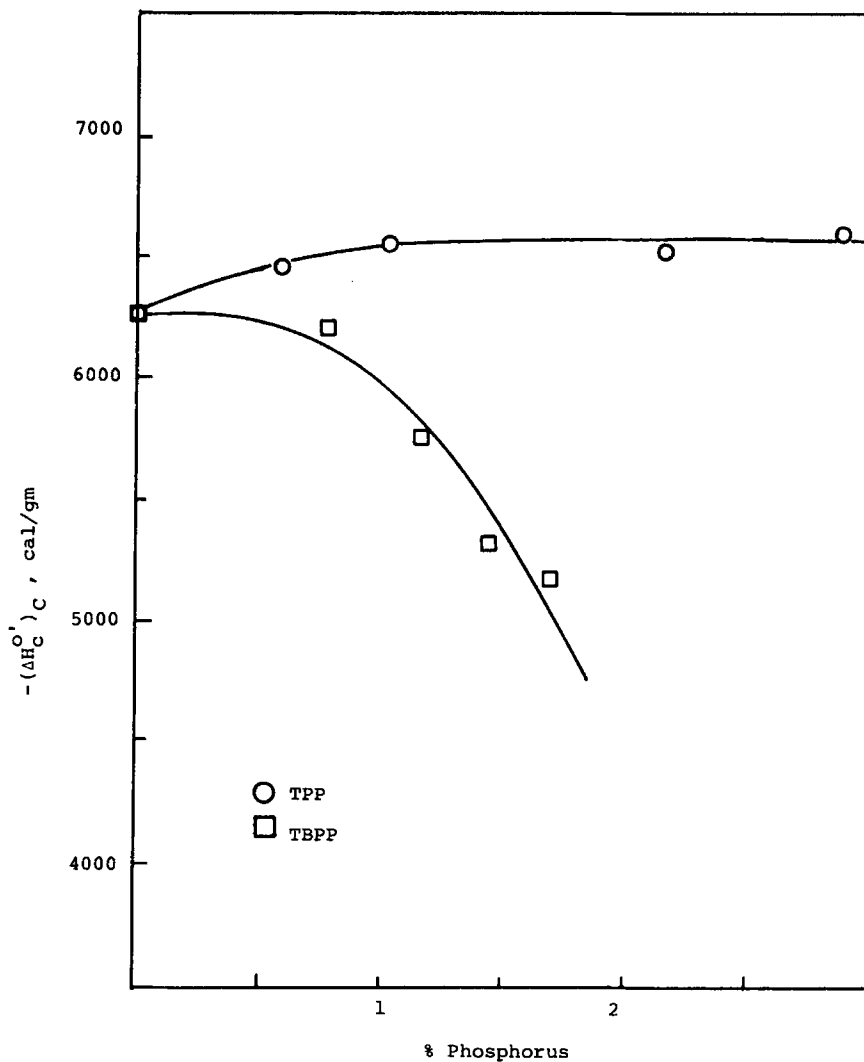Fig. 3. Residue of treated PCHDT fabrics.

Fig. 4. Heats of combustion of char.

content in the fabric is increased. However, with TBPP there is a signifi-
cant increase in the residue.

Determination of the heats of combustion of these chars (Fig. 4) indicates
that the TPP and TBPP chars are quite different thermochemically, and
apparently the chemical nature of the char is modified significantly when
larger quantities of phosphorus are present. Also, while bromine is
generally assumed to operate in the vapor phase when used as a flame
retardant,[5] the large differences in the heats of combustion of the char
suggest that some of the bromine may be effecting the decomposition in
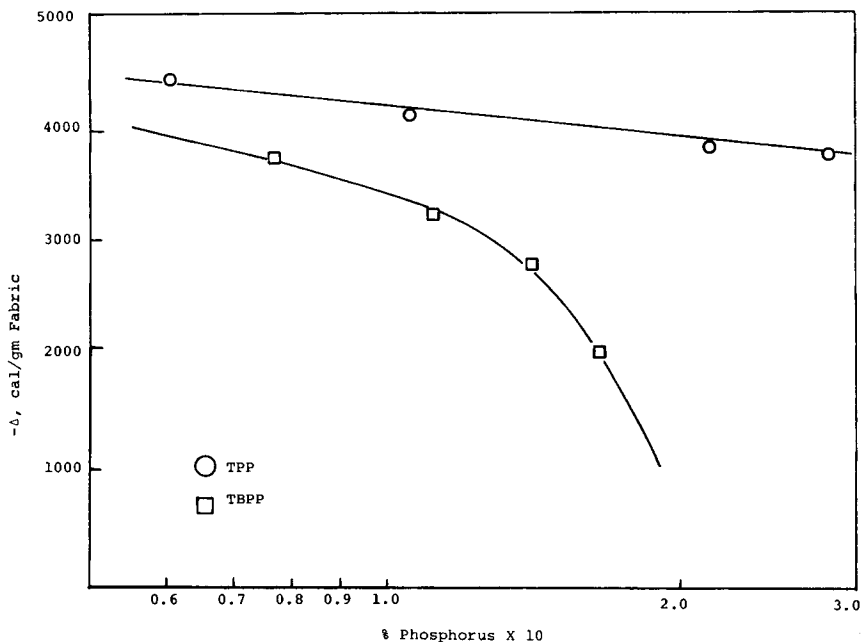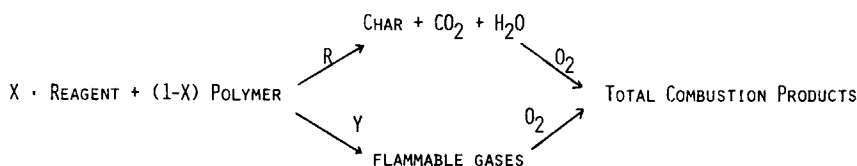the condensed phase.

Fig. 5. Heat parameters of treated PCHDT fabrics.

Using these data, corrections can be applied to the heats of combustion obtained for the fabrics and Δ values corresponding to the heat liberation in the open air can be calculated. These are the values which are expected to parallel the flame retardancy observed for the two treatments.

With TBPP, the incorporation of increasing amounts of phosphorus into the PCHDT fabric not only reduced the overall heat of combustion, but also increased the char residue to better than 50% at a level of 1.6% phosphorus. At the same time, the net heat evolved, indicated as Δ, was reduced from 5073 cal/g with no phosphorus to 3796 cal/g at 0.7% phosphorus and approximately 2100 cal/g at slightly less than 1.7% phosphorus.

In an analogous treatment, the fabric impregnated with TPP exhibited total heats of combustion which are essentially the same with increasing phosphorus content. In this case, the TPP was not effective in increasing the residue formation significantly, and the net heat values only decreased from 4463 cal/g at 0.6% phosphorus to 3805 cal/g at 2.85% phosphorus. Thus, this material would not be expected to exhibit good flame retardant properties. These net heat values are summarized in Figure 5. Since there is a linear relationship between the Δ for TPP treatments and the logarithm of the phosphorus content, it might seem that this is in some way related to the observed first-order kinetics for the thermal decomposition of polyester.[6,7] However, because of the ambiguity of treating heterogeneous kinetics, there is real danger of incorrect interpretation of

$$\text{CHAR + CO}_2 + \text{H}_2\text{O}$$

$$X \cdot \text{REAGENT} + (1\text{-}X) \text{ POLYMER} \quad \xrightarrow{\quad R \quad} \quad \xrightarrow{\quad O_2 \quad} \quad \text{TOTAL COMBUSTION PRODUCTS}$$

$$\xrightarrow{\quad Y \quad} \quad \text{FLAMMABLE GASES} \quad \xrightarrow{\quad O_2 \quad}$$

X = WEIGHT FRACTION OF TREATING REAGENT

R = WEIGHT FRACTION OF TREATED POLYMER CONVERTED TO CHAR

Y = WEIGHT FRACTION OF TREATED POLYMER CONVERTED TO FLAMMABLE GASES

$$\Delta = Y(\Delta H_c^{o\,\prime})_{\text{POLYMER}} + X\,(\Delta H_c^{o\,\prime})_{\text{REAGENT}}$$

Fig. 6. Corrections for the oxygen bomb technique.

the data at this point. It is significant, however, that the data for the two treatments in this study are compatible with current theory even though they are not easily interpretable in terms of mechanisms. It is obvious, however, that the mode of action of the TPP is vastly different from that of the TBPP. Finally, it must be remembered that these data represent net heat liberated and are not corrected for extraneous factors such as the heats of combustion of the reagents.

Corrections based on Figure 6 can be applied to these data in order to increase their mechanistic significance. The upper reaction in Figure 6 contributes very little to the total heat liberated. The major contribution to the heat of combustion of the polymer term is due to the combustion of the flammable gases generated from the polymer and the reagent:

$$\Delta = Y(\Delta H_c{}^{\circ\prime})_{\text{PCHDT}} + X(\Delta H_c{}^{\circ\prime})_{\text{reagent}}.$$

Solving this expression for Y gives the equation

$$Y = \frac{\Delta - X(\Delta H_c{}^{\circ\prime})_{\text{reagent}}}{(\Delta H_c{}^{\circ\prime})_{\text{PCHDT}}}.$$

Thus Y, the fraction of treated polymer converted to flammable gases, is related to the net heat attributable to the polyester portion but separated from the contribution owing to the decomposition of the reagent. The expression for Y also reduces to a form in which all the necessary parameters are easily measurable. The results of this type of treatment as applied to treated polyester are shown in Table III and are summarized graphically in Figure 7.

The data for TPP-treated samples show decreasing values of Y for increasing phosphorous content. But even with approximately 2.7% phosphorus, the fabric is still decomposing in such a way that about 30% of the polyester is being converted into the flammable volatile compounds which serve as fuel for the flame. As was observed with the Δ values, a linear relationship exists between $Y/(1 - X)$, the fraction of polyester

TABLE III
Corrected Thermochemical Data for Treated PCHDT Fabrics

Reagent	X	%P	$-\Delta$	Y	$Y/(1-X)$
TPP	0.0579	0.6	4463	0.5941	0.6306
	0.1019	1.05	4192	0.5094	0.5671
	0.2084	2.14	3882	0.3639	0.4597
	0.2777	2.85	3805	0.2808	0.3887
TBPP	0.1751	0.77	3796	0.5885	0.7134
	0.2615	1.15	3200	0.5083	0.6883
	0.3221	1.42	2894	0.4304	0.6349
	0.2776	1.66	2106	0.2779	0.4464

converted to flammable gases, and the logarithm of the phosphorus content. As before, the mechanistic significance of the linearity is somewhat ambiguous.

With TBPP, the fraction of treated polyester converted to flammable gases, $Y/(1-X)$, increases more rapidly than with TPP when the lower levels of phosphorus contents in the fabric are compared. This indicates that the polyester burns more easily with small amounts of the TBPP as a flame retardant, and that in char formation the effects of scaffolding[8] are greater than those of the inhibition reaction at the lower percentages of phosphorus from TBPP. After the TBPP and TPP lines cross (Fig. 7), the inhibition reaction dominates, and the TBPP is clearly more efficient than TPP in reducing the fraction of treated polyester converted to
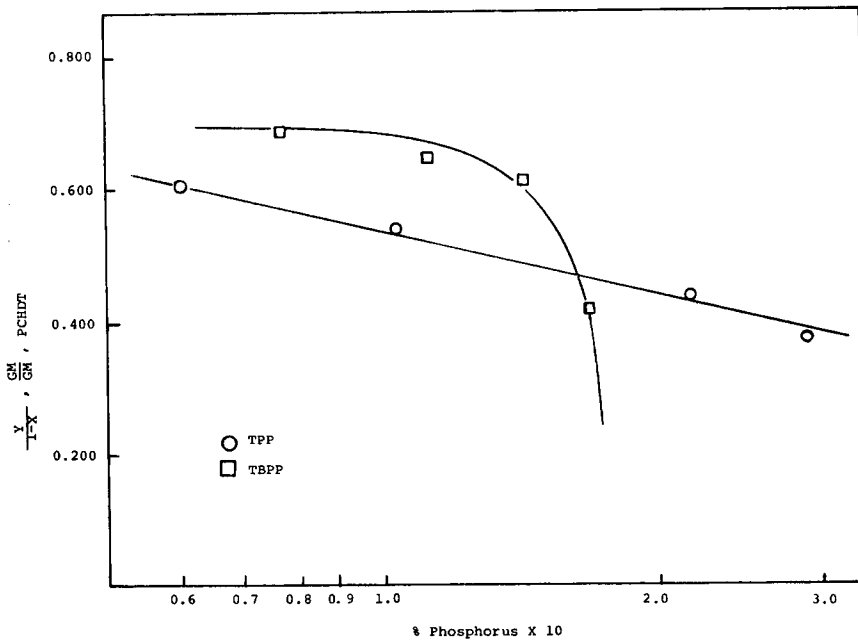

Fig. 7. Estimated fuel formation for treated PCHDT.

flammable gases. Also, these results indicate that using a semidurable flame retardant finish such as TBPP, which can be hydrolyzed back into the range of low percentages of phosphorus, may create a polyester fabric that presents an increased hazard. This apparently greater hazard which has been indicated thermochemically confirms a visual observation that many investigators have made while conducting actual burn tests.

The further utility of this method has been demonstrated in studies of blends containing polyester. It has been established that most synthetic polymers burn rather well when suspended by a carbonaceous grid formed from combustion of cellulosic or other nonmelting materials.[9] If polyester is blended with cotton cellulose, the molten polymer is not permitted to drip away and the combined system is flammable.

The calorimetric heats of combustion of cotton cellulose and a series of cotton/polyester blends were measured and are tabulated in Table IV.

TABLE IV
Heat of Combustion of Polyester and Cotton Cellulose

Fiber	$-(\Delta H_c^{\circ\prime})_F$	R	$-(\Delta H_c^{\circ\prime})_C$	$-\Delta$, cal/g
Cotton cellulose	4013	0.015	7900	3890
Cotton/polyester[a]				
87.5/12.5	4145	0.031	6354	3948
75/25	4328	0.039	6216	4086
62.5/37.5	4535	0.045	6916	4224
50/50	4757	0.052	6911	4398
35/65	4907	0.046	7512	4561
20/80	5159	0.066	6264	4746

[a] Dacron type 54.

In this case, the presence of the nonthermoplastic cotton allowed the combustion experiments to be carried out at the 45° angle so that there was no appreciable amount of material lost from the burning fabric owing to melting and dripping. These data show that there is a linear relationship between the per cent of cotton and the heat liberated (Fig. 8). As the cotton cellulose is decreased from 100% to 20% in a cotton/polyester blend, the heat liberation increases from 3890 cal/g for pure cotton to 4746 cal/g for a fabric containing 80% polyester. This indicates that the combustion of the polyester portion is a significant factor in such blends.

SUMMARY AND CONCLUSIONS

This study of PCHDT fabric treated with TPP and TBPP using oxygen bomb calorimetry has shown that the amount of heat liberated in the open air, Δ, decreases with increasing phosphorus content of the fabric. The char formation in the treated fabrics is affected by competing scaffolding and inhibition effects, and the percentage of phosphorus on the fabrics determines which effect predominates. The heats of combustion of the
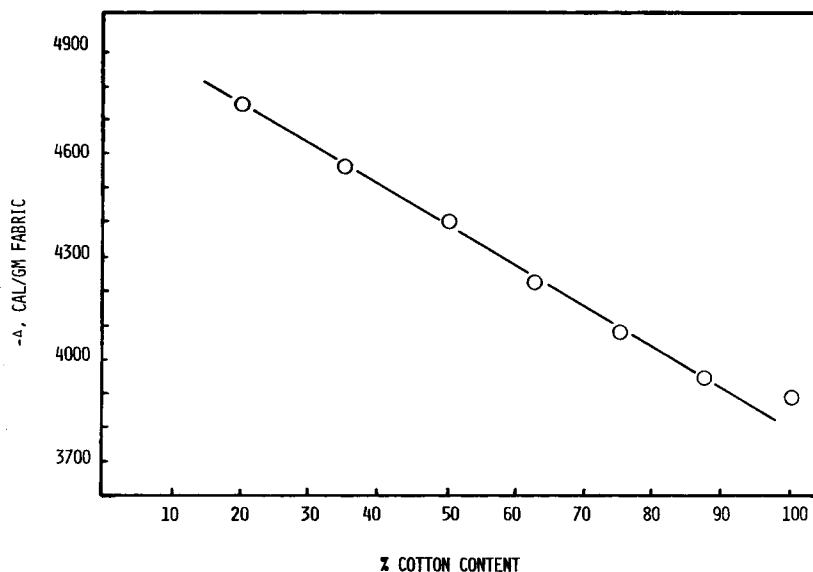
Fig. 8. Heat parameters of cotton/polyester blends.

char suggest that some of the bromine in TBPP may be effecting the decomposition in the condensed phase of the treated polyester. Also, while the TBPP was more efficient than the TPP in reducing the fraction of treated polyester converted to flammable gases at high add-ons, the quantities of treated PCHDT converted to flammable gases indicates that using a semidurable flame retardant finish such as TBPP creates a polyester fabric which may be a greater hazard than before the fabric was treated with low amounts of the flame retardant.

Secondly, the study shows that the method of Yeh and Barker can be used successfully on a polyester which has a melting point high enough to allow the fabric integrity to be maintained long enough for ignition. However, there is an inherent error in this method in assuming complete combustion of all volatilized materials. In theory, this error could be eliminated by modifying the equation $\Delta = (\Delta H_c^{\circ\prime})_{\text{polymer}} - R(\Delta H_c^{\circ\prime})_{\text{char}}$ to include a term $-B(\Delta H_c^{\circ\prime})_{\text{smoke}}$, where B = weight fraction of smoke and $(\Delta H_c^{\circ\prime})_{\text{smoke}}$ = standard specific heat of combustion of the smoke. The problem encountered is that it is not easy to collect the numerous smoke particles and to determine the fraction of smoke B and $(\Delta H_c^{\circ\prime})_{\text{smoke}}$.

Thirdly, this method has also been shown to produce meaningful data on the combustion of fiber blends. Even though the problem of smoke generation is encountered in these systems too, the data correlate qualitatively with previous observations of fabric burning characteristics. Cotton/polyester blends produce heat in direct relationship to their fiber content, and the heat liberated increases as the per cent polyester in the blend increases.

Efforts are currently in progress to confirm the results of these investigations by isoperibol calorimetry.[10]   It is hoped that in this way the systematic errors introduced by smoke generation and other forms of incomplete combustion can be eliminated.   However, in the meantime, the applicability of static bomb calorimetry techniques as qualitative probes of polyester flammability has been clearly demonstrated.

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