

# Flame Retardant Polyesters Based on Bromine Derivatives

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## Synopsis

Unsaturated polyesters containing halogens in the backbone of the polymer chain were synthesized. Derivatives used had brominated functional groups such as tetrabromobisphenol A, tetrabromophthalic anhydride, and dibromoneopentyl glycol. These were compared to chlorine-containing polyesters based on HET acid and tetrachlorophthalic anhydride and an additive exhibiting a synergistic effect of phosphorus and halogen, trichloroethyl phosphate. Optical properties before and after artificial weathering (up to 1650 hr), were determined on cast specimens, and mechanical properties (flexural strength, modulus, and hardness) and flame retardancy were determined on glass fiber laminates. The flammability tests consisted of the "oxygen index" and the "self-extinguishing time" tests, which were correlated for various halogen concentrations and different compositions. The efficiency of bromine in flame retardancy has been found to be much higher than that of chlorine. The minimal concentration of bromine required for self-extinguishing is 10–12%, as compared with 20–25% for chlorine. A general performance index for polyesters has been derived which incorporates both flame and weather resistivity factors of the modified polyesters.

## INTRODUCTION

Some methods for obtaining flame retardant polyesters were described by Namitz<sup>1</sup> and Lyons.<sup>2</sup> While the use of special additives (chlorinated paraffins, antimony, phosphorus, and halogen derivatives) was initially adopted, it was later suggested<sup>2,3</sup> that modified polyesters based on built-in reactive groups be used, in order to overcome the gradual diffusion of the additives into the atmosphere. On the other hand, there exists a distinct deterioration of optical and mechanical properties upon aging<sup>4</sup> which is only aggravated by the halogen derivatives.

The flammability mechanism of polyesters and other polymeric systems has been extensively analyzed in the literature,<sup>5–10</sup> as was the specific role of the halogens in flame retardancy.<sup>1,2,5,11–13</sup> It is claimed that the halogens serve as free-radical scavengers, converting the radicals produced during the burning of the polymer into halide radicals of lower activity. It has been stated that the brominated products have an advantage over their chlorinated counterparts<sup>2</sup> due to the weaker bond strength of the former (65 kcal/mole in the Br—C bond compared with 81 kcal/mole for the Cl—C bond).

The problem of the weathering resistance of polyesters and other useful polymers has been the target of many researchers.<sup>14–17</sup>

In this work both the flame retardancy and weather resistance were investigated in an attempt to reach an optimal balance of properties. Flame retardancy was imparted to the system by means of reactive bromine derivatives built into the main skeleton of the polymer chain.

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TABLE I  
 Polyester Compositions

Reactive material	Mole ratio				Halogen, wt-%	Cooking time, hr	Final acid number
	Reactive material	Phthalic anhydride (PA)	Maleic anhydride (MA)	Propylene glycol (PG)			
None	0	1	1	2.05	0	5.5	48
TBBP-A	0.05	1	1	2.03	3	8	49
	0.12	1	1	1.97	6	6	56
	0.15	1	1	1.78	7.8	8	50
	0.2	1	1	1.9	10	7	56
	0.28	1	1	1.82	13	8.25	53
	0.33	1	1	1.77	15	8.25	48
	0.39	1	1	1.71	17	8	25
TBPA	0.12	0.88	1	2.05	6	12	51
	0.15	0.85	1	2.05	8	10	40
	0.2	0.8	1	2.05	10	6	52
	0.24	0.76	1	2.05	12	7	51
	0.29	0.71	1	2.05	14	8	55
	0.34	0.66	1	2.05	16	5	53
TCPA	0.43	0.57	1	2.05	10	10	50
	0.58	0.42	1	2.05	13	10	52
	0.68	0.32	1	2.05	15	10	41
	0.79	0.21	1	2.05	17	10	39
	0.96	0.04	1	2.05	20	10	38
	1.0	0	1	2.05	20.6	10	

## EXPERIMENTAL

Three modified polyesters based on the following bromine derivatives were prepared: tetrabromophthalic anhydride (TBPA), tetrabromobisphenol A (TBBP-A), and dibromoneopentyl glycol (DBNPG). Their behavior at various bromine contents was compared with that of polyesters based on chlorine derivatives—HET acid (chlorendic anhydride) and tetrachlorophthalic anhydride (TCPA)—and an unmodified polyester to which trichloroethyl phosphate (TCEP) was incorporated.

The basic polyester is made with propylene glycol and phthalic and maleic anhydrides, all in stoichiometric ratios, with a 5% excess of the glycol. At the end of the polymerization reaction (acid number less than 50), the resin was diluted with 30% by weight styrene monomer. In the modified polyesters the original acid or alcohol was partially replaced by the equivalent halogen derivative at the desired halogen concentration. Details on the various compositions are given in Table I. Crosslinking was performed with the aid of 2% methyl ethyl ketone peroxide and 0.5% cobalt naphthenate. Both clear casts (2 mm thick) and laminates with glass fiber (by hand lay-up) were prepared. Glass cloth was used when evaluating mechanical properties and weathering resistance, while glass mat served in the fire test samples.

### Mechanical Properties

Modulus and strength in flexure were chosen as representing the contribution of the polymer matrix to the laminate. These were tested according to ASTM 790 on a Hounsfield Tensometer. Hardness was also measured, according to ASTM-2583, using a Barcol Impressor Model 934.

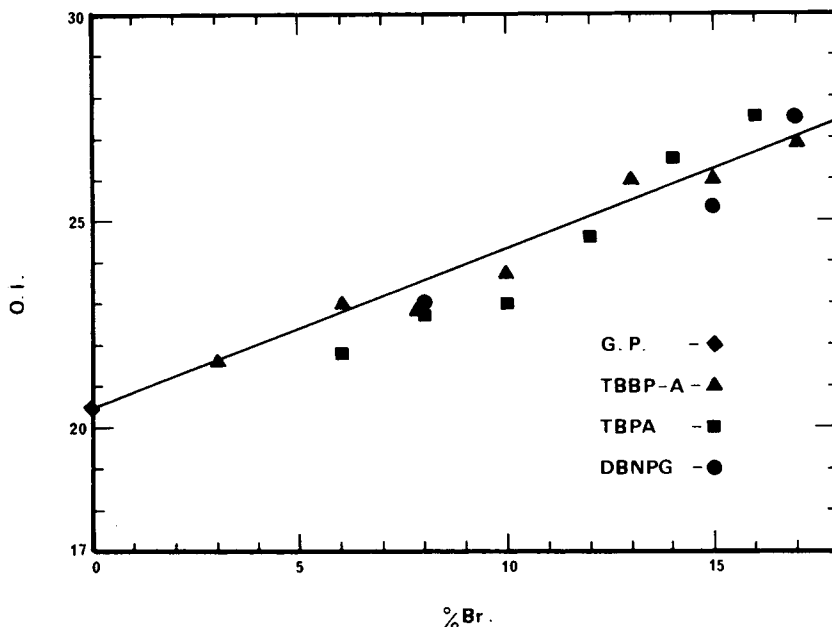


Fig. 1. Correlation between *O.I.* and percent bromine in polyester.

### Optical Properties

Transmission of visible light through clear, cast resin plates (unreinforced) was measured on a Beckman DB spectrophotometer in the wavelength range of 320–800 nm. Transmittance at 700 nm (the region of the peak) was frequently taken as representative for performance evaluation. The optical density

$$O.D. = \log I_0/I$$

where  $I$  represents the intensity of transmitted light relative to  $I_0 = 100\%$ , was utilized as a criterion for resistance to weathering effects. Low values for *O.D.* are obviously desired.

### Fire Tests

Flame retardant properties were measured by either the “self-extinguishing time” (ASTM D635) or by the “oxygen index” (ASTM 2853) method. In the first test the major task was to measure the time elapsed between removal of the bunsen burner and complete self-extinguishing of the sample. This was taken as the average time for 10 standard specimens of 5-in. length each. Satisfactory results are considered when these times are below 60 sec.

The “oxygen index” test was first offered by Fenimore and Martin<sup>18</sup> and later modified and discussed by others.<sup>19–23</sup> It is defined as the minimum volumetric fraction of oxygen in an  $O_2-N_2$  blend required to support the flame under the specified conditions, about 3 min prior to extinguishing. The linear velocity of the gas was fixed at  $4 \pm 1$  cm/sec, and the samples were 10 cm long, 6 mm wide, and 2 mm thick. The instrument was built according to the modifications suggested by Learmouth and Twaite.<sup>19</sup>

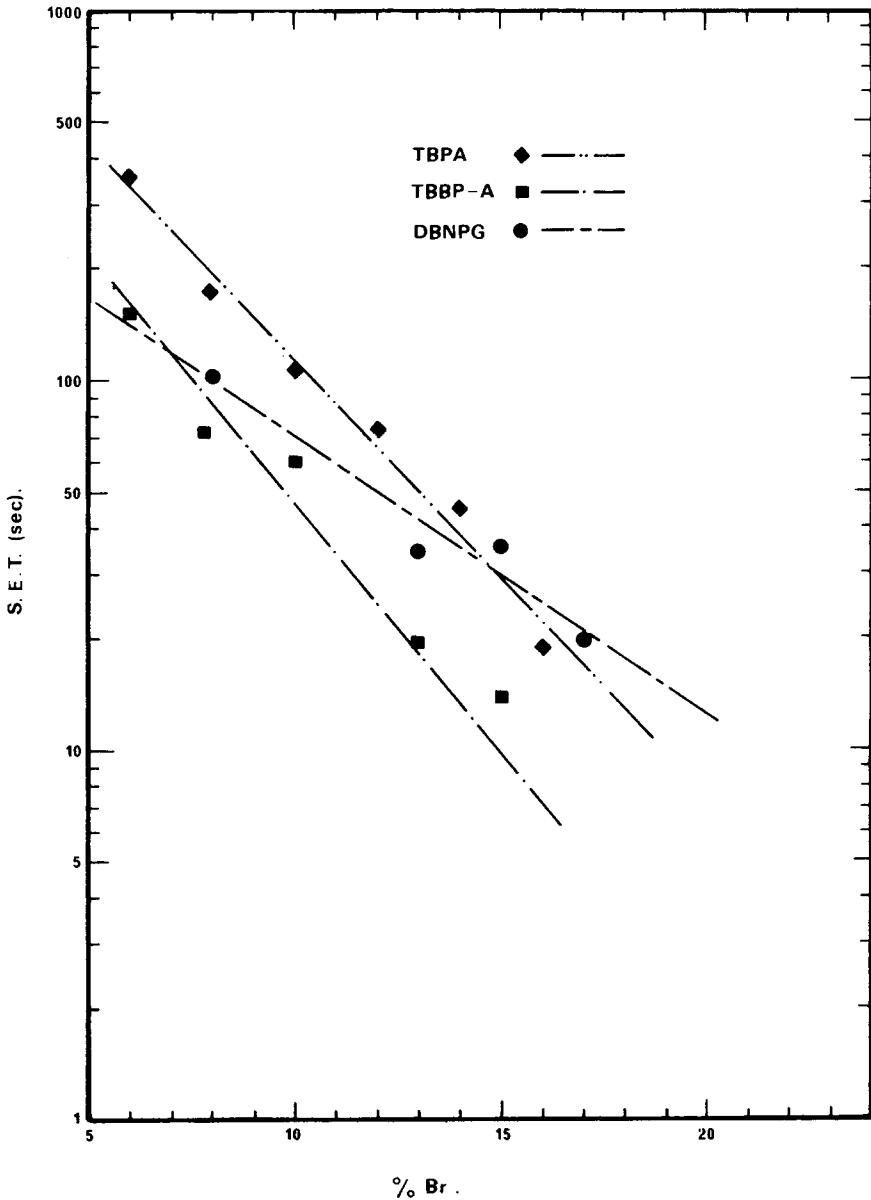


Fig. 2. Correlation between S.E.T. and percent Br in Polyester.

### Weathering

Accelerated weathering was performed in an Atlas xenon-lamp Weather-Ometer (WOM, 2.5kw). The cycle consisted of 5 min of "rain" every hour. Samples were exposed for periods of up to 1650 hr, with intermediate observations. Natural weathering was performed on a rack on the roof of the Faculty building, Technion City, Haifa, inclined at 45° to the horizontal and directed toward the south, for periods of 4, 8, and 11 months. Effects on mechanical and optical properties as well as microscopic studies of structural failures in the scanning electron microscope (Jeol Model JSM-03) served as indicators for the role of polymer composition in weather resistance.

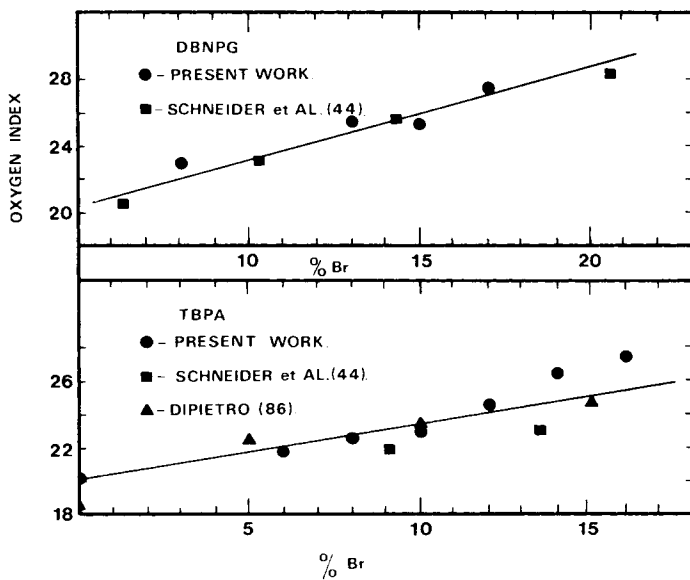


Fig. 3. Comparison of *O.I.* values of the present work and data from the literature: (●) present work; (■) Schneider et al.<sup>24</sup>; (▲) Di Pietro.<sup>25</sup>

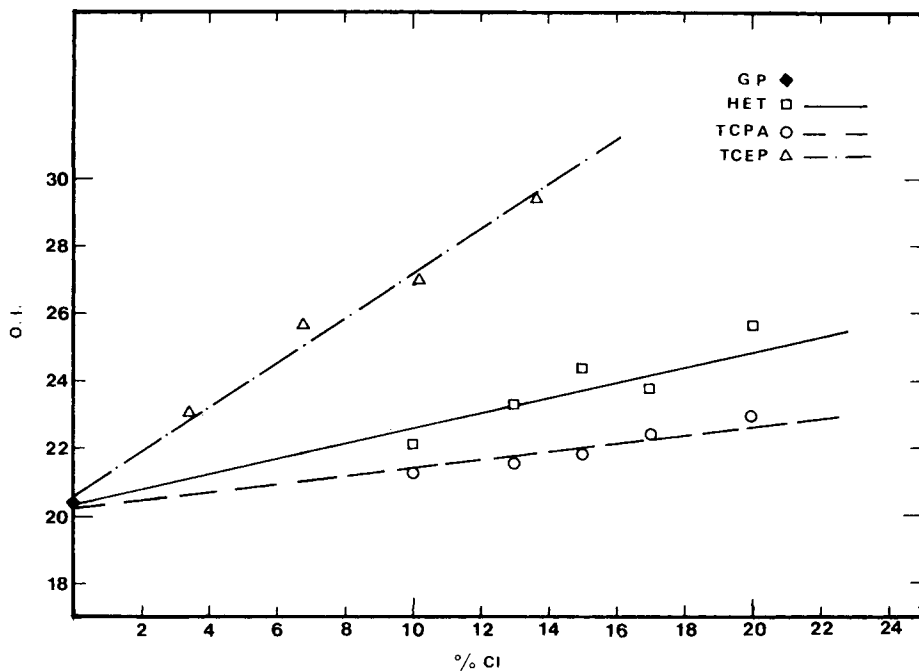


Fig. 4. Correlation between *O.I.* and percent chlorine in polyester. (◆) GP; (□) HET; (○) TCPA; (△) TCEP.

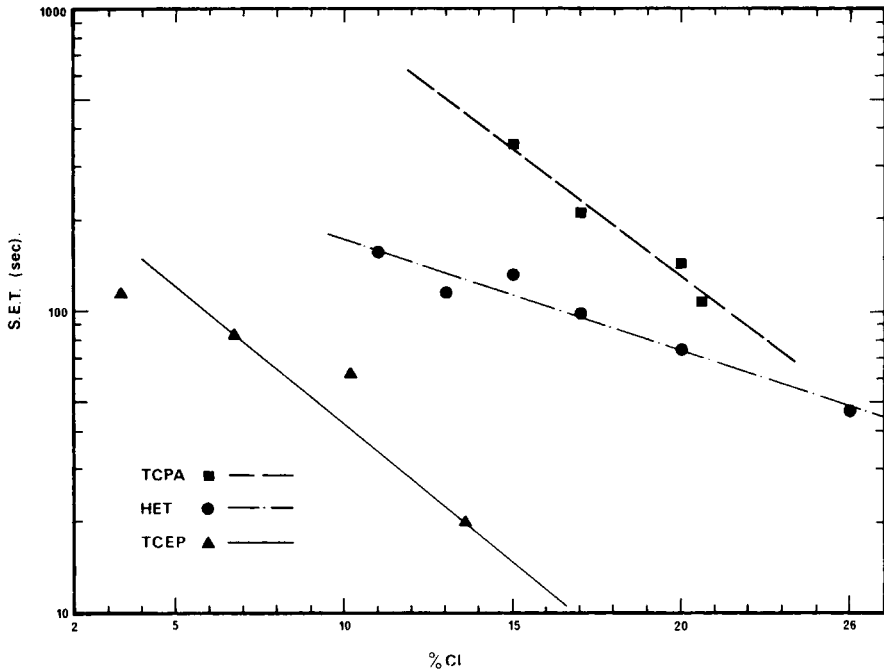


Fig. 5. Correlation between S.E.T. and percent chlorine in polyester. (■) TCPA; (●) HET; (▲) TCEP.

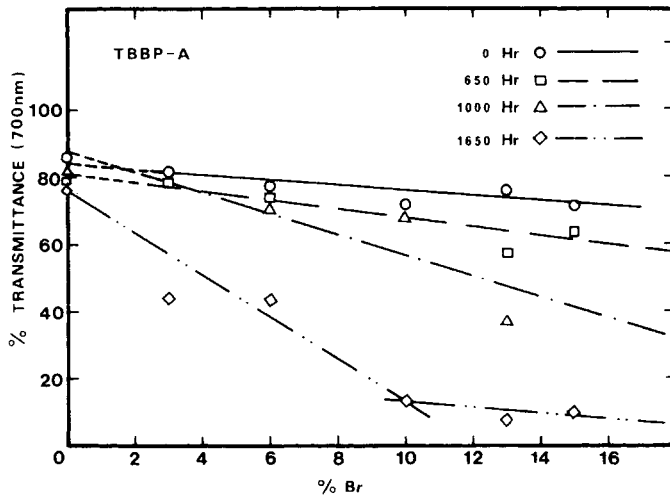


Fig. 6. Dependence of light transmittance at 700 nm on percent Br in polyester containing TBBP-A: (○—) 0 hr; (□—) 650 hr; (△—) 1000 hr; (◇—) 1650 hr.

## RESULTS AND DISCUSSION

### Flame Retardancy

The relationship between the bromine content of the modified polyesters and the oxygen index of their laminates is shown in Figure 1. A linear correlation

TABLE II  
Fire Properties of the Polyester Compositions

Reactive material	Halogen wt-%	Self-extinguishing time (S.E.T.), sec	Oxygen index ( <i>O.I.</i> )
None	0	burns	20.4
TBBP-A	3	burns	21.6
	6	150	23.0
	7.8	72	22.8
	10	60	23.7
	13	19.5	26.0
	15	14	26.0
TBPA	17	3.8	26.9
	6	354	21.8
	8	174	22.7
	10	108.3	23.0
	12	75.4	24.6
	14	45.3	26.5
TCEP	16	18.7	27.5
	3.4	116.3	23.1
	6.8	84.5	25.7
	10.2	62.5	27.0
TCPA	13.6	19.7	29.4
	10	burns	21.3
	13	burns	21.5
	15	353	21.8
	17	213	22.4
	20	143	23.0
HET	20.6	107	24.1
	10	154.5	22.1
	13	116	23.3
	15	131	24.4
	17	99	23.8
	20	75	25.7
DBNPG	25	46.7	28.0
	8	103	23.0
	13	34.9	25.5
	15	36	25.3
	17	19.7	27.5

(calculated by least-squares analysis) between the *O.I.* and percent bromine does not differentiate between the three modified polyesters (with some scatter). However, the S.E.T. flame test results are described by three straight lines on semilog coordinates, as shown in Figure 2. Increasing the bromine content results in a decrease in the S.E.T., with the lowest S.E.T. values obtained from TBBP-A and the highest from TBPA, while DBNPG lies in-between, except at higher bromine contents. It is interesting to compare these results with other data published in literature for the *O.I.*-Br correlation, Figure 3.<sup>24,25</sup> Similar correlations for chlorine-containing polyesters are shown in Figures 4 and 5. More details are given in Table II.

While low values of *O.I.* in the range of 15 were found for some untreated polymers, the natural limiting value is obviously 21 (equivalent to the oxygen

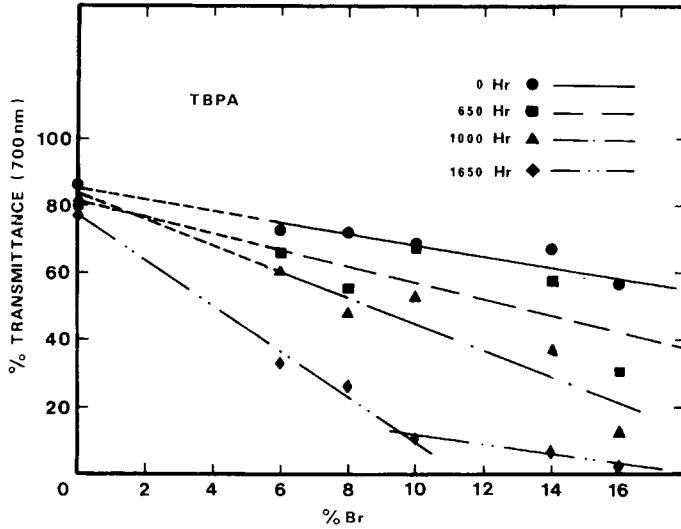


Fig. 7. Dependence of light transmittance at 700 nm on percent Br in polyester containing TBPA: (●—) 0 hr; (■—) 650 hr; (▲—) 1000 hr; (◆—) 1650 hr.

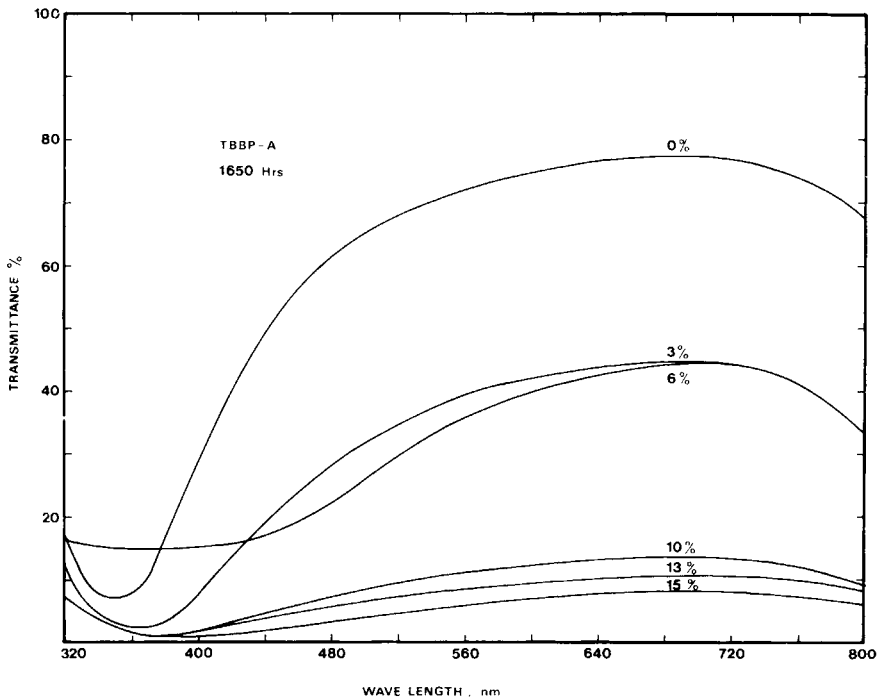


Fig. 8. Light transmittance spectra of polyester containing TBBP-A after 1650 hr in WOM.

content of air). However, higher values are needed for acceptable fire protection. In this work a critical value, S.E.T. = 60 sec, was chosen. This is equivalent to an *O.I.* of 26.0 for the bromine derivatives and implies concentrations of bromine exceeding 13–14%. Utilizing the same criterion for chlorine-modified polyesters



TABLE III  
Percent Light Transmittance at 700 nm for Polyester Castings

Reactive material	Halogen, wt.-%	0 <sup>a</sup>	Percent light transmittance		
			650 <sup>a</sup>	1000 <sup>a</sup>	1650 <sup>a</sup>
None	0	86	80	82	77
TBBP-A	3	82	79	81	44.5
	6	77.5	74	71	44
	10	72	72	68	14
	13	76	57	37	8
	15	72	64	—	10.5
TBPA	6	72.5	66	60	33
	8	72	55	48	26
	10	69	67	53	10.5
	14	67	58	37	7
	16	57	31	13	3
TCEP	3.4	74.5	43 <sup>b</sup>	72	—
	6.8	82	69	74	—
	10.2	79	68	62	—
	13.6	78.5	72	78	—
TCPA	10	70	40 <sup>b</sup>	10	—
	13	77	43	18	—
	15	70	19	12	—
	17	79.5	5	2	—
	20	81	8	4	—
HET	10	78	63 <sup>b</sup>	53	—
	13	84	46	34	—
	15	83.5	66	11	—
	17	85	71	9	—
	20	82	55	9	—

<sup>a</sup> Hours in Weather-Ometer (WOM).

<sup>b</sup> After 525 hr in WOM.

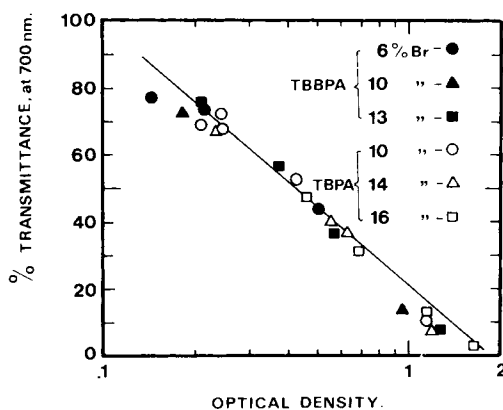


Fig. 9. Correlation between *O.D.* and light transmittance at 700 nm.: TBBP-A-(●) 6% Br; (▲) 10% Br (■) 13% Br; TBPA-(○) 10% Br; (△) 14% Br; (□) 16% Br.

(*O.I.* = 26.0 for HET) requires about 20% chlorine for equivalent performance. The fire performance of TBBP-A seems better than that of TBPA at the same percent bromine, as can be seen in Table II. The use of TBPA flame retardant polyesters was also mentioned by others.<sup>26-29</sup> Among the chlorine derivatives, the additive TCEP exhibits the best results as a flame retardant, through the

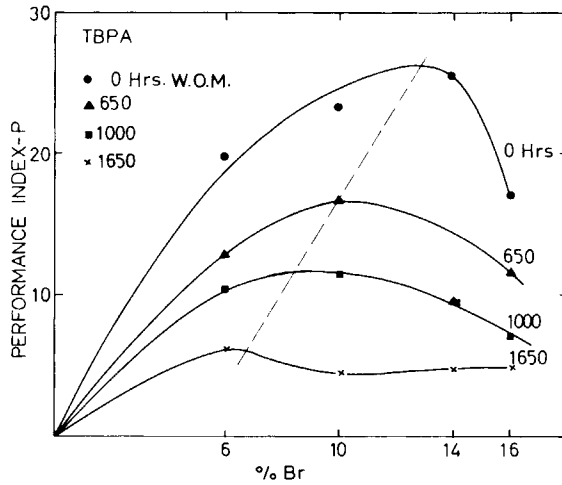


Fig. 10. Dependence of performance index on percent Br in TBPA-containing polyester, after exposure to WOM for zero to 1650 hr.

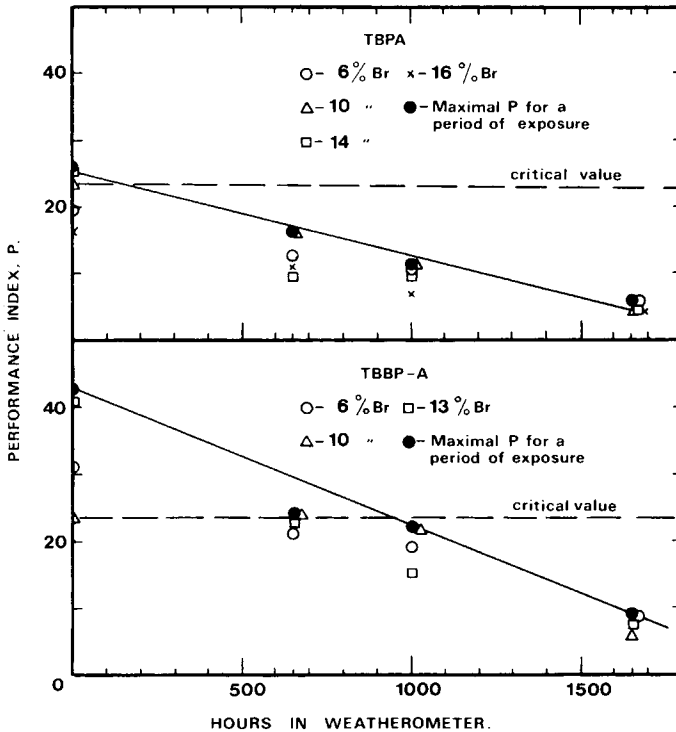


Fig. 11. Dependence of performance index on WOM time for TBBP-A- and TBPA-containing polyesters. TBPA; (O) 6% Br; ( $\Delta$ ) 10% Br; ( $\square$ ) 14% Br; (x) 16% Br; TBBP-A; (O) 6% Br; ( $\Delta$ ) 10% Br; ( $\square$ ) 13% Br. ●, Maximal P.

dual (synergistic) effect of Cl and P. By drawing horizontal lines in Figure 4, the equivalence between chlorine and phosphorus is roughly estimated as 1% P = 8.5% Cl. When  $O.I. = 23.0$ , 12% Cl in HET or 3.4% Cl plus 1% P in TCEP are required. On the other hand, the use of TCEP has severe drawbacks due to its leaching out upon exposure to weather. It also reduces the mechanical

TABLE IV  
Optical Density of Various Polyester Compositions After Accelerated Weathering

Reactive material	Halogen, wt-%	0 hr <sup>a</sup>	Optical density		1650 hr <sup>a</sup>
			650 hr <sup>a</sup>	1000 hr <sup>a</sup>	
None	0	—	0.156	0.134	0.179
TBBP-A	3	0.140	0.195	0.181	0.451
	6	0.148	0.216	0.238	0.505
	10	0.182	0.234	0.255	0.968
	13	0.212	0.371	0.582	1.237
	16	0.236	0.402	0.634	1.268
TBPA	6	0.198	0.306	0.372	0.641
	10	0.211	0.296	0.431	1.142
	14	0.236	0.402	0.634	1.268
	16	0.466	0.684	1.120	1.637
TCEP	3.4	0.19	0.48 <sup>b</sup>	0.208	—
	6.8	0.155	0.225	0.195	—
	10.2	0.168	0.23	0.275	—
	13.6	0.17	0.208	0.173	—
TCPA	10	0.22	0.512 <sup>b</sup>	1.28	—
	13	0.178	0.48	1.0	—
	15	0.22	0.98	1.7	—
	17	0.167	1.48	1.62	—
	20	0.16	1.36	1.5	—
HET	10	0.175	0.27 <sup>b</sup>	0.355	—
	13	0.145	0.44	0.62	—
	15	0.147	0.245	1.25	—
	17	0.14	0.212	1.3	—
	20	0.155	0.34	1.3	—

<sup>a</sup> Hours in Weather-Ometer (WOM).

<sup>b</sup> After 525 hr in WOM.

properties since it acts as a plasticizer. The use of TCPA is limited, due to its low chlorine content, even when all the PA in the resin is replaced by TCPA. In this case, only a synergistic additive will be useful.

It is interesting to note that for equivalent fire retardancy the weight of chlorine required is about twice that of bromine, which means about 4:1 on a molar basis.

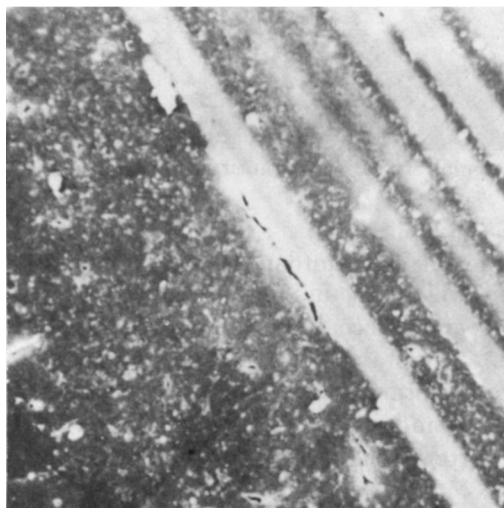


Fig. 12. Electron micrograph of general-purpose polyester after 1650 hr in WOM.

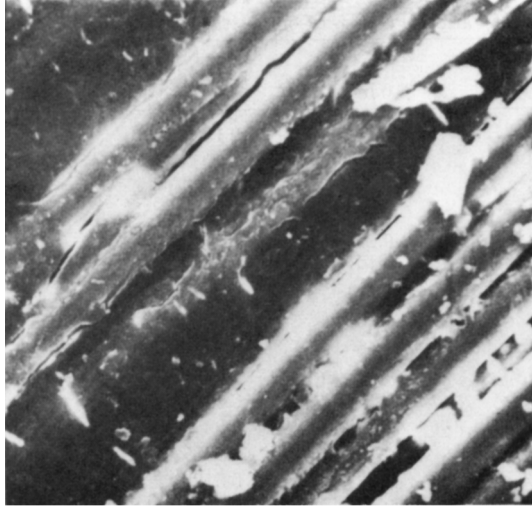


Fig. 13. Electron micrograph of TBBP-A-modified polyester containing 10% Br after 650 hr in WOM.

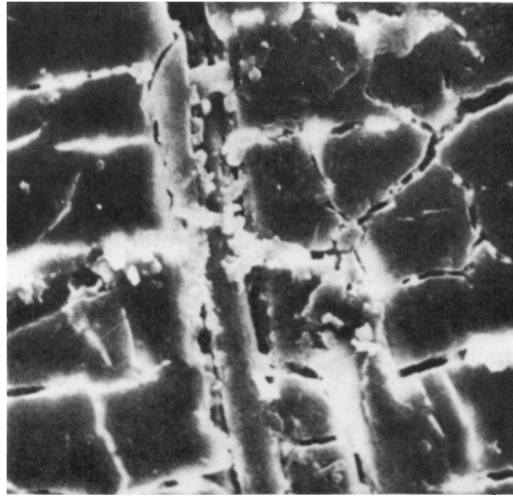


Fig. 14. Electron micrograph of TBBP-A-modified polyester containing 10% Br after 1000 hr in WOM.

Both methods for testing fire retardancy are satisfactory. The O.I. represents a universal criterion, which is found to be reliable and reproducible for most materials, including foams and coatings. It was also correlated with the specific heat of combustion.<sup>8</sup> The standard conditions (flow rate of gases, dimensions of the sample, and temperature of the test) must be closely followed. The S.E.T. method is more specific and sensitive but is limited to rigid materials only and suffers from some scatter of the results, thus calling for a large number of test samples.

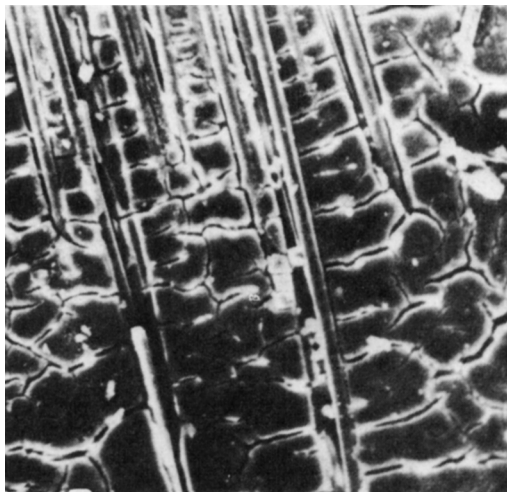


Fig. 15. Electron micrograph of TBBP-A-modified polyester containing 10% Br after 1650 hr in WOM.

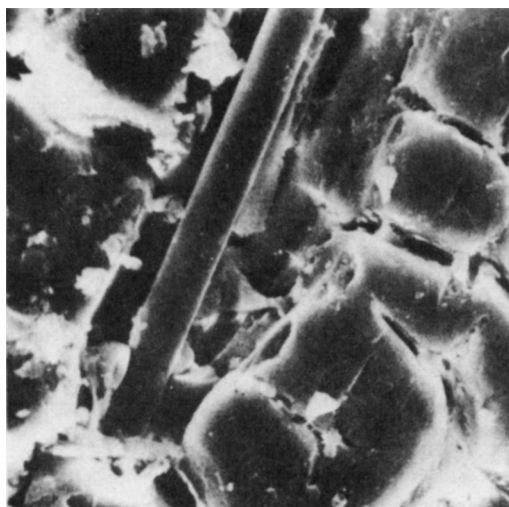


Fig. 16. Electron micrograph of TBBP-A-modified polyester containing 13% Br after 1650 hr in WOM.

### Weathering Resistance

Light transmittance at 700 nm served as a sensitive indicator for the effect of weather on the Br-modified polyesters. Figures 6 and 7 verify the effect of exposure time in the Weather-Ometer (WOM) at various bromine contents. An increase of bromine in the composition decreases the light transmittance and at the same time enhances the sensitivity to UV radiation. Again, the performance of TBBP-A surpasses that of TBPA. Typical visible light transmittance spectra for TBBP-A polyesters are shown in Figure 8 after 1650 hr in the Weather-Ometer. The deleterious effect of bromine on the system is remarkable. Table III summarizes the weatherability of various halogen-modified polyesters. The Cl derivatives are even more sensitive to weathering effects than the Br derivatives.

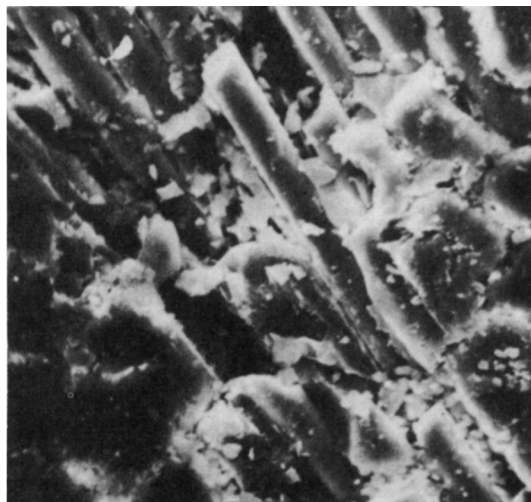


Fig. 17. Electron micrograph of TBBP-A-modified polyester containing 17% Br after 1000 hr in WOM.

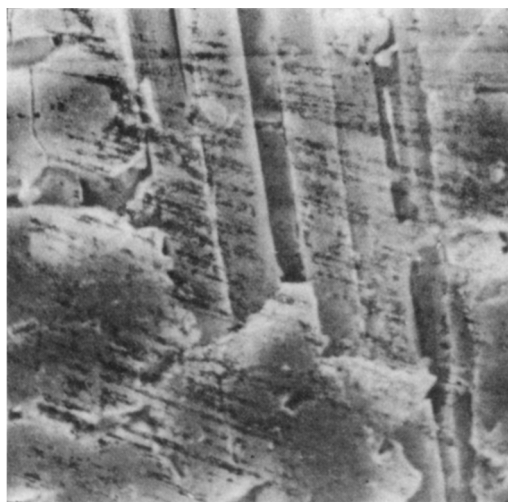


Fig. 18. Electron micrograph of TBPA-modified polyester containing 10% Br after 1650 hr in WOM.

### Performance Index

In order to express the combined effects of flame and weather resistance, an arbitrary performance index  $P$  is proposed:

$$P = \frac{10}{\log (\text{S.E.T.}) \cdot (O.D.)_t}$$

wherein S.E.T. represents the sensitive criterion for fire retardancy, while  $(O.D.)_t$  (the time-dependent optical density during artificial weathering) was chosen to represent the change in light transmittance. Data for  $O.D.$  are given in Table III and in Figure 9, in which the optical density is related to the light transmittance at 700 nm. There is a small decrease in S.E.T. with exposure time (prob-

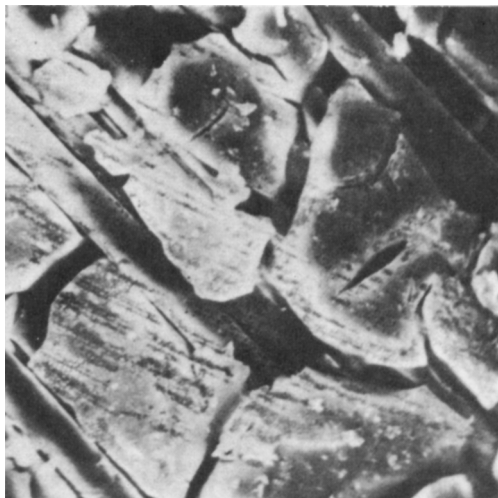


Fig. 19. Electron micrograph of TBPA-modified polyester containing 16% Br after 1650 hr in WOM.



Fig. 20. Electron micrograph of TBBP-A-modified polyester containing 17% Br after eight months of natural weathering.

ably due to advanced crosslinking), but its effect on the performance index is not significant.

The performance index offers an absolute numerical value which takes into account the contradictory effects of the halogen content on flame retardancy and weathering resistance. Figures 10 and 11 show typical values for  $P$  as a function of bromine content and exposure time in the Weather-Ometer.

The performance index exhibits a maximum value that serves as an optimum peak, which varies with the bromine content and the exposure time. The decrease in  $P_{\max}$  with exposure time results from the controlling effect of the weatherability on the general performance.

If we choose critical values of 60 sec for S.E.T. and a light transmittance limit of 70%, one obtains a critical value for the performance index of  $P = 23.5$ . Figure 11 demonstrates the importance of utilizing  $P_{\text{crit}}$  as a sensitive estimate for the

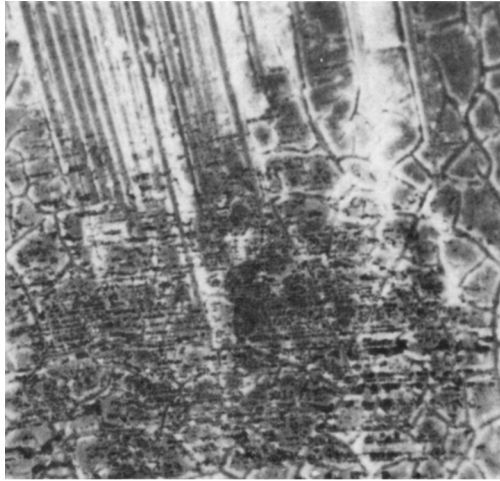


Fig. 21. Electron micrograph of TBBP-A-modified polyester containing 17% Br after 11 months of natural weathering.

predicted lifetime of some modified polyesters. The advantage of TBBP-A over TBPA is apparent. However, as indicated, the performance index was arbitrarily chosen as a product of two parameters, so that various combinations of these may appear. In spite of its limitations, it serves its purpose as a rough quantitative characterization of the general performance.

### **Mechanical Properties**

Moduli and flexure strength of all halogen-modified polyesters (reinforced with glass fiber) were about 10% lower than for the unmodified polyesters. On exposure in the Weather-Ometer, various simultaneous reactions take place: postcuring, which enhances modulus and strength, together with photolysis, which causes emission of HBr and eventually chain scission (the latter effect shows up at higher values of Br).

In general, the mechanical properties of these reinforced polyester samples are not suitable as sensitive criteria for failure when compared with optical properties and surface analysis criteria. However, at high Br concentrations, there exists a marked decrease in mechanical properties.

### **Analysis of Surface Failure by Means of Scanning Electron Microscopy**

The use of SEM for surface analysis provides a valuable tool for performance evaluation. Various combinations of modified polyester castings, after exposure to either accelerated or natural weathering, demonstrate the progress of failure: cracking of the polymeric layer above the fibers, delamination of the fibers, and finally complete breakdown of the top layer and separation of phases. A series of selected photographs clearly demonstrates this process, Figures 12–21. The effect of the presence of bromine in reducing weatherability is clearly seen. There seems to be a general similarity between the type and progress of surface failures for both the naturally and the accelerated weathered polyesters with an approximate acceleration ratio of 1:8 (1000 hr in WOM, equivalent to 11 months on the roof). This is comparable to the correlation of 1:6 found by Blaga et al.<sup>30</sup>



## CONCLUSIONS

1. 10–12% Br or 20–25% Cl is required in order to achieve adequate flame retardancy in the modified unsaturated polyester samples.

2. The performance of the modifiers, in descending order, was found to be TBBP-A, DBNPG, HET, TBPA, TCPA, and TCEP. Both acids and glycols were partially replaced by the reactive substitutes. The replacement of the styrene monomer by bromostyrene was not investigated. It was, however, recently mentioned in the literature.<sup>31,32</sup>

3. The presence of the halogen derivative significantly reduces the weathering resistance of the polyester. The most sensitive properties are the optical and surface properties.

4. A useful performance index was proposed, serving as quantitative characteristic of general behavior.

5. In practice, performance may be improved by utilizing synergistic components (P or Sb), pigments, UV absorbers, and gel coats in addition to replacement of the styrene monomer.

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