

## **Influence of Structural Effects of Halogen and Phosphorus Polyol Mixtures on Flame Retardancy of Flexible Polyurethane Foams**

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### **Synopsis**

The role of mixtures of reactive bromine and phosphorus flame-retardant polyol intermediates as well as the individual bromine and phosphorus reagents in suppressing combustion of flexible polyurethane foams was investigated by means of the oxygen index flame test and charring techniques. Bromine alone appears to contribute to flame retardancy in the solid as well as the vapor phase. A substantial portion of the bromine from both aliphatic and aromatic bromide flame retardants was accounted for in the char, and this is also true when phosphorus is present. Ionic bromine appears to be the most effective elemental form. Like phosphorus, bromine alone in foams is also observed to increase the yield of char. Aliphatic bromide in mixture with phosphonate or phosphate gave enhanced flame retardancy, whereas, mixtures with phosphite are not beneficial. Maximum flame retardancy and char yields correlate well for bromine mixed with phosphate and phosphonate, whereas the relationship does not hold with phosphites. Charring experiments at 500°C with foams containing both phosphorus and bromine generally afforded a constant P/Br ratio, suggesting a specific chemical interaction for flame retardancy. Phosphate flame-retardant efficiency was sensitive to concentration of phosphorus in the foams. On the other hand, phosphonate and phosphite exhibited a constant level of fire resistance at phosphorus levels greater than 0.3%.

### **INTRODUCTION**

It is well known that halogen contributes to flame-resistant properties of polyurethanes when used in combinations with phosphorus-containing reagents. It is commonly believed that their combined action is synergistic, i.e., producing greater flame retardancy than would be seen from cumulative additive effects of the individual reagents.<sup>1,2</sup> In spite of these claims, however, there is little evidence in the literature of an effort to explain either the high flame-retardant efficiency of phosphorus-halogen compounds or, in fact, whether true synergism is involved. The present study was undertaken to gain an insight into the various factors which explain how or why bromine polyols contribute to flame retardancy when used with phosphorus-containing polyols as a first step toward an understanding of the concept of synergism.

In order to determine how mixtures of bromine and phosphorus materials contribute to flame retardancy, it was decided to first evaluate the effect of the flame-retardant reagents themselves. Thus, this study is divided into three distinct phases: (1) a study of aliphatic and aromatic bromine-containing polyols, (2) an investigation of the effect of phosphate, phosphonate, and phosphite polyols, and (3) a study of the combined effect of (1) and (2).

## EXPERIMENTAL

### Flame-Retardant Reagents

**Aliphatic Bromides.** The aliphatic organic bromide diol, 2,2-bis(bromomethyl)-1,3-propanediol, more commonly known as dibromoneopentyl glycol (DBNG), was purchased from the Dow Chemical Company and used without further purification (mp 109–110°C). In view of its solid nature and in order to facilitate blending of the foaming components this bromide was predissolved in the polyether polyol NIAX Polyol LG-56) by heating a mixture at 70°C for 1.5 hr to give an 18 wt-% solution. Then, as required, this stock solution was blended with additional polyether polyol to obtain the desired proportion of flame retardant in the foams.

**Aromatic Bromides.** An aromatic bromide triol was prepared by propoxylating a reaction product of tetrabromophthalic anhydride (Michigan Chemical Corporation) and a typical flexible-foam polyether polyol, NIAX Polyol LC-60 (Union Carbide Corporation), as follows.

Sodium acetate, 2.4 g, and 3000 g (1.0 mole) of NIAX Polyol LC-60 (an alkylene oxide adduct of glycerin containing largely primary hydroxyl endgroups with OH number about 60 mg KOH/g) were placed in a previously dried 5-liter four-necked flask equipped with a stirrer, thermometer, dropping funnel, and reflux condenser. The contents of the flask were kept under a positive pressure of dry nitrogen and heated to 100°C. Tetrabromophthalic anhydride, 576 g (0.535 mole), was added portionwise during 25 min, and then 2.1 g stannous octoate was added. The reaction mixture was heated for 5 hr at 100°, after which propylene oxide was added until the oxide commenced to reflux; uptake, 74 g (1.22 mole). The reaction mixture was then heated at 83° and 1 mm pressure to remove volatiles. Analysis revealed the following properties: bromine, 11.91%; hydroxyl number, 42.80 mg KOH/g; acid number 0.337 mg KOH/g; viscosity, 1832 cps at 25°C; Gardner color, 1.

**Phosphorus-Containing Reagents.** Studies were conducted on three different commercially available phosphorus-containing flame-retardant polyols, a phosphate, a phosphonate, and a phosphite. The properties of these reagents are summarized in Table I.

### Foaming Procedure

Flexible foams used in this study were produced in 14 × 14 × 6-in. cardboard boxes using the standard one-shot hand-batch technique based

TABLE I  
Properties of Phosphorus Polyols Investigated

Chemical identification	OH No., mg KOH/g	P, %
Phosphate-containing polyol	300	11.1
Diethyl-N,N-bis(2-hydroxyethyl)- aminomethylphosphonate	440	12.2
Tris(dipropylene glycol)phosphite	395	7.1-7.3

on 500 g polyol. Formulations were standardized as follows (in parts by weight): NIAX Polyol LG-56, 100; water, 4; silicone surfactant, 0.5; NIAX Catalyst A-1, 0.1; NIAX Isocyanate TDI, varied; and stannous octoate, varied; the isocyanate index is 105. The blend of flame retardant and polyol, the surfactant, and the isocyanate were weighed into a  $\frac{1}{2}$ -gal container, fitted with a baffle, and stirred for 60 sec with a high-speed stirrer at 2700 rpm. The mixture was allowed to stand for 15 sec, and then stirring was continued for another 15 sec. During the 15-sec stirring period, but after 5 sec had elapsed, a solution of the NIAX Catalyst A-1 in the water was added, and after 10 sec the stannous octoate was added from a syringe. When the 15 sec of stirring was complete, the mixture was quickly poured into the mold, whereupon the mass foamed. The cream and rise times were recorded. The foams were allowed to stand at ambient laboratory conditions for two days before testing.

#### Flammability Tests

The oxygen index flammability test was essentially conducted as described in ASTM Method D2863-70.<sup>3</sup> The foam sample size for the oxygen index determination was  $2 \times \frac{1}{2} \times 6$  in., the dimensions used by ASTM D1692-67T. Specimens were supported by the device's fork holder, and the samples were ignited by means of the flammability tester's propane torch. For reignition, samples were cut to expose fresh surface. Before ignition, each foam specimen was allowed to stand in the oxygen index apparatus for 2-3 min to permit time for the gaseous mixture to diffuse into the cells of the foam.

#### Charring Procedure

Laboratory-size flexible foam buns ( $13 \times 13 \times 8$  in.) were allowed to age for one week at ambient conditions prior to cutting for pyrolysis samples. Charring was carried out in air to be consistent with normal combustion conditions. Because the amount of char produced could be related to the charring procedure, a consistent technique was employed. Prior to the actual charring, 2.5-3.0 g and 5-6 g samples for the lower and higher charring temperatures, respectively, were rolled and inserted in a 100-ml capacity (2 in. high with 2.5 in. top diameter) crucible and heated to 50°C in a vacuum oven to constant weight. The specimen size used was  $0.5 \times 2 \times 6$

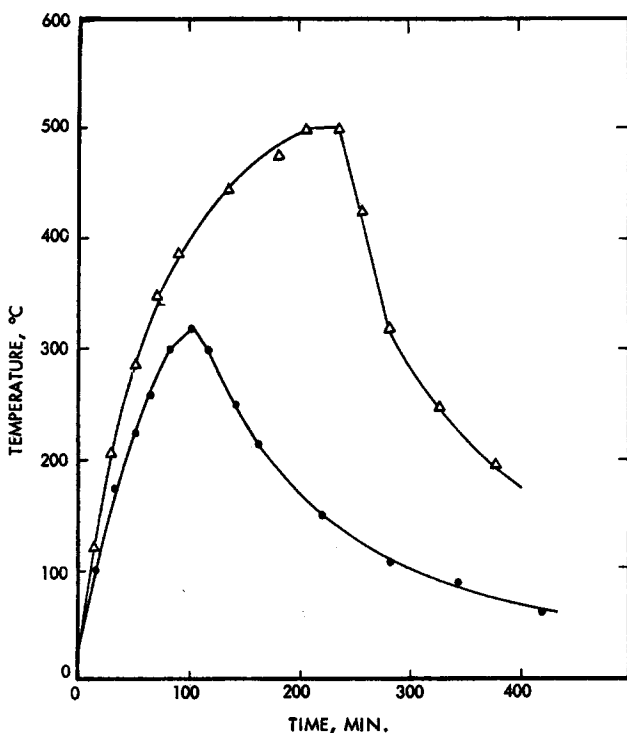


Fig. 1. Typical heating rate curves for charring studies.

in. The crucibles were then placed in a high-temperature furnace and the temperature raised. The samples were either heated at 300°C for 45 min or at 500°C for 30 min, then the furnace power was turned off. The samples were allowed to cool to ambient temperature while setting in the furnace. Typical curves showing rate of heat-up and cooling for the two temperatures employed is shown in Figure 1. The char weights were then recorded. Samples which did not contain phosphorus and/or bromine did not give chars under the conditions employed.

## RESULTS AND DISCUSSION

### Flame Resistance and Char Content of Foams Containing Only Bromine

Flexible foams were prepared with dibromoneopentyl glycol (DBNG) and a propoxylated adduct of a condensate of tetrabromophthalic anhydride with a typical high primary (50%), 3000-molecular-weight trifunctional flexible-foam polyol, hereafter referred to as TBPA/foam polyol/PO adduct, to give increasing concentration of bromine. These two compounds were selected to represent an aliphatic and aromatic bromine source, respectively. To get an understanding of the relationship between flam-

mability and amount of char produced, the tendency to char at several concentrations of bromine in flexible foams was evaluated. Charring temperatures employed throughout were 300° and 500°C for 45 and 30 min, respectively.

**Flammability.** Oxygen index values as a function of bromine content and the amount of char formed at 300° and 500°C are compared in Figure 2 for DBNG. It is obvious that the degree of flame resistance is not a linear function of the bromine content. Instead, the plots pass through an initial maximum in flame retardance at 2% bromine, which then falls off and finally shows an increase in oxygen index (OI) at 5% bromine. It should be pointed out that the same trend was previously observed, and an explanation involving variation of volatile flammable species as a function of a critical concentration of bromine in the solid phase was offered.<sup>4</sup>

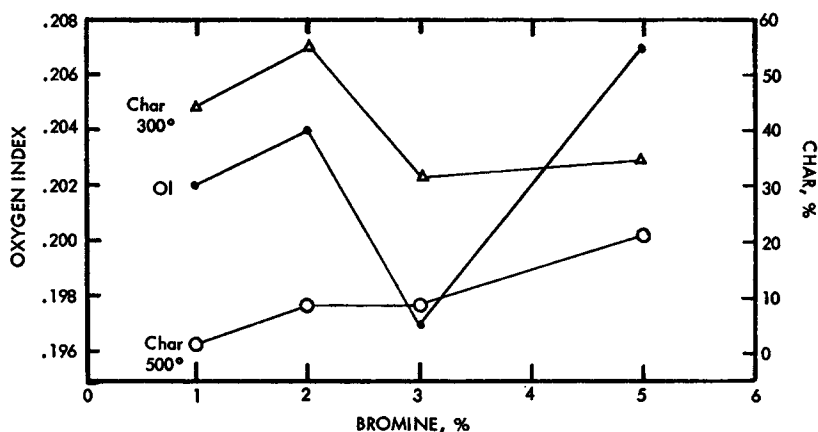


Fig. 2. Degree of char and flammability resistance of flexible foams containing dibromoneopentyl glycol.

Of the foams examined containing up to 5% aliphatic or aromatic bromine, only those containing DBNG at 3% and 5% bromine were rated SE by ASTM D 1692-67T (2.8 and 1.8 in. burned, respectively).

**Charring.** Unexpectedly, elemental analysis of the char revealed the presence of substantial amount of bromine for both charring temperatures employed. The amount of aliphatic bromine in the foams accounted for in the 300° and 500°C chars is illustrated in Figure 3. At a charring temperature of 300°C, greater than 70% of the bromine was found in the char for all the foams containing aliphatic bromide. Furthermore, bromine found in the char is a linear function of the bromine content of the foam. At the higher charring temperature (500°C), the bromine concentration in the chars leveled to a constant value of 4% to 5.5% halide. Essentially the same results were observed with the aromatic bromide at each charring temperature.

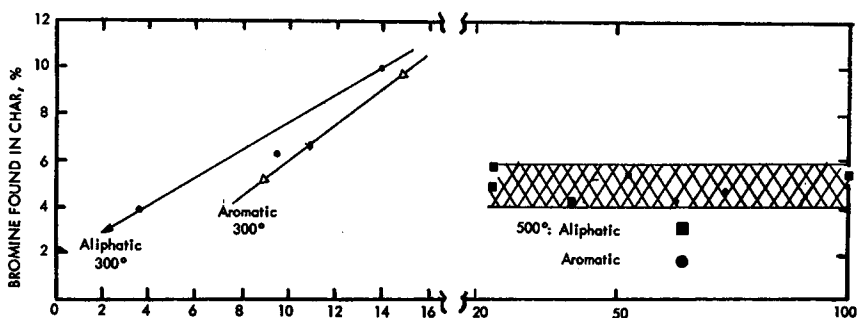


Fig. 3. Comparison of amount of bromine found in char vs. concentration employed in foam.

Table II gives the results from analysis of some of the chars for ionic bromine. With the use of aliphatic bromine, 34% of the bromine present in the original foam appeared in ionic form from char of foam rated SE by ASTM D 1692-67T. This represented 50% of the total bromine present in the char. On the other hand, all of the original bromine content (1%) of a non-SE foam appeared in nonionic form. Additionally, in the presence of phosphorus, a constant level of about 1.0% ionic bromine was found in the chars, regardless of the initial concentration of bromine in the foams or the type of phosphorus compound employed. A uniform phosphorus-to-ionic bromine ratio of 1 was observed for all cases. The high retention of bromine may be due to the formation of heat-resistant phosphorus and/or nitrogen-containing bromide salts.

A significant contribution of bromine to flame retardancy in the solid phase of combustion (in addition to its effect in the gaseous phase) could be implied from the charring results. For example, from Figure 2 it can be seen that the amount of char formation at 300°C followed about the same pattern as the flammability curve. This relationship is especially strong at the lower concentration of bromine but shows some deviation at 5% bromine. That is, as the OI increased or decreased, the amount of char exhibited a corresponding increase or decrease. Maximum OI was achieved

TABLE II  
Ionic Bromine Content of Chars

Phosphorus description	Char Content, 300°C/45"						
	Foam*		Calcd.		Found		Ionic Br, %
	Br, %	P, %	Br, %	P, %	Br, %	P, %	
—	0.995	—	2.26	—	3.05	—	0.26
—	2.98	—	9.56	—	6.24	—	3.21
Phosphate	2.03	0.520	3.65	0.933	1.35	1.09	1.19
Phosphonate	2.03	0.498	5.24	1.29	0.95	1.28	1.12
Phosphite	1.04	0.302	3.46	1.01	2.96	0.78	1.09

\* All foams contained aliphatic bromine from DBNG.

at 5% bromine and a relatively low char level (35%). The correlation with ASTM D 1692-67T, however, is somewhat erratic. Maximum char (55%) was produced when 2% bromine was in the foam and the flame resistance was not quite sufficient to pass the ASTM flame test. Additionally, minimum char (31%) and minimum OI was reached at 3% bromine where the flame resistance was just adequate to pass by the ASTM test.

It appears that there is some dependency of flame resistance and the amount of char, especially at the lower level of bromine. Inasmuch as control foams without bromine did not yield char under our test conditions, it could be inferred that only a low level of bromine is required to produce about 30–55% char in flexible foams. Clearly, the OI and ASTM flame tests appear to be measuring different aspects of flame resistance by bromine materials.

### Influence of Various Phosphorus Polyols on Charring and Flame Resistance

Various phosphorus polyols which possess phosphate, phosphite, and phosphonate functional groups were compared for their flame retardance efficiency. Description of each of these phosphorus compounds is given in the experimental section. Foams were prepared with phosphorus contents (0.3% to 1.0%) to correspond with product devoid of splits, shrinkage, and with the highest degree of open-cell character as permissible.

**Flammability.** Oxygen index values as a function of phosphorus content of the foams are plotted in Figure 4. At the lower level of phosphorus (0.3%) studied, the phosphate exhibited a significantly lower OI than the

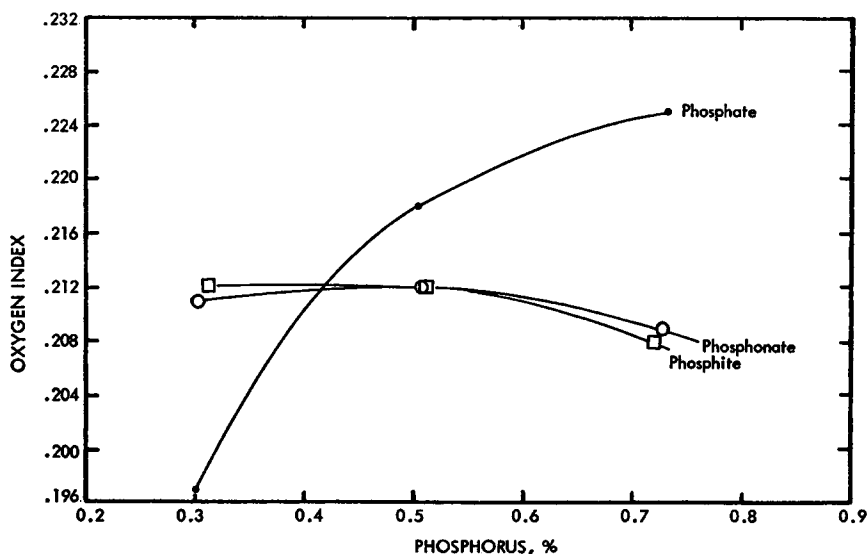


Fig. 4. Relationship of oxygen index with phosphorus content of foams.

phosphonate or phosphite. However, substantial increase in OI was noted above 0.4% phosphorus for the phosphate, whereas the fire resistance of the phosphonate and phosphite remained essentially unchanged. In fact, apparent leveling appeared at an OI of 0.212 and about 0.3% phosphorus for the phosphonate and phosphite. No rationale is offered for this behavior at this time, but the observed limiting value for the latter two phosphorus derivatives was above the 0.210 value, which was found to be the minimum level required to gain a self-extinguishing rating by ASTM D 1692-67T. In fact, reasonably good correlation between flame resistance by OI and the ASTM test methods for all phosphorus compounds investigated seemed to hold. On the other hand, it was previously seen that this relationship is not true for flame retardancy by bromine derivatives.

**Charring.** Extensive charring studies with rigid polyurethane foams prepared with a variety of nonreactive phosphorus compounds as well as a few phosphorus polyols have been previously reported.<sup>5,6</sup> The investigators found that essentially all of the phosphorus from both types of reagents in the foam was accounted for in the char. Based on these results, theories suggesting that phosphorus compounds inhibit combustion in the solid state have been hypothesized.<sup>1,5,7</sup> In the present study with flexible foams, it was also found that most of the phosphorus originally present in the foam was found in the char.

To understand the stability of the phosphorus alcohols utilized in this investigation, TGA curves were obtained over a broad temperature range in air. The curves are presented in Figure 5. Marked differences are exhibited in their initial decomposition as well as rate of weight loss. It may be that this behavior is reflected in controlling the char content of their foams. In fact, this appears largely the case, but the analogy only holds for the charring experiments at the higher temperature (500°C).

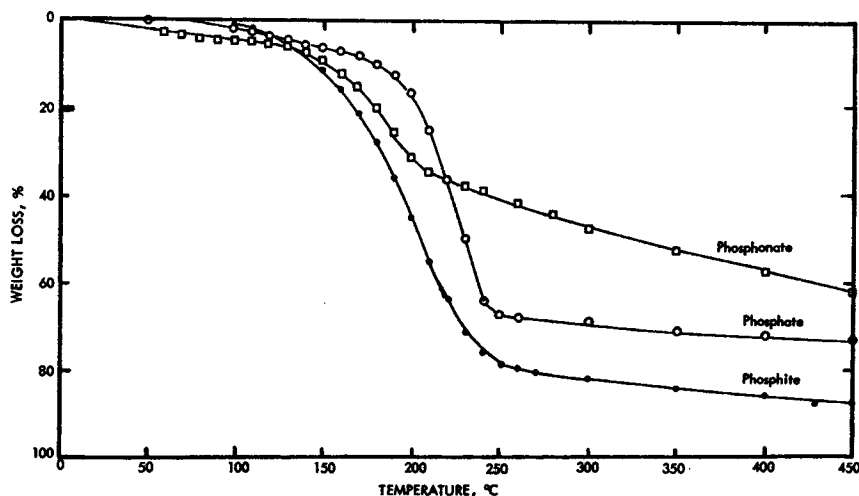


Fig. 5. Comparative TGA for various phosphorus alcohols.



### Phosphorus-Bromine Relationships with Suppression of Combustion

Experiments were designed to determine if there are phosphorus-bromine interactions during combustion when the elements are part of two separate flame-retardant reagents. Accordingly, flammability and charring studies were performed in air as described in the experimental section.

**Flammability.** Flammability was studied from the standpoint of the influence of the amount of bromine in a foam on the contribution of the various phosphorus types to flame resistance. To illustrate the effect, foams containing 0.5% phosphorus from the phosphate and varying amounts of bromine were compared with foams containing the same level of phosphorus from a phosphonate and varying amounts of bromine. In a second experiment, foams containing 0.3% phosphorus from a phosphite were compared (this level of phosphorus represents optimum for practical foams from the phosphite). A plot of the data is shown in Figure 6. The curves show that the effectiveness of mixtures of flame retardants containing phosphorus and bromine is related to the chemical type of phosphorus. At 0.5% phosphorus, it is readily apparent that bromine contributes only slightly more effectively to flame resistance in the presence of phosphate as compared to phosphonate. Again, OI values of greater than 0.210 were observed to produce SE-rated foams by ASTM D 1692-67T. This was true for all three phosphorus types studied.

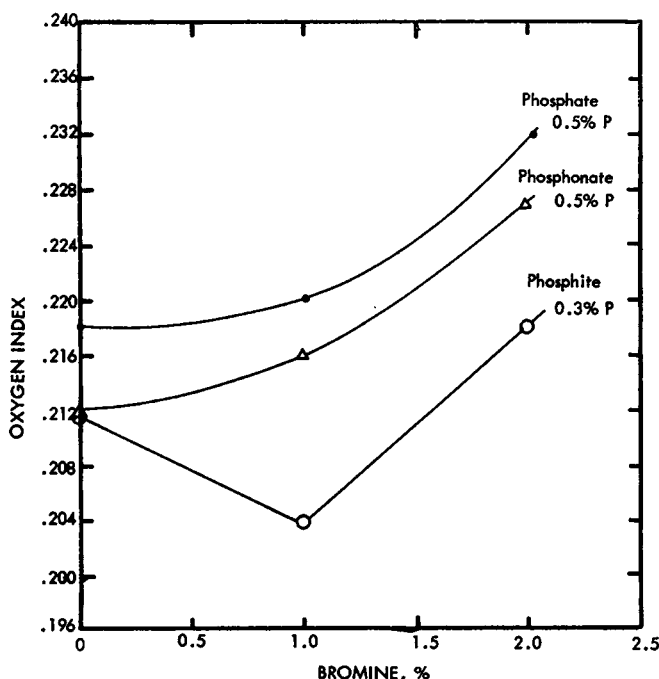


Fig. 6. Flame resistance vs. bromine content of foams at two levels of phosphorus.

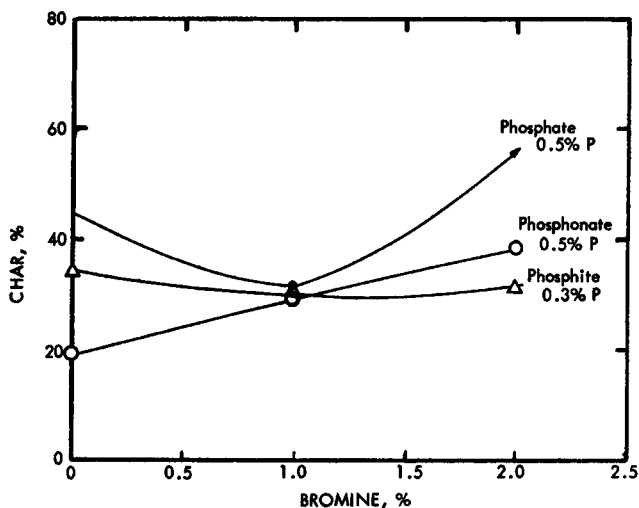


Fig. 7. Effect of bromine concentration on char yields at two levels of phosphorus at 300°C.

With 0.3% phosphorus from a phosphite and varying amounts of bromine, the OI curve passed through a minimum in flame resistance. This surprising behavior is reminiscent of that previously seen for foams containing aliphatic bromine materials alone (Fig. 2). Flammability ratings by ASTM D 1692-67T also exhibited a minimum effect at 0.3% phosphorus from phosphite and 1% bromine (and was rated burning by this test).

Correlations of flame resistance with char yields for the above experiments are shown in Figure 7. Char yields are influenced most notably by phosphate and phosphonate with increasing amounts of bromine. A linear relationship of char yield as a function of phosphorus from phosphonate is apparent, while a curve passing through a minimum in flame retardancy was caused by the phosphate. Maximum char yields were reached at 0.5% phosphorus from each the phosphate and phosphonate with 2% bromine, where maximum flame resistance was also observed. On the other hand, the amount of char (30%) from foams containing phosphite are insensitive to added bromine, and the degree of flame resistance was just sufficient at 2% bromine to pass the flame tests. Consequently, it appears that there is a relationship between flame resistance and the amount of char formed only in those instances where the phosphorus is of the phosphate and phosphonate type.

**Charring.** The relationship of the degree of char formation and the amount of phosphorus and bromine contributed from their various sources was also studied.

From 80% to 100% of the phosphorus originally present in the foams was accounted for in the 300°C chars. These values were consistent for the diverse phosphorus types studied and the concentration of bromine present in the foams. However, the phosphorus content of the 500°C chars showed

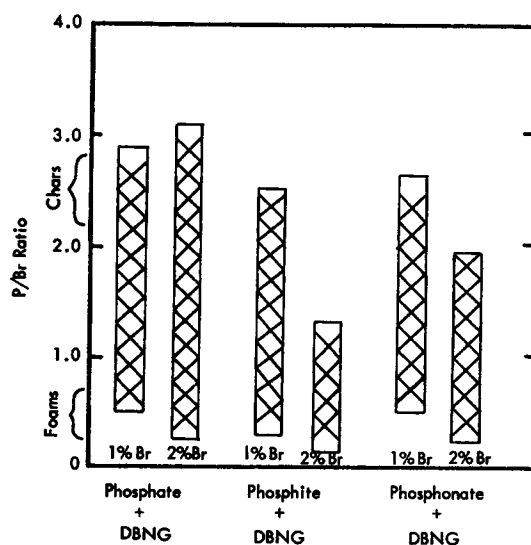


Fig. 8. Variation of P/Br ratio of foams vs. chars (500°C) for various flame retardants.

variability, ranging from 33% to 88%. In the latter study, phosphate gave the higher retention of phosphorus content (55–85%). Consequently, in the presence of bromine, some phosphorus escaped into the gas or tar at 500°C. Of the phosphorus compounds, phosphate was most stable in the presence of bromine.

The quantity of bromine (from DBNG) present at 1% and 2% in the foam which was accounted for in the char in mixtures with phosphorus was erratic, but bromine was observed in all cases. With the 300°C chars, the highest concentration found ranged from 45% to 85% bromine for phosphite, while 30–35% and 10–20% bromine were observed in the phosphate and phosphonate chars, respectively. Interestingly, the bromine content of the 500°C chars leveled off to constant value of 7–9% for mixtures with phosphorus supplied by phosphate and phosphonate, whereas the quantity was 4–5% bromine for the phosphite case. In this latter charring study (500°C), a constant P/Br ratio indicative of a chemical interaction is suggested. These relations are more clearly shown in the bar graph of Figure 8, where the P/Br changes in the foams are compared to their 500°C chars. The results show that the P/Br ratio approached a value of 2.5–3.0. The higher the ratio in the foam, the greater the loss of bromine. High retention of phosphorus is likely due to formation of compositions of phosphorus.

Unlike the aliphatic series of bromides (as in the above experiments), the aromatic source of bromine at 3% bromine in the foams gave a narrower concentration range at 35–55% bromine for all phosphorus compounds studied in the 300°C chars. The chars obtained at 500°C did not reveal bromine in two of the four cases. There seemed to be little correlation between bromine retention in chars and P/Br ratio in foams for aromatic bromine compounds.

TABLE III  
Properties of Flexible Foams Containing Phosphorus Polyols

Foam properties	Control	Phosphate			Phosphite			Phosphonate		
		0.299*	0.505	0.732	0.312*	0.510	0.720	0.301*	0.507	0.730
Density, pcf	1.56	1.45	1.55	1.77	1.65	1.76	1.70	1.45	1.44	1.85
Air porosity, ft <sup>3</sup> /min/ft	117	116	116	19	46	0	0	5	1	43
Tensile strength, psi	14.2	14.0	13.0	14.6	18.0	12.7	7.4	15.9	12.1	13.2
Elongation, %	158	149	123	119	159	95	83	176	142	122
Tear resistance, lb/in.	2.26	1.86	1.72	1.86	2.40	1.60	1.57	2.24	1.81	2.08
90% Compression set, %	5	7	8	17	15	26	65	55	45	13

\* Per cent phosphorus in foam.

TABLE IV  
Comparison of Foam Properties for Various Bromine/Phosphorus Ratios

Foam properties	Control	DBNG/Phosphate		Bromine/Phosphorus, %		DBNG/Phosphonate		Bromine, %	
		1.02/0.520	2.03/0.520	1.04/0.302	2.04/0.305	1.04/0.499	2.03/0.498	0.99	1.93
Density, pcf	1.56	1.80	1.96	1.91	1.95	1.68	1.74	1.57	1.57
Air porosity, ft <sup>3</sup> /min/ft	117	68	8	91	3	50	27	125	94
Tensile strength, psi	14.2	14.3	—	18.9	—	15.9	18.1	15.7	17.1
Elongation, %	158	122	—	187	—	143	155	182	180
Tear resistance, lb/in.	2.26	1.02	—	1.51	—	1.31	1.26	2.20	2.31
4-Inch ILD, lb/50 in. <sup>2</sup>									
25% Deflection	35	37	36	32	37	36	39	37	41
65% Deflection	64	75	79	68	78	69	78	68	75
25% Return	24	26	25	22	24	23	24	24	26
Return value	69	70	69	68	64	64	62	66	63
Load ratio	1.86	2.02	2.18	2.12	2.09	1.96	2.01	1.87	1.85
90% Compression set, %	5	63	—	18	—	20	25	4	6

### Foam Properties

A summary of the foam physical properties containing the flame-retardant reagents of this study is presented in Tables III and IV.

It is known that flexible foams flame retarded with aliphatic bromine-containing polyols possess physical properties essentially the same as controls. However, formulations containing phosphorus polyols presented some difficulty in processing and produced foams with inferior properties such as high 90% compression sets, higher density, and lower tensile and load values.

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