

Diffusion of Additives and Deterioration with Passage of Time in Polypropylene

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ABSTRACT: The diffusion of additives and the deterioration with the passage of time in polypropylene (PP) were studied by using the UL flaming test and the oxygen index test to measure the flame retardancy. The weight change was also measured. The decreases with the lapse of time were observed for multiple flame retardants. Aliphatic brominated compounds showed the best result for flame retardancy in the initial stage of combustion. The best flame retardants for PP to inhibit the deterioration of flame retardancy with the passage of time were brominated hydrocarbon with more than two aromatic rings connected by a functional group or isocyanurate, and phosphates connected with a branching aliphatic hydrocarbon. The weight of the

loss was plotted as a function of aging time and temperature to elucidate why the flame retardancy deteriorated. The apparent diffusion constant depends on the temperature and the rate was expressed with the Arrhenius equation. The concentration of flame retardant in PP was calculated by the constant and the equation at arbitrary time after thermal aging. The relation between the performance and chemical structure of the additives was also discussed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2152–2162, 2006

Key words: polypropylene; additives; combustion; diffusion; migration

INTRODUCTION

The flame retardancy of plastics and other flammable materials have been actively researched.^{1–3} Among them, the flame retardancy of polypropylene (PP) is very important because it is widely used for various purposes and it has a large production rate.^{4,5} Japanese newspapers reported that ignition accidents of TV sets occurred from January to June in 1990.⁶ Actually, 47 accidents happened in 1988 according to the Annual Report of Consumers. Including the accidents that were not officially announced, 600 or more cases were suspected to have occurred.⁷

The companies in the home electrical products trade launched a self-imposed control for the back covers of TV sets. In contrast, other companies in home electrical goods focused on the danger of fire. For example, there were cases reported in which warmed toilet seats caught fire.⁸ Flame retardant PP is spreading to parts materials for home electrical goods, including warmed toilet seats, because PP blended with flame

retardants shows good flame retardancy and chemical resistance.

Halogenated flame retardants and other flame retardants, including phosphorous, nitrogen, and metal hydroxide, are well known as flame retardants for PP. PPs treated by flame retardants are thus expected to show excellent flame retardancy. Moreover, the effect is necessary to continue in long periods of service. Namely, it is important that material contained in the plastic is confined in the plastic and does not to migrate into it.

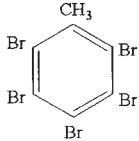
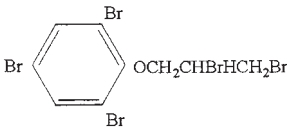
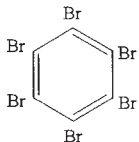
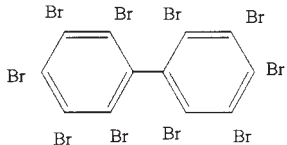
However, additives such as flame retardants, lubricants, and other chemicals tend to diffuse into PP and are volatile from the surface.^{9–14} Thus, studies have been conducted to analyze migration phenomena.^{15–20} There is a report about the migration of phosphorus flame retardants in a printed circuit board.²¹

In these situations, detailed studies have also been conducted on the change in concentration with the passage of time under various conditions of many stabilizers and antistatic agents for PP and polyethylene.^{22–25}

The flame retardancy at the initial stage and after aging, the migration rate and the activation energy, and the relation between the rate and the chemical structure have been studied and analyzed for PP with various flame retardants added to it.

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TABLE I
First Group of Flame Retardants

Chemical structure	Name	Code
$\text{CH}_2\text{BrCHBrCHBrCH}_2\text{Br}$	Tetrabromobutane	TBB
	Pentabromotoluene	5BT
	2,4,6-Tribromophenyl-2',3'-dibromopropylether	TBP-DB
	Hexabromobenzene	HB
	Decabromobiphenyl	B-10
$(\text{CH}_2\text{BrCHBrCH}_2\text{O})_3\text{PO}$	Tris(2,3-dibromopropyl)phosphate	TDBP

EXPERIMENTAL

Specimens and chemicals

The PP used in this study is a homopolymer with a melt flow rate of 9.0 (manufactured by Tokuyama Soda Co., Ltd.). The names, chemical structures, and acronym codes of the flame retardants are shown in Tables I, II, and III. The melting points and percentages of flame retardants and antimony oxide (Sb_2O_3) in PP are listed in Table IV.

Preparation of specimens

The compounds of PP and flame retardants were processed by a 50-mm extruder at 210°C. Each specimen was blended with 0.15 wt % phenolic antioxidant, 0.2 wt % thioetheric antioxidant, and 0.1 wt % scavenger for halogen. For the flame retardancy tests, the pellets blended with additives were fed into a press die and processed to make a 127 × 12.7 × 2 mm (length/width/thickness) specimen by cooling under high pressure (10 MPa) after heating for 600 s at 200°C.

The specimen size for oxygen index measurement was 127 × 7 × 3 mm (length/width/thickness). For

the migration test the specimen was 122 × 107 × 3 mm (length/width/thickness).

Methods of measurement

UL flaming and oxygen index tests

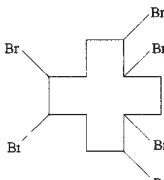
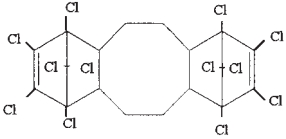
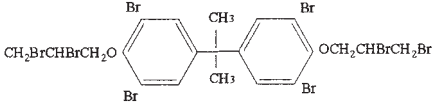
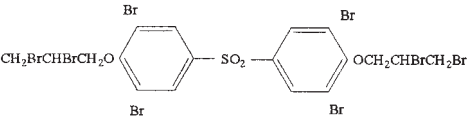
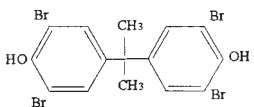
A UL-94V flaming tester was used for the measurement of flame retardancy. The flaming combustion time was observed according to the UL-94 vertical test method where a 20-mm blue flame was applied to heat specimens for 10 s. Each specimen was heated twice and the average was calculated by measuring the five specimens 10 times.

The oxygen index was measured with an ON-1 type flaming tester according to specimen K 7201 of Japanese industrial standard JIS K 7201.

Migration and deterioration with passage of time

The specimens were placed in an annealing oven, taken out after prefixed times, and then held at room temperature. After 16 h, the UL flaming test was conducted. Another specimen was put into the same annealing oven at 145°C, taken out after a

TABLE II
Second Group of Flame Retardants

Chemical structure	Name	Code
	1,2,5,6,9,10-Hexabromocyclododecane	HBCD
	1,2,3,4,7,8,9,10,13,13,14,14-Dodecachloro 1,4,4a,5,6,6a,7,10,10a,11,12,12dodecahydro 1,4,7,10-dimethanodibenzo(a,e)cyclooctene (Dechlorane plus, brandname)	DCPS
	Tetrabromobisphenol A-bis(2,3-dibromopropyl ether)	TBA-DB
	Tetrabromobisphenol S-bis(2,3-dibromopropyl ether)	TBS-DB
	Tetrabromobisphenol A	TBA

prefixed time, and held at room temperature. The oxygen index was measured after 16 h.

The specimens used for the measurement of the migration rate (2b, 3c, 11c, 12c, 13c, 14b, and 16b) were annealed at 145, 130, and 110°C in the annealing oven. Their weights were recorded after being removed from the oven. The specimens were repeatedly placed into and taken out of the oven, and their weights were measured. The averages were calculated from the data obtained from three specimens.

A control specimen blended with additives except the brominated flame retardants was prepared in order to check the effect of the additives.

RESULTS

Flame retardancy tests

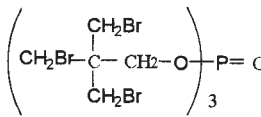
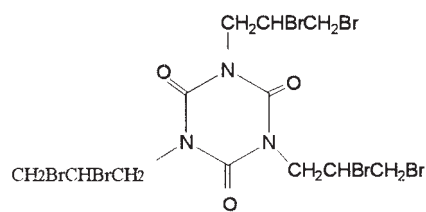
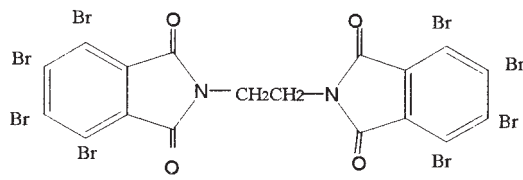
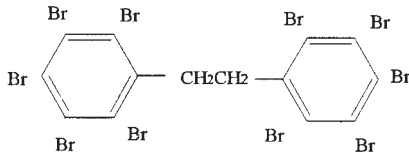
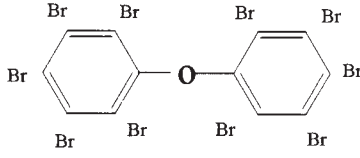
Various brominated flame retardants with aliphatic, alicyclic, and aromatic structures were used, as well as

those combined with other radical groups. The flame retardancy of the retardants immediately after processing and the change with the lapse of time are listed in Table V, in which the former is listed in the 0-h column.

The flame retardants, which were constructed of aliphatic or alicyclic brominated hydrocarbons such as TBB, HBCD, TBP-DB, TBA-DB, TBS-DB, TDBP, TBNP, and TDBIC, showed excellent effects on PP. (See Tables I–III for actual compound names throughout.) The PP blended with mixed retardants of $\leq 3.5\%$ brominated compounds and $\leq 2.0\%$ antimony oxide showed self-extinguishing qualities.

In particular, the effects of TBB, HBCD, TBP-DB, TBA-DB, and TBS-DB were higher. The self-extinguishing times were less than 1 s with 3.5 wt % additives and 2–3 s even at 1.9 wt %, which is much less than the usual rate of halogenated flame retardants. The performance of TDBP, TBNP, and TDBIC, which

TABLE III
Third Group of Flame Retardants

Chemical structure	Name	Code
	Tris(tribromoneopenyl)phosphate	TBNP
	Tris(dibromopropyl)isocyanurate	TDBIC
	Ethylene bis(tetrabromophthal)imide	EBTBPI
	Bis(pentabromophenyl)ethane	BPBPE
	Decabromodiphenyl ether	DBDE

are composed of aliphatic brominated hydrocarbon and a phosphate group or isocyanurate, were inferior to the above retardants and the self-extinguishing times were 1.2–6.9 s with 3.5 wt % additives.

PP blended with 5BT, HB, B-10, DBDE, EBTBPI, and BPBPE, which are composed of aromatic brominated hydrocarbons, did not show self-extinguishing qualities at 3.5 wt %. Only TBA was effective at 3.5 wt %. Amounts of 8 wt % halogenated compounds and 4 wt % antimony oxide were required for self-extinguishing, and the times were 15–40 s. Because the combustion of plastics is a vigorous reaction, the time is unstable. A stable time was obtained by adding 15 wt % flame retardants and 7.5 wt % antimony oxide or more.

The performance of halogenated retardants such as DCPS is generally inferior to those of brominated

ones, for example, HBCD in the case of alicyclic compounds. It is believed that radicals in a gaseous phase can be trapped more easily by the bromine radical emitted from an aliphatic brominated hydrocarbon than that of aromatic brominated or alicyclic chlorinated hydrocarbons because the dissociation energy of the former is lower than that of the latter.

Change of flame retardancy with passage of time

The flame retardancy changes with the passage of time of PP aged at 145°C are listed in Table V. The PP blended with TBB, which is an aliphatic brominated compound, burned after 30 min. In contrast, the self-extinguishing time of PP with HBCD (alicyclic brominated compound) became slightly longer after 5-h aging.

TABLE IV
Amount of Flame Retardants and Antimony Oxide in Specimens in Study

Sample no.	Flame retardant			Content (wt %)	Content of Sb ₂ O ₃ (wt %)
	Group	Name	mp (°C)		
1	Aliphatic bromine compound	TBB	110	3.5	2.0
2a	Alicyclic bromine compound	HBCD	151–153	3.5	2.0
2b				5.0	2.5
3a	Alicyclic chlorine compound	DCPS	>350	5.0	2.5
3b				20.0	10.0
3c				27.0	13.0
4a	Aromatic bromine compound (one aromatic ring)	5BT	280–284	3.5	2.0
4b				8.0	4.0
4c				15.0	7.5
5a		HB	315	3.5	2.0
5b				8.0	4.0
5c				15.0	7.5
6a	Aromatic bromine compound (two aromatic ring)	B-10	375	3.5	2.0
6b				8.0	4.0
6c				15	7.5
7a		DBDE	>290	3.5	2.0
7b				8.0	4.0
7c				15.0	7.5
8a		EBTBPI	>300	3.5	2.0
8b				8.0	4.0
8c				15.0	7.5
9a		BPBPE	354	3.5	2.0
9b				8.0	4.0
9c				15.0	7.5
10		TBA	178–180	3.5	2.0
11a	Aliphatic/aromatic bromine compound (one aromatic ring)	TBP-DB	43	1.9	1.0
11b				3.5	2.0
11c				5.0	2.5
12a	Aliphatic/aromatic bromine compound (two aromatic ring)	TBA- DB	85–90	1.9	1.0
12b				3.5	2.0
12c				5.0	2.5
13a		TBS-DB	60–80	1.9	1.0
13b				3.5	2.0
13c				5.0	2.5
14a	Aliphatic bromine compound/phosphate ester	TDBP	Liquid	3.5	2.0
14b				5.0	2.5
15		TBNP	181	3.5	2.0
16a	Aliphatic bromine compound	TDBIC	115	3.5	2.0
16b				5.0	2.5

There was no change in the self-extinguishing time of DCPS, which is a cyclic aliphatic compound. The self-extinguishing time of PP with 5BT and HB, which are brominated compounds with a single aromatic ring in each, became slightly longer after 5-h aging. No changes were observed for the PP with DBDE, EBTBPI, BPBPE, and TBA, except B-10, which has two aromatic rings.

The self-extinguishing time of PP with B-10 became slightly longer than 5BT and HB, which have

single aromatic rings. The specimen blended with TBP-DB, which is composed of single-ring aromatic and aliphatic groups, burned after 4-h aging. No change was observed in the case of the blends with TBA and TBS-DB, which are composed of two-ring aromatic and aliphatic brominated compounds.

Both TDBP and TBNP, which contain aliphatic and phosphate groups, were durable flame retardants. The extinguishing time of the blend with the former became slightly longer after 5-h aging. Con-

TABLE V
Self-Extinguish Time after Thermal Aging at 145°C

Sample no.	Flame retardant		Content (wt %)	Content of Sb ₂ O ₃ (wt %)	Self-extinguishing times aged at 145°C							
	Group	Name			0 h	0.5 h	1 h	2 h	3 h	4 h	5 h	50 h
1	Aliphatic bromine compound	TBB	3.5	2.0	0.2	Burn out	Burn out	—	—	—	—	—
2a	Alicyclic bromine compound	HBCD	3.5	2.0	0.1	—	—	—	—	—	1.1	—
3a	Alicyclic chlorine compound	DCPS	5.0	2.5	Burn out	—	—	—	—	—	Burn out	—
3b			20.0	10.0	8.0	—	—	—	—	—	7.5	—
3c			27.0	13.0	2.5	—	—	—	—	—	2.7	—
4a	Aromatic bromine compound (one aromatic ring)	5BT	3.5	2.0	Burn out	—	—	—	—	—	Burn out	—
4b			8.0	4.0	39.2	—	—	—	—	—	Burn out	—
4c			15.0	7.5	7.2	—	—	—	—	—	14.0	—
5a		HB	3.5	2.0	Burn out	—	—	—	—	—	—	—
5b			8.0	4.0	45.2	—	—	—	—	—	—	—
5c			15.0	7.5	6.3	—	—	—	—	—	12.5	—
6a	Aromatic bromine compound (two aromatic ring)	B-10	3.5	2.0	Burn out	—	—	—	—	—	—	—
6b			8.0	4.0	24.0	22.8	26.0	—	—	—	45.5	—
6c			15	7.5	5.5	—	—	—	—	—	11.1	—
7a		DBDE	3.5	2.0	Burn out	—	—	—	—	—	—	—
7b			8.0	4.0	14.5	—	—	—	—	—	—	15.8
7c			15.0	7.5	6.2	—	—	—	—	—	—	5.8
8a		EBTBPI	3.5	2.0	Burn out	—	—	—	—	—	Burn out	—
8b			8.0	4.0	20.2	—	—	—	—	—	22.3	18.9
8c			15.0	7.5	7.9	—	—	—	—	—	6.9	7.5
9a		BPBPE	3.5	2.0	Burn out	—	—	—	—	—	—	—
9b			8.0	4.0	16.3	—	—	—	—	—	—	17.9
9c			15.0	7.5	6.5	—	—	—	—	—	—	6.9
10		TBA	3.5	2.0	30.0	—	—	—	—	—	34.0	—
11a	Aliphatic/aromatic bromine compound (one aromatic ring)	TBP-DB	1.9	1.0	3.0	—	—	—	Burn out	—	—	—
11b			3.5	2.0	0.3	1.3	2.1	7.3	16.1	Burn out	Burn out	—
12a	Aliphatic/aromatic bromine compound (two aromatic ring)	TBA-DB	1.9	1.0	2.5	—	—	—	—	—	2.8	2.3
12b			3.5	2.0	0.1	—	—	—	—	—	0.1	0.1
13a		TBS-DB	1.9	1.0	3.2	—	—	—	—	—	3.8	3.0
13b			3.5	2.0	0.1	—	—	—	—	—	0.2	0.1
14a	Aliphatic bromine compound/phosphate ester	TDBP	3.5	2.0	3.1	—	—	—	—	—	4.2	—
14b			5.0	2.5	1.1	—	—	—	—	—	1.8	—
15		TBNP	3.5	2.0	6.9	—	—	—	—	—	6.0	7.2
16a	Aliphatic bromine compound	TDBIC	3.5	2.0	1.2	—	—	—	—	—	1.4	1.9
16b			5.0	2.5	0.5	—	—	—	—	—	0.4	0.4

Specimen = 127 × 12.7 × 2 mm.

versely, it did not change in the latter. TDBIC, which includes aliphatic and isocyanul groups, was also an excellent retardant because no change was observed in the self-extinguishing time.

The results can be summarized as follows. The largest change was observed after thermal aging at 145°C in the case of aliphatic compounds, which have relatively low molecular weight. The next largest changes were in the retardants that contained a single-ring aromatic as well as that combined with aliphatic compounds.

In contrast, the flame retardant composed of two aromatic rings showed excellent durability

against thermal aging, except B-10. The same tendency was observed for the two aromatic rings in it, as well as with those composed of two aromatic rings and an aliphatic group. The degree of change depended on the group adjacent to the linear aliphatic brominated radical against thermal aging. The changes in the self-extinguishing times decreased in the order of aromatic, phosphate, and isocyanurate.

In particular, the flame retardancy of the blend with isocyanurate and the compound composed of two aromatic rings connected by a functional group did not change. Branching aliphatic compounds,

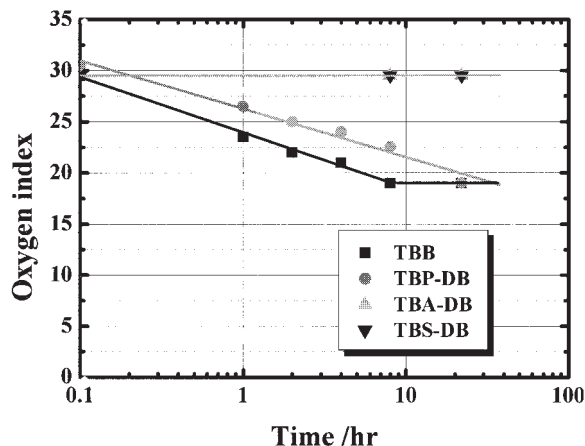


Figure 1 The dependence of the oxygen index on thermal aging.

such as TDBP, had smaller changeability against thermal aging than the linear one (TBNP).

Change of oxygen index by thermal aging

The oxygen indexes of the specimens aged at 145°C are shown in Table VI and Figure 1. The tendency of the oxygen index was similar to that of the UL flaming test. Namely, the oxygen index dropped rapidly after 1 h and it became the same level as that of nonblended PP after 8-h aging. The oxygen index of the blend with TBP-DB decreased like the blend with TBB and was as low as that of nonblended PP after 22-h aging. The oxygen index of the blends with 5BT and HB, which include a single aromatic ring, decreased. The oxygen index of the blends with TBA-DB and TBS-DB, which include two aromatics rings, did not decrease.

Compound B-10, in which the two aromatic rings directly connect, had a performance level that was midway between the single aromatic ring group and

two aromatic rings connected by functional group compounds.

Quantitative treatment of diffusion

The direct diffusion constant of the flame retardants was measured in an oven at 110, 130, and 145°C for specimens 2b, 3c, 11c, 12c, 13c, 14b, and 16b. The control specimen with additives and the same amount of antimony oxide without brominated flame retardants was prepared to measure the effect of brominated compounds. The decrease of the control specimen was 0.1–0.2 wt %. Specimens 3c, 12c, 13c, and 16b were the same as the control specimen.

The fugitive and residue rates listed in Table VII for the specimen aged at 110, 130, and 145°C were determined by the measurement of the weight loss of specimen 2b (HBCD). The fugitive rate (F_r) and the remain rate (R_r) were calculated as follows:

$$F_r = (C_0 - C)/C_0 \times 100 \quad (1)$$

$$R_r = C/C_0 \times 100 \quad (2)$$

where C_0 is 5 wt %, which is the initial concentration of the flame retardant, and C is the concentration at arbitrary time. The values of specimens 11c (TDB-DB) and 14b (TDBP) are listed in Tables VIII and IX, respectively. The residue rates of specimens 2b (HBCD), 11c (TBP-DB), and 14b (TDBP) as a function of aging time are plotted from Figures 2–4 using the remain rate.

The linear lines of three kinds of flame retardants showed a constant decrease with the passage of time by an exponential function. According to the above tendency, the loss is considered to depend on the first-order chemical reaction in which the decrease rate is proportional to the concentration. Thus, the equation is the following:

TABLE VI
Dependence of Oxygen Index on Thermal Aging

Flame retardant	Content (wt %)	Oxygen index aged at 145°C						
		Untreated	1 h	2 h	4 h	8 h	19 h	22 h
—	—	19	—	—	—	—	—	—
TBB	3.5	29.5	23.5	22	21	19	—	19
5BT	3.5	21.5	—	—	—	—	18.5	—
HB	3.5	21.5	—	—	—	—	19	—
B-10	3.5	22.5	—	—	—	—	22	—
TBP-DB	3.5	30.5	26.5	25	24	22.5	—	19
TBA-DB	3.5	29.5	—	—	—	29.5	—	29.5
TBS-DB	3.5	29.5	—	—	—	29.5	—	29.5
TDBP	3.5	25	—	—	—	—	—	23.5

Specimen = 127 × 7 × 3 mm; Content of Sb_2O_3 = 2.0 wt %.

TABLE VII
Migration of HBCD at 110, 130, and 145°C

Processing temp. (°C)		Processing time												
		6 h	18 h	22 h	23 h	43 h	47 h	70 h	71 h	95 h	115 h	116 h	141 h	159 h
145	Weight loss rate (wt %)	0.97	—	2.26	—	—	3.32	—	3.93	—	4.66	—	—	—
	(C ₀ - C)/C ₀ × 100	19.4	—	45.2	—	—	66.4	—	78.6	—	93.2	—	—	—
	C/C ₀ × 100	80.6	—	54.8	—	—	33.6	—	21.4	—	6.8	—	—	—
130	Weight loss rate (wt %)	0.69	—	—	1.51	—	2.34	—	—	3.27	—	—	3.73	—
	(C ₀ - C)/C ₀ × 100	13.8	—	—	30.2	—	46.8	—	—	65.4	—	—	74.6	—
	C/C ₀ × 100	86.2	—	—	69.8	—	53.2	—	—	34.6	—	—	25.4	—
110	Weight loss rate (wt %)	—	0.51	—	—	0.91	—	1.24	—	—	—	1.57	—	1.86
	(C ₀ - C)/C ₀ × 100	—	10.2	—	—	18.2	—	24.8	—	—	—	31.4	—	37.2
	C/C ₀ × 100	—	89.8	—	—	81.8	—	75.2	—	—	—	68.6	—	62.8

Content of HBCD = 5 wt %; specimen = 122 × 107 × 3 mm; data are averaged over 3 values.

$$-dC/dt = kC \tag{3}$$

$$K = Ze^{-\Delta E/RT} \tag{6}$$

where C is the concentration of the flame retardants, t is time, and k is the fugitive constant. Equation (1) then changes to the following:

$$\log(C_0/C) = k/2.303 \times t \tag{4}$$

where Z is a coefficient and R is the gas constant. The following equation can be obtained by deformation, which confirms the relation:

$$\ln [k] = -\Delta E/RT + \ln Z \tag{7}$$

The equation can be applied to the experimental data because the line is correctly proportional to the lapse of time, which is shown in Figures 2–4. The pseudo fugitive constant is written as follows:

$$k = -(2.303/t) \log(C/C_0) \tag{5}$$

The relations of Figure 5 are realized again. The fugitive constant; half-time of the loss of TBP-DB, HBCD, and TDBP; and 80% extant time of those at 50, 70, and 90°C were calculated and are listed in Table XI.

Fugitive constants k_{145} , k_{130} , and k_{110} , which are the constants at three temperatures, were obtained from the lines of Figures 2–4 and eq. (5). A summary of the fugitive constants is listed in Table X.

The practical service time can be calculated from the values in Table XI. A fire retardant is moved with diffusion in PP, and the fugitive constant of these fire retardants is estimated to happen by evaporation from the surface of PP. Elucidation of the spreading diffusion in PP and the evaporation from the surface of PP is a key point has not been elucidated yet.

Figure 5 presents the results of a plot of the logarithm of the fugitive constants and the reciprocal number of the absolute temperature in a graph. Accurate linear lines were obtained. The activation energies are constant. This means that the diffusion in PP and evaporation from the surface depend on the fugitive phenomena of the flame retardancy.

Clarification of which diffusion condition is a solid, liquid, or gas (steam) state has not been achieved, and it is a subject for future exploration. The reason for nondiffusion of the fire retardant cannot be made clear either. Among them, the “blooming” phenomena of TBA-DB have already been analyzed in detail,^{26,27} but

The fugitive constant and the activation energy can be expressed as follows:

TABLE VIII
Migration of TBP-DB at 110, 130, and 145°C

Processing temp. (°C)		Processing time								
		1 h	2 h	4 h	7 h	12 h	22 h	23 h	28 h	46 h
145	Weight loss rate (wt %)	0.85	1.27	2.04	2.89	—	—	4.70	—	—
	(C ₀ - C)/C ₀ × 100	17.0	25.4	40.8	57.8	—	—	94.0	—	—
	C/C ₀ × 100	83.0	74.6	59.2	42.2	—	—	6.0	—	—
130	Weight loss rate (wt %)	0.53	0.77	1.27	1.94	2.77	—	—	4.09	—
	(C ₀ - C)/C ₀ × 100	10.6	15.4	25.4	38.8	55.4	—	—	81.8	—
	C/C ₀ × 100	89.4	84.6	74.6	61.2	44.6	—	—	18.2	—
110	Weight loss rate (wt %)	—	0.30	0.42	—	—	1.70	—	—	2.52
	(C ₀ - C)/C ₀ × 100	—	6.0	8.4	—	—	34.0	—	—	50.4
	C/C ₀ × 100	—	94.0	91.6	—	—	66.0	—	—	49.6

Content of TBP-DB = 5 wt %; specimen = 122 × 107 × 3 mm; data are averaged over 3 values.

TABLE IX
Migration of TDBP at 110, 130, and 145°C

Processing temp. (°C)		Processing time										
		3 h	6 h	7 h	9 h	22 h	23 h	27 h	29 h	45 h	53 h	69 h
145	Weight loss rate (wt %)	0.20	—	0.40	—	—	—	1.12	—	—	—	—
	$(C_0 - C)/C_0 \times 100$	4.0	—	8.0	—	—	—	22.4	—	—	—	—
	$C/C_0 \times 100$	96.0	—	92.0	—	—	—	77.6	—	—	—	—
130	Weight loss rate (wt %)	0.09	0.17	—	—	0.43	—	—	0.52	0.70	—	—
	$(C_0 - C)/C_0 \times 100$	1.8	3.4	—	—	8.6	—	—	10.4	14.0	—	—
	$C/C_0 \times 100$	98.2	96.2	—	—	91.4	—	—	89.6	86.0	—	—
110	Weight loss rate (wt %)	0.03	—	—	0.07	—	0.12	—	—	—	0.24	0.29
	$(C_0 - C)/C_0 \times 100$	0.6	—	—	1.4	—	2.4	—	—	—	4.8	5.8
	$C/C_0 \times 100$	99.4	—	—	98.6	—	97.6	—	—	—	95.2	94.2

Content of TDBP = 5 wt %; specimen = 122 × 107 × 3 mm; data are averaged over 3 values.

those of many other flame retardants and plastics remain unsolved.

DISCUSSION

Deterioration of flame retardancy by thermal aging

Generally speaking, the deterioration of the flame retardants measured by the UL flaming test and the oxygen index after thermal aging at 145°C is considered to be caused by the following:

1. decomposition of the flame retardants,
2. an unknown reaction between the flame retardants and PP, and
3. a decrease of the concentration of the flame retardants in PP through diffusion from the center part of PP to the surface.

The decomposition of the flame retardants should be considered first. Thermogravimetric analyses tests showed that the retardants did not decompose at 145°C. They colored the PP at 200–300°C kneading and process-

ing temperatures, but clear degradation was not observed. After further aging, the melt flow rate of the blend increased, meaning the blend decomposed. However, the flame retardancy did not decrease.

The color of the blends in this study did not change after thermal aging. Therefore, decomposition was not the cause of the thermal deterioration of the flame retardants.

The possibility of an unknown reaction between PP and the flame retardants was discussed. PP is one of the most inert polymers compared to other industrial plastics. When we want to react PP with additives, it is indispensable to first pretreat it, for example, by blending with a grafted polymer with maleic anhydride. Therefore, the possibility of an unknown reaction being the cause of deterioration seems to be small.

Diffusion was discussed in detail, the results of which follow. TBB diffused into PP and the concentration dropped rapidly. The molecular weight of HBCD is larger than TBB and the steric chemical structures are complicated, so the diffusion is presumed to be less rapid.

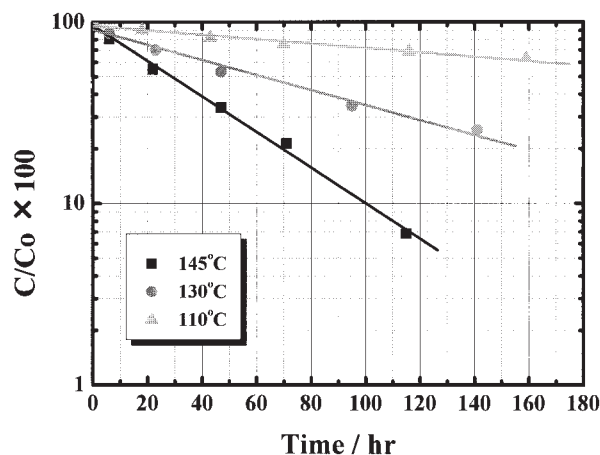


Figure 2 The decrease of HBCD in PP as a function of aging time.

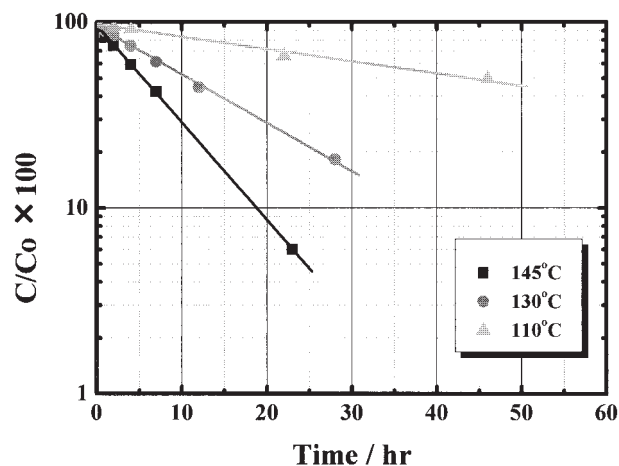


Figure 3 The decrease of TBP-DB in PP as a function of aging time.

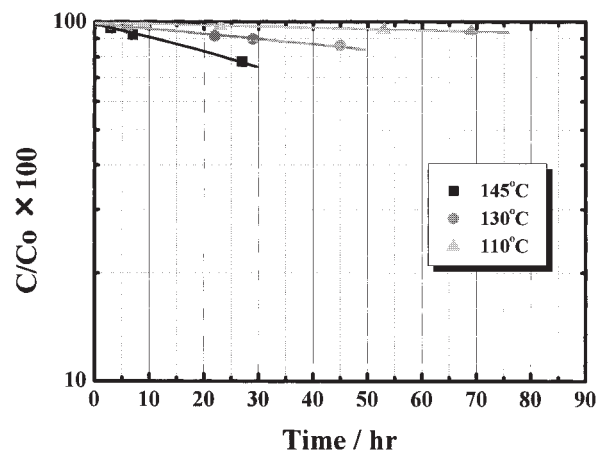


Figure 4 The decrease of TDBP in PP as a function of aging time.

Furthermore, DCPS, one of the alicyclic chlorinated compounds, has a very large molecular weight and the chemical structure is intricate. This seemed to prevent the diffusion. In contrast, the diffusions of 5BT and HB, which have a single aromatic ring, and TBP-DB, which is composed of single-ring aromatic and aliphatic groups, were larger. Diffusion of a single aromatic ring compound is large, because the chemical structure of a single-ring aromatic ring is relatively simple compared to the 12-member alicyclic ring in HBCD. The same cause can be supposed in the cases of DBDE, EBTBPI, BPBPE, TBA, TBA-DB, and TBS-DB, which have double aromatic rings.

The only exception was B-10. It is composed of double aromatic rings but the rings are connected directly. Thus, the structure is so simple that it can be diffused in the PP matrix.

The diffusion of TDBP, which includes linear aliphatic and phosphate, is much smaller than TBP-DB, which includes aliphatic and single-ring aromatic. Because TDBP connects aliphatic groups to each other in three directions, TDBP has little diffusion in PP.

In contrast, the diffusion constant of TBNP, which has branching aliphatic and phosphate, in PP is nil because the branching structure does not make it move into PP. The diffusion of TDBIC is not observed. The reason is because of the character of the triazine ring or by the three directions of the aliphatic group. If diffusion is the main factor in the deterioration of the flame retardancy, the order of the diffusion is single-aliphatic > single-aromatic > phosphate > isocyanuric = double-aromatic rings, except directly connected ones. It is reasonable in the affinity between PP and the flame retardants.

The flame retardants that melt during processing were dispersed in PP as small droplets because the melting point is less than the processing temperature. If the melting point is higher than the processing

TABLE X
Migration Constant and Activated Energy

Flame retardant	Temperature (°C)	Estimated diffusion constant	Activation energy (kcal mol ⁻¹)
TBP-DB	145	1.23×10^{-1}	19.2
	130	6.55×10^{-2}	
	110	1.60×10^{-2}	
HBCD	145	2.30×10^{-2}	18.3
	130	1.07×10^{-2}	
	110	3.01×10^{-3}	
TDBP	145	9.64×10^{-3}	21.5
	130	3.51×10^{-3}	
	110	9.07×10^{-4}	
TBA-DB		Not diffusion (each temp.)	
TBS-DB		Not diffusion (each temp.)	
DCPS		Not diffusion (each temp.)	
TDBIC		Not diffusion (each temp.)	

temperature, the diameter of the dispersed particle is larger than that of the melted retardants. The solid particle with a larger diameter is trapped in the polymer network, so it hardly diffuses into it. Therefore, 5BT, HB, and B-10 (melting point > processing temperature) can be expected to produce a small deterioration of the flame retardancy. However, the self-extinguishing times of 5BT, HB, and B-10 were extended with 145°C aging.

Thus, the flame retardant whose melting point is higher than the temperature of PP processing diffuses easily and breaks away from the PP.

Effect of chemical structure on migration rate

Studies have reported that the concentration of the additives decreased through diffusion in the plastics and by evaporating from the surface with the lapse of time, which was demonstrated by measuring the concentration of the additives from the initial to final

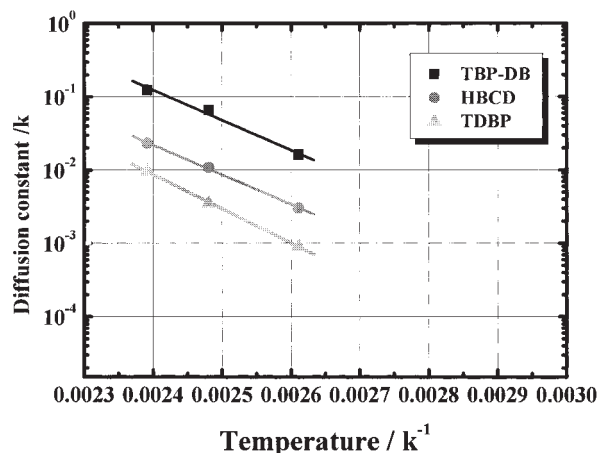


Figure 5 The migration constant at various temperatures.

TABLE XI
Migration Rate, Half-Time, and 80% Residue Period

Flame retardant	Temperature (°C)	Estimated diffusion constant	Half-value period	80% Remaining life	Activation energy (kcal mol ⁻¹)
TBP-DB	90	3.7×10^{-3}	190 h	60 h	19.2
	70	7.8×10^{-4}	890 h, (37 days)	285 h (12 days)	
	50	1.4×10^{-4}	5000 h, (200 days)	1600 h, (67 days)	
HBCD	90	8.2×10^{-4}	845 h (35 days)	270 h (11 days)	18.3
	70	1.9×10^{-4}	3650 h (150 days)	1200 h (50 days)	
	50	3.5×10^{-5}	825 days (27 months)	260 days (9 months)	
TDBP	90	1.9×10^{-4}	3650 h (150 days)	1200 h (50 days)	21.5
	70	3.4×10^{-5}	850 days, (28 months)	275 days (9 months)	
	50	4.8×10^{-6}	6000 days, (200 months)	1950 days, (65 months)	

stages. They also clarified that the diffusion constant depended not only on the reciprocal number of the molecular weight of the additives but also on the chemical structure of the individual compounds.

By contrast, there have been few reports on the change of flame retardants with the passage of time: how long it exists, its concentration, and its effect on flame retardancy. One example of the few studies previously conducted is that two or more aromatic rings or an isocyanurate group in the additives have an effect on reducing the change of flame retardants with the passage of time in PP.^{28,29}

CONCLUSION

Aliphatic brominated group flame retardants for PP were found to be superior to aromatic group ones. The chemical structure by which the flame retardancy of PP did not change with the passage of time was specified. It was constructed with double aromatic rings that connect with another radical group.

The durable flame retardants were the compounds with a triazine ring such as isocyanurate and phosphate, which has a branching aliphatic hydrocarbon such as neopentyl. Although the flame retardants whose melting points are higher than the processing temperature of PP were expected to show excellent durability, a difference was not observed for the self-extinguishing time. TBP-DB, HBCD, and TDBP diffused and left the surface of the PP, which was why the flame retardancy decreased. The rate was proportional to the concentration of the residue in PP.

Furthermore, the rate was expressed by the Arrhenius plot so that the arbitrary concentration in PP could be calculated at arbitrary time and temperature. The control of the phenomena was supposedly attrib-

utable to the evaporation speed from the surface or the transfer speed in PP could not be fully elucidated.

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