Boron Compounds as the Fire Retardants for Cellulose*

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セルロースの難燃化剤としてのホウ素化合物

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1. Introduction

There are great many fires in Japan as well as in many countries in the world. Wooden houses are very comfortable for people, but they have some unavoidable defects. One of them is fire-hazard. In order to protect the wood from the damage, chemical treatments have been investigated and DAP (diammonium

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phosphate) and MAP (monoammonium phosphate) have been recommended as the most effective fire retardants. But, recently a shocking paper[1] was reported, that is, nitrogen fire retardants evolve the hydrogen cyanide when it is heated under the high temperature and oxygen deficient conditions. And this fact has been confirmed by our papers.[2,3]

Therefore, the new chemical which has no danger should be investigated. After the several surveyings, we reached the conclusion of the adoption of boron compounds. These compounds has no nitrogen, so these can not generate any hydrogen cyanide, then boron does not exert any bad influences on human beings because boric acid is used for eye lotion showing safety.

In this paper, the effects of boron compounds on the fire retardation have been studied by paper combustion test, pyrolysis-gas chromatography, thermogravimetric and differential thermal analysis.

2. Experimental

2. 1 Paper combustion test

This procedure was reported previously,[4] namely, filter papers (Toyo Filter Co. No. 2) cut by the size of 6×13 cm are soaked in the solution of various concentrations such as 1, 2, 3 and 4% of fire retardants. After 6 minutes, the papers are picked up and are dried on a vinyl wire. After two days, the papers are weighed and the percentage of chemicals added is calculated.

Then, a paper is set vertically using a frame and is burnt with a Teclu burner having a 2 cm flame. At that case, 1 cm of flame is contacted with the lower end of paper. After 12 seconds, the paper is separated from the burner and the residual paper is weighed.

When we write a table showing the relation of chemicals added and weight loss after combustion test, the minimum limit of the fire retardant may be determined.

2. 2 Water-repellency test

In order to prepare the various concentrations of silicone solution, various volumes of benzene solution were added to original silicone liquor (Shin-Etsu Silicone, Polon-T, Shin-Etsu Chemical Co.). Test specimens of filter paper, the size of which is 3×6 cm, were drawn horizontally with 1 cm interval by a pencil. After the papers were soaked in the solutions, dried and the percentages of chemicals added were calculated.

One centimeter of the lower part of the paper was soaked in water in a laboratory dish, and the elevation of water was measured with the progress of time such as 2, 3, 4 and 5 minutes.

2. 3 Pyrolysis-gas chromatography

Specimens were prepared as follows, namely, cellulose powder (Toyo Filter Co.) was mixed with the solution of several fire retardants and dired under vacuum. The chemicals added were 39% for MAP, 43% for DAP, 30% for Na-Borate, 18%

for boric acid and 29% for B-mixture.

Two to three milligrams of every specimen was heated in a "Yanagimoto Pyrolysis-Pipetter GP-1000 type" at 700°C. Pyrolysis gas was analyzed by "Hitachi K 23 gas chromatograph".

The conditions are as follows:

Stationary phase: Activated carbon 60-80 mesh, 2 m
Carrier gas: Helium, 40 mℓ/minute
Bath temperature: 135°C

Charts obtained were copied on a semi-transparent paper, the each peak was cut off, weighed by a microbalance and the area was calculated. On the other hand, the calibration curves for each gas were prepared using standard gases.

2.4 TG-DTA

The specimens were prepared by the same way in PGC. The chemicals added were 38% for MAP, 41% for DAP, 26% for Na-borate, 20% for boric acid and 30% for B-mixture.

An apparatus named "Thermoflex-standard type" of "Rigaku Denki Co." was used. Two to three milligrams of specimen was weighed in a platinum pan, and heated in an electric furnace. The weight loss and the difference of temperature between the specimen and standard Al_2O_3 were recorded during the heating.

The conditions are as follows:

Rate of temperature elevation: 20°C/minute
TG range: 10 mg
DT range: ±250 μV
Atmosphere: Air, 20 ml/minute

3. Results and Discussion

3.1 Ability of four single fire retardants

Four single fire retardants were tested by paper combustion test. The results are shown in Table 1.

The minimum limit showing fire-retardation was 5.0% for MAP, 5.3% for DAP and 6.2% for Na-borate, respectively. Boric acid did not show any effects. And in the case of Na-borate, sometimes afterglow and the spread of combustion were observed. For example, a paper added 12.4% Na-borate showed the large weight loss, 62.7%.

3.2 Prohibition of afterglow

3.2.1 Mixing of boric acid with Na-borate

The results are shown in Table 2. Ten percent addition of boric acid to Na-borate did not give good results for the prohibition. In case of 20% addition, the afterglow was suppressed significantly, but a little spread of combustion was observed. In case of 30% addition, the afterglow was seen, but it was limited in the carbonized area and the spread to cellulosic area was prohibited.

In case of 40% addition, the afterglow duration was very short and the spread

Table 1. Paper combustion test for single fire retardants

Fire retardants / Broad order (%)	MAP		DAP		Na-borate		Boric acid	
	added (%)	Weight loss (%)	added (%)	Weight loss (%)	added (%)	Weight loss (%)	added (%)	Weight loss (%)
2							2.6	72.4
3	3.7	55.6	3.5	51.8			3.1	67.9
	3.7	49.8	3.5	49.7			3.3	69.6
	3.7	22.1	4.2	49.8				
4	4.3	36.9	4.4	36.7	4.9	42.8	4.3	65.7
	4.4	41.8	4.5	33.8			4.8	66.8
	4.6	37.9	4.9	42.2				
5	5.0	10.3	5.1	28.2	5.0	59.4	5.2	68.3
	5.0	8.7	5.3	8.2	5.1	45.4		
6	5.3	8.4	5.7	6.4	6.2	13.9		
	5.7	9.6	6.0	6.4	6.2	19.6		
7	5.8	8.4			7.4	14.6	7.1	65.6
	5.9	7.7			7.5	16.3	7.5	70.0
8	8.5	6.5	8.3	6.3	8.1	9.6	8.0	65.5
			8.4	5.8	8.2	15.9		
			8.5	5.4	8.5	19.9		
9	9.0	8.4						
	9.1	6.1						
10	10.8	6.2	10.6	4.8			10.0	74.2
	10.9	5.5	10.8	4.9			10.0	64.0
11	11.4	4.9					10.2	67.7
12					12.2	10.3		
					12.4	62.7		
13					13.8	10.9		
17					17.2	5.2		
18					18.4	10.2		

Table 2. Paper combustion test for various boron-mixtures

Boric acid added to Na-borate (%)	Fire retardant added to paper (%)	Weight loss after combustion test (%)	Afterglow (seconds)	Spread of combustion
10	8.3	16.0	60	+
	8.7	24.0	195	+
	9.2	5.9	40	+
20	9.5	9.1	25	+
	9.7	4.7	40	+
	10.8	4.1	27	+
30	8.4	5.1	17	−
	9.4	4.4	30	−
	10.6	8.0	13	−
40	9.1	6.8	13	−
	9.2	4.9	25	−
	10.6	6.4	8	−

of combustion was not observed.

As the conclusion, the addition of more than 30% boric acid is able to prohibit the afterglow and the spread of combustion.

3. 2. 2 Treatment with silicone plastics

The results are shown in Table 3. Na-borate was added to filter paper in the range of 7.7 to 8.5%, then the silicone plastics were added in the range of 7.4 to 8.9%. The weight loss after combustion test was only 5.8 to 7.3%. Though the duration of afterglow was a little longer, the spread of combustion was not observed.

3. 3 Ability of boron-mixture fire retardant

According to the results of 3. 2. 1 experiment, boron-mixture solutions of various concentrations were prepared by mixing 70% of Na-borate and 30% of boric acid. The paper combustion test using the solutions showed the results as in Table 4. In this case, the addition of 6% was the minimun limit for the fire retardation.

Table 3. Paper combustion test for silicone coating

Na-borate added (%)	Silicone added (%)	Weight loss after combustion test (%)	Afterglow (seconds)	Spread of combustion
7.7	7.9	7.3	50	—
8.0	8.9	6.9	55	—
8.5	7.4	5.8	90	—

Table 4. Paper combustion test for boron-mixture

Boron-mixture added (%)	Weight loss after combustion test (%)
4.4	54.4
4.7	14.0
5.0	50.0
5.3	44.6
5.5	23.1
5.8	11.6
6.0	8.6
6.4	8.2
6.4	5.7
7.6	7.3
7.8	8.1
8.0	7.0
10.2	5.6
10.9	6.2
11.1	3.7
16.3	4.5
16.6	4.9
16.8	4.8

3. 4 Water-repellency of paper treated with silicone

The results are shown in Table 5. In case of the addition of less 3.8%, the length of water absorption after the immersion of 5 minutes was the more of 2.0 cm. In case of the addition of less 5.6%, the length was the more of 1.0 cm. Then, in case of the addition of more 5.7% showed the length of less 1.0 cm, which is the good water-repellency.

Table 5. Water-repellency test of filter paper coated with silicone

Immersion time (min) / Silicone added (%)	Length of water absorption (cm)				Length in broad order (cm)
	2	3	4	5	
0	3.1	3.8	4.3	4.7	4
2.9	0.8	1.2	1.7	2.0	2
3.2	1.1	1.6	2.2	2.7	|
3.4	0.4	0.7	1.0	1.2	|
3.7	1.0	1.5	1.7	2.2	|
3.7	0.7	1.0	1.2	1.7	|
3.8	0.8	1.2	1.6	2.0	↓
3.8	0.6	0.8	1.1	1.4	1
4.8	0.7	1.1	1.4	1.7	|
4.9	0.2	0.5	0.7	0.9	|
5.4	0.3	0.6	0.8	1.1	|
5.6	0.4	0.6	0.8	1.2	↓
5.7	0	0	0.4	0.5	0
6.3	0.2	0.4	0.6	0.9	|
6.6	0	0	0.2	0.5	|
7.4	0.1	0.3	0.3	0.5	|
7.6	0	0	0	0.1	↓

3. 5 Variation of gases generated

Famous fire retardants MAP and DAP caused the large reduction in toxic and combustible carbon monoxide, and also large reduction in combustible methane, ethylene and ethane, and then enlargement of water which contribute to the effective fire retardation.

Boric acid showed no difference in gas composition except a some enlargement of water. Na-borate showed intermediate effects between MAP-DAP and boric acid.

At last, boron-mixture showed the considerable good effects on the reduction of toxic and combustible gases and the enlargement of water, though the results were a little inferior than MAP and DAP.

The volumes of gas (mℓ) generated from 1 g of cellulose are shown in Table 6, and those from 1 g specimen are shown in Table 7. The data in Table 6 will be useful theoretically, and those in Table 7 will also be effective practically.

Table 6. Pyrolysis-gas chromatography of cellulose treated with various fire retardants (mℓ from 1 g of cellulose)

Specimen / Gas	Cellulose	Cellulose treated with				
		MAP	DAP	Na-borate	Boric acid	B-mixture
CO	349	36	32	194	323	58
CH_4	64	15	14	40	65	15
CO_2	19	22	21	61	24	52
H_2O	162	572	622	398	249	361
C_2H_4	25	Tr.	Tr.	15	25	Tr.
C_2H_6	8	Tr.	Tr.	Tr.	5	Tr.

Table 7. Pyrolysis-gas chromatography of cellulose treated with various fire retardants (mℓ from 1 g of specimen)

Specimen / Gas	Cellulose	Cellulose treated with				
		MAP	DAP	Na-borate	Boric acid	B-mixture
CO	349	22	18	137	265	41
CH_4	64	10	8	28	53	11
CO_2	19	13	12	43	19	36
H_2O	162	348	361	286	212	252
C_2H_4	25	Tr.	Tr.	10	21	Tr.
C_2H_6	8	Tr.	Tr.	Tr.	4	Tr.

Table 8. Thermogravimetric analysis of cellulose treated with various fire retardants

Specimen / Temp. (°C).	Cellulose	Cellulose treated with				
		MAP	DAP	Na-borate	Boric acid	B-mixture
200	0	1.5	1.1	1.6	2.9	2.0
300	1.8	36.4	37.0	5.3	1.4	3.0
400	81.6	7.6	9.4	54.9	55.8	36.6
500	7.0	9.3	13.6	25.4	14.1	5.4
600	3.7	11.9	16.5	5.7	9.7	15.0
700	0	9.4	9.8	0	1.5	13.8
Total	94.1	76.1	84.4	92.7	85.4	75.8

3.6 Thermogravimetric analysis

Though untreated cellulose descreased by over 80% at 400°C, those treated with MAP and DAP decreased by less 50% at the same temperature and then decreased gradually. Each cellulose treated with Na-borate and boric acid showed the similar tendency to untreated cellulose. (Table 8).

The cellulose treated with boron-mixture showed a little similar tendency to

that treated with Na-borate or boric acid but the velocity was more slow and the total reduction at 700°C was minimum, which was the best results.

3.7 Differential thermal analysis

DTA diagrams of various fire retardants, cellulose, and that treated with the fire retardants are illustrated in Figure 1.

Cellulose has main three peaks, namely, first one is an endothermic peak (a345),

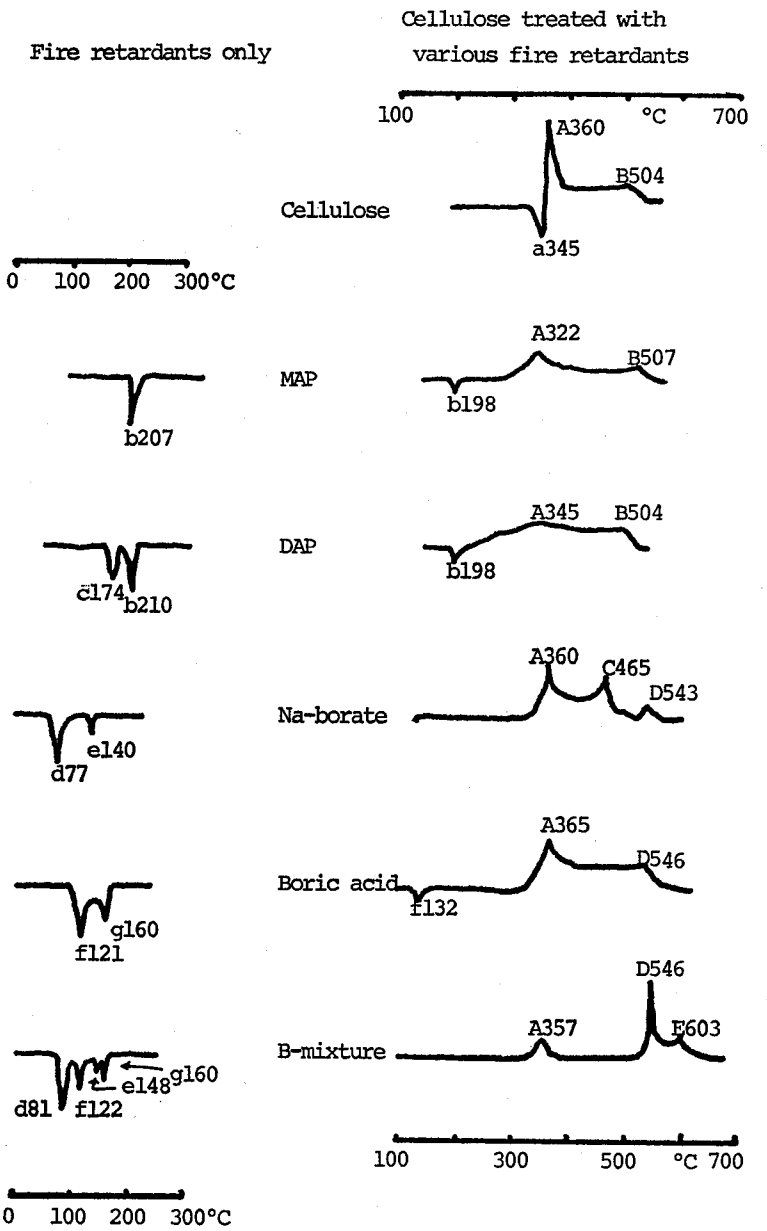

Fig. 1. DTA diagrams of cellulose treated with various fire retardants.

second is an exothermic peak (A360) and third is a broad exothermic peak (B504).

MAP has a only endothermic b peak at 207°C, and suppressed the sharp peak A of cellulose. DAP has two endothermic peaks, and also suppressed the sharp peak A. These two diagrams are similar each other, but MAP seems to suppress the B peak more than DAP.

Na-borate showed two endothermic peaks, and first one (d 77) meant the evaporation of water of crystallization. Na-borate did not suppress the A peak of cellulose and got C and D peaks dividing B peak. Boric acid had two peaks (f, g) and did not suppress the A peak, and C peak by Na-borate has disappeared.

Boron-mixture showed a synthetic pattern of the diagrams of Na-borate and boric acid, but suppressed A peak significantly and showed a sharp peak D and a new peak E. Therefore, it is recognized that the B-mixture acts a special performance different from Na-borate and boric acid. And also, this diagram is different from those treated with MAP and DAP. The theoretical clarification[5] of this performance should be investigated.

4. Conclusion

Wood treated with several fire retardants containing nitrogen is sometimes invaded by fungi and generates a little amount of hydrogen cyanide.

Mixing of boric acid with Na-borate produced a special effective fire retardant. Boron compounds are such safe chemicals as the fact that boric acid is used for eye lotion. Then, they act as fungicide. Additionally, they are not expensive.

Silicone has a good water-repellency, anti-afterglow and heat-resistant properties. As the cost of it is expensive, new water-repellant with heat-resistance should be explored.

5. Summary

1) MAP and DAP are very excellent fire retardants, but it has been reported that a little amount of hydrogen cyanide is generated under oxygen deficient and high temperature conditions. Therefore, new safe chemicals were surveyed and boron compounds were selected as the prospective chemicals.

2) Na-borate showed afterglow and the spread of combustion, and boric acid did not show any good effects.

3) Silicone coating on the paper treated with Na-borate inhibited the afterglow and the spread of combustion.

4) Mixing of 30% boric acid and 70% Na-borate showed a good results for the fire retardation of cellulose.

5) According to pyrolysis-gas chromatography, B-mixture caused the large reduction of toxic carbon monoxide, combustible methane, ethylene and ethane. Additionally, it caused the enlargement of water which acts effectively fire retardation.

6) Thermogravimetric analysis showed that B-mixture gave the best result at 700°C. Differential thermal analysis showed that B-mixture acts a new per-

formance different from Na-borate or boric acid.

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要　　約

MAP（リン酸水素一アンモニウム）と DAP（リン酸水素二アンモニウム）は優秀な防火薬剤であるが，近年，酸素不足かつ高温の条件下で，小量であるが，青酸ガスを発生させることが報告された。そこで安全な薬剤を検索の結果，ホウ素系薬剤を選択して試験することとした。

ホウ砂は防火効果はあったが残じんと延焼をひきおこし，ホウ酸は防火効果がなかった。ホウ砂にホウ酸を30％以上混合することによって，その欠点をおさえることができた。シリコーン樹脂も残じんと延焼をおさえる効果があり，さらに撥水性も与えた。

PGC（熱分解ガスクロマトグラフィー）によると，同薬剤は有毒ガスの一酸化炭素の発生を著しく減少させ，可燃性のメタン・エタン・エチレンの発生を減少させ，さらに防火効果を高める水の発生を増大させた。

TG・DTA（熱重量・示差熱分析）によると，ホウ素系混合物は，加熱重量減少率を最小におさえ，さらにホウ酸やホウ砂を単独に用いるときと異なる新しい作用をすることがわかった。