

## Flame Retardancy Effects of Halogenated Phosphates on Poly(ethylene Terephthalate) Fabric

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### Synopsis

A chemical research on the flame retardancy effect of halogenated phosphates on poly(ethylene terephthalate) fabric was carried out by thermogravimetry, infrared spectral analysis, and mass spectrometry. The following conclusions were drawn: (1) The flame retardancy effect of halogenated phosphates such as tris(2,3-dibromopropyl) phosphate is due to altering the pyrolysis reaction of polyester by aldol condensation. (2) The probability that liberated halogen compounds from the phosphates act as radical acceptors in a flame zone may be low. (3) Incorporation of halogen elements into phosphates appear to depress evaporation of phosphates, which act as acidic catalysts in aldol condensation from the condensed phase.

### INTRODUCTION

This paper describes flame retardancy effects of halogen-containing phosphates on poly(ethylene terephthalate) fabric. A number of studies on the flame retardation of polyester fabric have been reported.<sup>1-5</sup> Halogen and/or phosphorus compounds are available; tris(2,3-dibromopropyl) phosphate (TBPP) is a well-known flame retardant for polyester fabric. Bostic et al.<sup>4</sup> studied thermochemically an effect of phosphorus- and halogen-containing flame retardants on combustion. Low heat evolution of combustion by incorporation of flame retardants contributes to flame retardation. Koch et al.<sup>5</sup> have reported that phosphorus and bromine compounds operate as flame inhibitors in a flame zone. However, these views cannot provide a satisfactory explanation as to how halogen and phosphorus compounds operate as flame retardants.

Recently, fundamental research on combustion of polymers has been carried out. Martin<sup>6</sup> pointed out that the burning of polymers was a diffusion flame sustained by generated fuel gases from the polymers and that polymer pyrolysis occurred at or near a melted polymer surface. This burning model has been supported by other investigators, but it has been debatable whether polymer pyrolysis at the surface is only thermal decomposition or oxidative degradation. Gas composition measurements showed that oxygen just above the melted polymer surface was present in a small concentration and that oxidized compounds could not be detected in flame gases just above the surface. On the basis of these measurements, Martin<sup>6</sup> and Fenimore and Jones<sup>7</sup> concluded that polymers involving poly(methyl methacrylate) and poly(oxyethylene) did not

react with oxygen at the surface; the pyrolysis products oxidized subsequently in the flame. On the other hand, from the calculation of residence time of generated gases in the region of high temperature (450–550°C) where pyrolysis products may be readily oxidized, Burge and Tipper<sup>8</sup> concluded that oxidative degradation occurred at a melted surface of polyethylene; but oxidative degradation was not important for poly(methyl methacrylate) which decomposed at lower temperature. A similar oxidative degradation for polypropylene was recognized by Stuetz et al.<sup>9</sup>

These reports indicate that when polymers that decompose readily below the temperatures of a melted polymer surface (around 400°C) burn, the characteristics of thermal decomposition may influence the burning process. Introduction of phosphorus compounds into the polymer results in lowering the threshold temperature for degradation,<sup>10–12</sup> so it is predictable that flame retardancy effects of phosphorus compounds can be attributed to variations of the mode of thermal decomposition.

## EXPERIMENTAL

**Materials.** Tripropyl phosphate (I) and tris(2,3-dichloropropyl) phosphate (II) were prepared from the corresponding alcohol and phosphorus oxychloride according to the method of Evans et al.<sup>13</sup> Tris(1,3-dichloropropyl) 2-phosphate (III) was prepared by the method of Yoshino et al.,<sup>14</sup> which involves the reaction of epichlorohydrin with phosphorus oxychloride. Products were identified by IR and NMR spectroscopy.<sup>15,16</sup> Tris(2,3-dibromopropyl) phosphate (IV) was provided by the Marubishi Oil Co.

Other chemicals were analytical-grade commercial materials and used without further purification.

**Fabric and Fabric Treatment.** 100% Polyester fabric used throughout this study was obtained from Kuraray Co. Ltd.: 75 denier, 120 × 90, plain weave, weight 94 g/m<sup>2</sup>.

The fabric (10 × 16 cm) was scoured in methanol to remove all residual spinning oils and then immersed in a benzene solution of the phosphorus compounds. The fabric was then squeezed using a nip roll of a laboratory pad and dried under reduced pressure.

**Flame Retardancy Test.** The oxygen index test (ASTM D-2863-70) was used to evaluate a limiting oxygen index of the treated fabrics.

**Thermogravimetry.** A Shinku-Riko thermogravimetric analyzer DGC-3 was used. All analyses were run in air atmosphere at a programmed rate of 2.0°C/min.

**Analysis of Degraded Product.** Ground sample (60 mesh) contained in a Pyrex tube connected to a liquid nitrogen trap was pyrolyzed at the prescribed temperature for 1 hr in nitrogen atmosphere. Infrared spectra of residual products were examined as KBr disks using a Nihon-Bunko spectrophotometer IRA-1. The products condensed in the trap were methylated according to the method of Pochinokand and Portyagina<sup>17</sup> and analyzed by GC/mass spectrometry using a Nihon-Denshi GC-Mass spectrometer JMS-07. A separation column (3 mm I.D. × 1 m) containing 5 wt-% of SE-30 coated on Cellite 545 (60–80 mesh) was used. The column was heated in a temperature range from 60° to 280°C.

## RESULTS AND DISCUSSION

## Flame Retardancy Test

Results of the oxygen index test (Table I) show that the phosphorus compound II, III, and IV had satisfactory flame retardancy, but that compound I had no flame retardancy. Replacement of hydrogen by halogen in tripropyl phosphate led to enhanced flame retardance. It is well known that combinations of phosphorus with halogen are favorable in enhancing flame retardancy; a system with bromine is more effective than one with chlorine.<sup>18</sup> This different effectiveness is said to be due to the ability to trap radicals in a flaming zone. A similar synergistic effect of phosphorus and halogen was recognized in this experiment using a series of halogenated *n*-propyl phosphates, I, II, and IV; the improved effectiveness of halogen was in the following order: Br > Cl >> H. However, when the *sec*-propyl phosphate was used, the effectiveness was higher than that of II, comparable to that of IV (Table I). This result indicates that the chemical structure of halogenated phosphates affects flame retardancy properties and that another mode of action than the radical trapping ability may be operative. The thermal reaction of polyester in the presence of halogenated phosphates was studied.

## Thermogravimetry

Introduction of phosphorus compounds into poly(vinyl alcohol)<sup>10</sup> and cellulose<sup>11</sup> results in formation of a large amount of carbonaceous residue including polyene structure on heating. Formation of the residue inhibits evolution of flammable gases, and hence these polymers have flame retardancy.

TABLE I  
Oxygen Index Testing for Treated Polyester Fabric

Flame retardant	Add-on, %	Phosphorous content, %	Halogen content, %	Oxygen index, %
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> PO (I)	4.8	0.6		24.9
	9.9	1.4		24.1
	17.0	2.3		23.0
$\begin{array}{c} (\text{CH}_2\text{CHCH}_2\text{O})_3\text{PO (II)} \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$	1.4	0.1	0.7 <sup>a</sup>	23.7
	3.9	0.3	2.0	25.0
	7.7	0.6	3.7	25.9
	11.4	0.8	5.6	28.5
$\left( \begin{array}{l} \text{ClCH}_2 \\ \diagdown \quad \diagup \\ \text{CHO} \\ \diagup \quad \diagdown \\ \text{ClCH}_2 \end{array} \right)_3 \text{PO (III)}$	5.3	0.4	2.6 <sup>a</sup>	28.1
	10.6	0.7	5.2	31.6
$\begin{array}{c} (\text{CH}_2\text{CHCH}_2\text{O})_3\text{PO (IV)} \\   \quad   \\ \text{Br} \quad \text{Br} \end{array}$	1.9	0.1	1.2 <sup>b</sup>	24.6
	6.3	0.2	4.2	28.3
	9.2	0.3	6.1	28.6
	12.0	0.5	7.9	31.6
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> PO	6.7	0.6		27.6
Original				22.4

<sup>a</sup> Cl wt-%.

<sup>b</sup> Br wt-%.

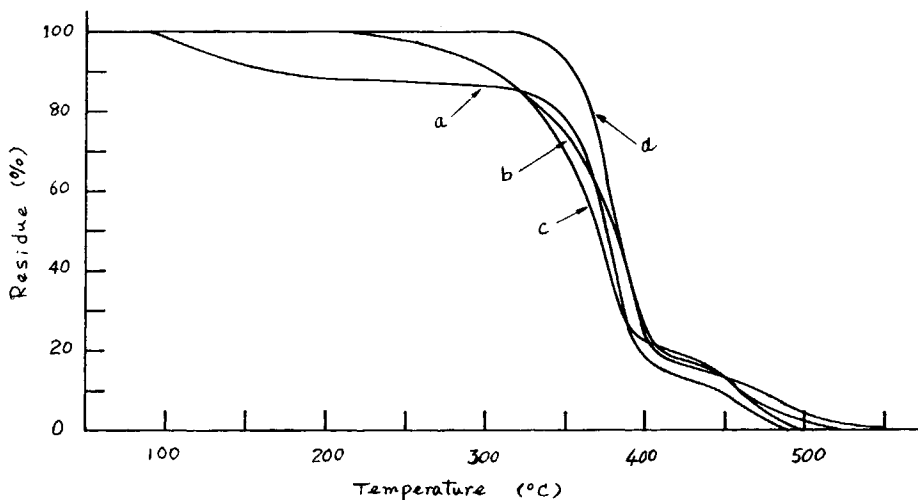


Fig. 1. Thermogravimetric curves for treated polyester fabrics: (a) treated with compound I; (b) treated with compound II; (c) treated with compound IV; (d) untreated.

Typical thermogravimetric curves of the three treated fabrics with phosphates I, II, and IV are shown in Figure 1. All the treated fabrics with phosphorus compounds decomposed at lower temperatures than the untreated and left no residue; but there were differences in detail. For the fabric treated with I, the thermal degradation proceeded in two stages. In the first, degradation occurred at a temperature of 90°C with a weight loss of 13 wt-%; a thermally pseudostable stage followed up to 320°C. The second degradation occurred at 320°C; the weight loss curve in this stage was similar to that of the untreated fabric which decomposed at 320°C. For the fabrics treated with II and IV, the thermal degradation proceeded in one stage. The degradation occurred at 210°C; the rate of weight loss was slow. These thermogravimetric behaviors were different from those reported previously for poly(vinyl alcohol)<sup>10</sup> and cellulose.<sup>11</sup>

Changes in phosphorus and halogen contents in residues on heating are listed in Table II. In the case of the fabric treated with I, no phosphorus compounds could be found in the residue at 330°C where the second degradation was proceeding; so all the added phosphate may evaporate before the second degradation occurs. This assumption is supported by the facts that the amount of the weight

TABLE II  
Phosphorus and Halogen Contents in Residual Product

Flame retardant	Phosphorus content, %			Halogen content, %		
	Untreated	330°C	390°C	Untreated	330°C	390°C
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_3\text{PO}$	2.2	0	0			
$(\text{CH}_2\text{CHCH}_2\text{O})_3\text{PO}$	1.5	0.4	0.2	10.5 <sup>a</sup>	1.0	0
$\text{Cl Cl}$ $(\text{CH}_2\text{CHCH}_2\text{O})_3\text{PO}$	0.8	0.6	0.3	12.4 <sup>b</sup>	0.8	0
<b>Br Br</b>						

<sup>a</sup> Cl wt-%.

<sup>b</sup> Br wt-%.

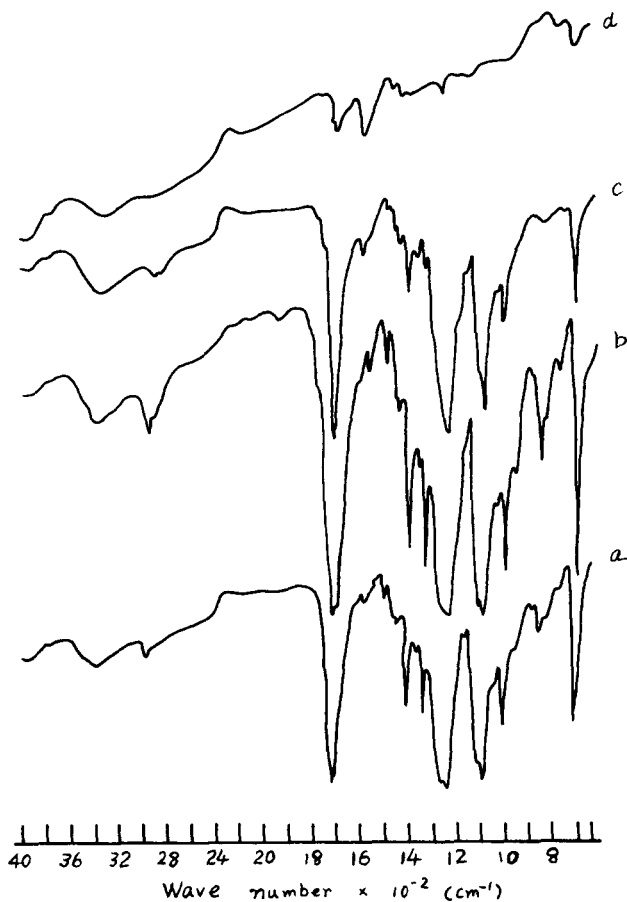


Fig. 2. Infrared spectra of residual products of polyester fabric: (a) nondegraded; (b) degraded at 360°C; (c) degraded at 420°C; (d) degraded at 450°C.

loss in the first stage is comparable to that of initially added phosphate, namely, 16 wt-%, and that the weight loss curve in the second is similar to that of untreated fabric. A considerable amount of phosphorus compounds could be found in the residues when the fabrics treated with II and IV were pyrolyzed even at 390°C, while most of the halogens were liberated before the main thermal degradation.

These results suggest that the presence of phosphorus compounds in a condensed phase above the degradation temperature of polyester fabric is essential for enhancing flame resistance and that the probability that liberated halogens from the phosphates act as a radical acceptors in the flame zone is low.

### Analysis of Degradation Products

#### *Infrared Spectrum of Residual Products*

In order to reveal the mode of action of phosphorus compounds in the thermal reactions of polyester, infrared spectra of residual products are shown in Figures 2 and 3 for polyester fabric and the treated fabric with IV, respectively.

For polyester fabric, no change could be observed up to 420°C in spite of a

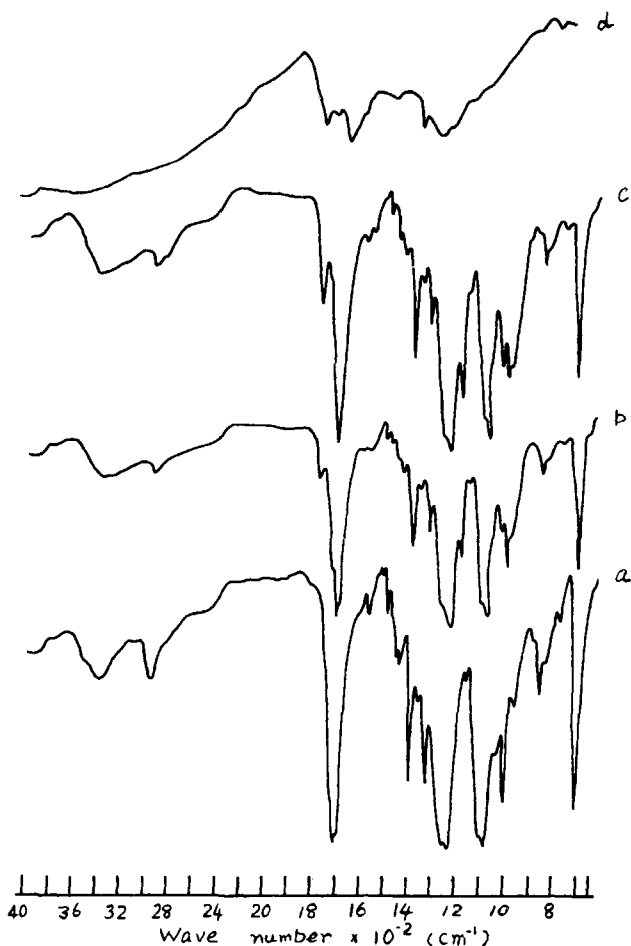


Fig. 3. Infrared spectra of residual products of the polyester fabric treated with compound IV: (a) nondegraded; (b) degraded at 360°C; (c) degraded at 390°C; (d) degraded at 420°C.

weight loss of more than 75%. At 420°C, the absorption of  $\text{CH}_2$  groups at 2958 and  $1344\text{ cm}^{-1}$  and that of  $\text{C}=\text{C}$  groups at  $1600\text{ cm}^{-1}$  became strong. At 450°C, the absorptions due to  $\text{CH}_2$ ,  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$ , and aromatic groups became less intense; the absorption of  $\text{C}=\text{C}$  groups became more intense. Similar changes were observed in the spectrum of the fabric treated with I. For the fabric treated with IV, some changes could be observed at a lower temperature of 360°C: new absorption bands at 1780, 1200, 1030, and  $990\text{ cm}^{-1}$  appeared. These bands are attributed to  $-\text{C}(=\text{O})-\text{O}-\text{CH}=\text{CH}_2$  groups. These bands could be observed in

the spectrum of the fabric treated with III.

Comparison of spectral results suggests that the presence of phosphorus compounds in a condensed phase accelerates alkyl-oxygen scission at ester links, perhaps by acid catalysis.

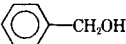
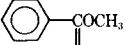
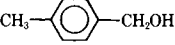
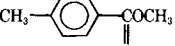
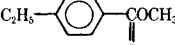
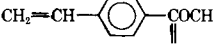
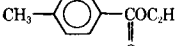

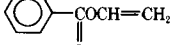

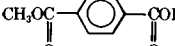
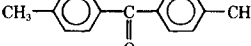
#### *GC/Mass Spectrum of Nongaseous Product*

Results of GC/mass spectrometric analyses of nongaseous products from polyester fabric and the fabrics treated with the three phosphorus compounds

I, II, and IV are listed in Table III. The main products from polyester fabric were benzoic esters, terephthalic esters, and ketones, and agree with those already reported by investigators.<sup>19-21</sup> From the fabric treated with I, degradation products, except for tripropyl phosphate, were similar to those from polyester fabric; little effect of incorporation of compound I on thermal degradation can be recognized. On the other hand, marked changes in composition could be observed for the fabrics treated with II and IV: a large amount of benzyl alcohols and little of benzoic esters and ketones. Incorporation of compounds II and IV changed the course of thermal degradation of polyester. Formation of benzyl alcohols could be detected also in degradation products from the fabric treated with ammonium phosphate (Table III), so it can be assumed that acid-catalyzed aldol condensation,<sup>22</sup> perhaps by phosphoric acid, results in the formation of benzyl alcohols from aromatic ketones.

If altering the pyrolysis reaction by aldol condensation contributes to enhanced

TABLE III  
Analysis of Nongaseous Product

Compound	Relative peak area, %				
	Original fabric	Fabric with I	Fabric with II	Fabric with IV	Fabric with NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>
	6.9	18.9	55.7	72.7	38.7
	25.9	19.3			
	1.6	8.7	8.2	12.6	17.5
	4.9	5.8			
	3.6	3.6			
	1.6	1.3			
	13.5	9.5	0.7	4.4	3.9
	15.7	8.6	23.0	2.4	11.9
	15.2	3.5			
	3.5	1.6			
	2.9	2.3	2.2		
	4.0	3.4	5.1	7.2	8.5
(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> PO		11.6			

flame resistance, the presence of phosphorus compounds as acids in a condensed phase is important; combination of halogen and phosphate is not an essential requirement. An additional experiment was carried out: nonvolatile trihexyl phosphate was used as a flame retardant. The result of the flammability test (Table I) shows that trihexyl phosphate, in spite of having no halogen, is better than compound II and comparable to IV in effectiveness.

The principal conclusions from this work are as follows: (1) The flame retardancy effect of halogen-containing phosphates such as tris(2,3-dibromopropyl) phosphate is due to its altering the pyrolysis reaction of polyester by aldol condensation. (2) The probability that liberated halogen compounds from phosphates act as radical acceptors in a flame zone may be low. (3) Incorporation of halogen elements into phosphates appear to depress evaporation of phosphates, which act as acidic catalysts in aldol condensation, from the condensed phase.

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