



Title	Fire Retardation of Plywood with Boron Compounds
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Citation	北海道大學農學部 演習林研究報告, 43(1), 57-72
Issue Date	1986-02
Doc URL	http://hdl.handle.net/2115/21173
Type	bulletin (article)
File Information	43(1)_P57-72.pdf



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Fire Retardation of Plywood with Boron Compounds*

By

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ホウ素化合物による合板の難燃化

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欧 文 要 旨

Various fire retardants were surveyed and boron compounds seem excellent from a viewpoint of safety, because toxic gases such as sulfur dioxide or hydrogen cyanide are not produced during pyrolysis of treated materials.

Treating methods for plywood were studied and a vacuum impregnation showed an excellent result, that is a duplicate impregnation composed of 30-minutes vacuum, air drying and 30-minutes vacuum.

Lauan plywoods treated with Boron-mixture were combusted according to JIS A 1322. The test standard was modified to a convenient type, which can use a smaller size (15 cm square) specimen. The specimens loading 5% or more of Boron-mixture fairly improved the weight loss in the combustion test.

Treated plywoods were analyzed by a pyrolysis-gas chromatography. As the results, a toxic and combustible carbon monoxide decreased, combustible methane decreased and uncombustible water vapor which is the depressor of temperature of fire circumstance increased with increase of the fire retardants.

Key Words: Fire retardant, Boron-mixture, Plywood, Vacuum impregnation, Pyrolysis-gas chromatography.

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* Received August 30, 1985.

A part of this paper was presented at the 34th Annual Meeting of the Japan Wood Research Society, Nagoya, April, 1984.

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1. Introduction

In our laboratory, an effective and safe fire reardant has been searched. Diammonium phosphate, that is DAP, is a famous and effective fire retardant, but when the material treated with the DAP is heated at high temperature and oxygen insufficient condition, it generates a small amount of hydrogen cyanide (HCN)^{1,2)}. And some fire retardants including sulfur compounds such as ammonium sulphate, generate sulfur dioxide (SO₂)³⁾ which damages our throats and respiratory organs. Halogen compounds including such as bromine (Br) give us very stimulative smell.

At last, we arrived at Boron compounds, that are fairly safe chemicals, for example, boric acid is used for eye lotion. They may be a little inferior to DAP in a point of efficacy of fire retardation, however, the problem of safety for human beings is considered most important. The toxicity of sodium borate is fairly low, that is, the LD₅₀ is estimated as 0.5 to 5 g/kg for human body⁴⁾. And that of boric acid is estimated as 15 to 30 g/kg for adults and 3 to 6 g/kg for children⁵⁾. Recently, the Central Medicines Council of Japan eliminated the ointment made of boric acid for burn or scratch⁶⁾. It says that it is useful for the medical treatment of eye, but long-term and continuous treatment for burn, little hurt and eczema showed the examples of diarrhea or a disease of kidney. And Dr Isozaki pointed that there were two reports on the death of child in 1918 and 1943 caused by boric acid ointment. Of course, boron compounds are not completely safe chemicals, but they must be most reliable fire retardants at present. Additionally, boron compounds are fairly effective as an insecticide and are used widely for the purpose in Japan⁷⁾. And also boric acid is effective to hinder the enzymatic activity of *Fomitopsis pinicola*, *Flammulina velutipes*, *Coriolus versicolor*, *Coniophora puteana* and *Phellinus igniarius*^{8,9)}. Then, boron compounds are water soluble, this point is a merit, because several solvents sometimes poison human or the other animals.

We have tested the treatment of boron compounds for paper as cellulose,¹⁰⁾ so we would like to step in the treatment of wood. Recently, Wegner and Holms¹¹⁾

applied the boron fire retardant to cellulosic loose-fill insulation and got a fairly good results. It is a difficult point to get homogenous material. Therefore, at first, a thin plywood was chosen as the raw material.

Next problem is the treatment method, a general method is conventional vacuum — pressure process using mixed chemicals¹²⁾. Several convenient methods, such as soaking, painting, pressure impregnation and vacuum one will be tried.

Recently, WHITE¹³⁾ applied 8 organic or inorganic fire retardant/resistant coatings on plywood and significantly improved the fire resistance of the plywood. KIKUCHI, MIYANO & YAMAGISHI¹⁴⁾ evaluated the fire-retardant plywood by JIS A 1321, ISO ignition test and Oxygen Index Method, and clarified the conditions for 3rd class of Fire Retardancy.

Next, there is also a problem about the test method, which should be convenient and useful for a fairly small size specimen. From this point, JIS A 1322¹⁵⁾ method was modified to be suitable for the above-mentioned purpose.

At last, the problem of generated gas is important for a solvation of the mechanism of fire retardation and also for the safety of people in the occasion of fire emergency. Pyrolysis-gas chromatography method was applied for the purpose. Now, related toxicological problem are highlighted and reported by Susan L. LEVAN¹⁶⁾ and BRENDEN¹⁷⁾ in the last IUFRO D5 Conference in Madison, USA. Of course, the smoldering¹⁸⁾ or smoking¹⁷⁾ of wood products is important and should be still more investigated.

2. Experimental

2.1 Materials

Plywood used for this experiment has a dimension of 90 cm × 180 cm × 2.4 mm. The surface veneer is so-called Red Lauan. These plywoods were purchased from a shop of building materials at the price of ¥ 500 per one sheet of plywood. The plywood was cut to size of 15 cm square with a sawing machine of the Laboratory of Wood Processing. According to the JIS A 1322, the size of a test specimen is 20 × 30 cm. The size was considerably decreased to this 15 cm square. By this modification the materials, chemicals, laboratory room space and labor were fairly economized.

Used chemicals are boric acid and anhydrous sodium borate, both 1st grade from Yoneyama Chemical Industry Co. and diammonium phosphate (DAP), 1st grade from Kanto Chemicals Co.

2.2 Loading of fire retardants

Boron-compounds solution was prepared as follows: 3 parts of boric acid were added to 10 parts of sodium borate according to the previous report¹⁰⁾. Because, this ratio showed excellent results on the weight loss after combustion test, afterglow and spread of combustion. This will be called B-mixture from now on.

2.2.1 Soaking

The solution of 1, 2, 3, 4, 5 and 6% of the B-mixture and DAP were pre-

pared. Five hundred ml of the solutions were put in each glass dish of diameter of 22 cm. Three plywoods were each soaked in the dishes for 3, 6, 24 and 48 hours, and taken out of the dishes and air-dried until they became constant weight. Loading percent was calculated on base of air dry weight of the plywood.

2.2.2 Painting

The aqueous solutions of the B-mixture, that are 4, 8, 12 and 16%, were painted with a brush on a surface of the plywood, respectively. After air drying, second painting was tried. The solutions over 8% needed hot water to dissolve the chemicals. This experiment was tried only on the B-mixture, because it has a problem of crystallization of the chemical on surface of the plywood.

2.2.3 Pressure impregnation

The plywoods were put in an autoclave, and heated slightly to a pressure of 1 kg/cm² and maintained for 30 minutes. Concentration of the chemical was 4%. After cooling, the specimens were taken out and air dried.

2.2.4 Vacuum impregnation

A dish containing a fire retardant was put in a desiccator. The concentrations of the fire retardant were 2, 4, and 6%. Several plywoods were put in the dish. The desiccator was vacuumed with a water jet pump for 30 or 60 minutes. And an additional case is a vacuum for 30 minutes, air drying and then a vacuum for 30 minutes.

2.3 Combustion test

A fire-retardant-treated material was heated in a combustion box according to JIS A 1322 (Testing Method for Incombustibility of Thin Materials for Buildings), as shown in Fig. 1. A used burner for the combustion test is named Mecker burner, the inner diameter of which is 22 cm. Only town gas was sent without any air. The burner was put at the point shown in the Figure. Length of the flame was adjusted at 65 mm. And the distance between the mouth of the burner and the test specimen was 50 mm.

Time of heating was 40, 50, 60, 70 and 80 seconds. Untreated plywood was not ignited within 30-second heating. And the specimen was penetrated through with combustion by over 90-second heating, and the afterflame became 0 second and the weight loss attained a constant value.

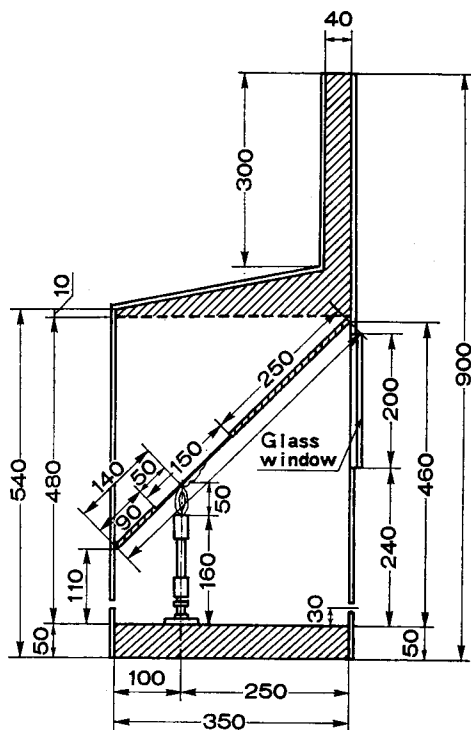


Fig. 1. An apparatus modified from JIS A 1322.

Therefore, 40 to 80 seconds are suitable for the time of heating.

After the combustion test, the weight loss, length and width of carbonized area and afterflame were observed.

2.4 Pyrolysis-gas chromatography

Several small particles were scraped from the plywood. The weight is about 3 mg, and they were weighed accurately with a Mettler micro-balance. These specimens were soaked in the various concentration (1, 2, 3, 4, 5 and 6%) liquors for 60 minutes, then air dried. Those were weighed again and the loadings of the chemicals were calculated.

A Yanagimoto GCP-1000 type pyrolysis pipetter was connected

to a Yanagimoto G8 Gas Chromatography. Generated gases were detected by a TCD (Thermal Conductivity Detector). Analysis conditions are as follows:

1. Stationary phase: Activated carbon, 60 to 80 mesh, 2 m, 3 mm ϕ .
2. Carrier gas: Helium, 15 ml/minute. Second pressure, 5 kg/cm².
3. Bath temperature: 180°C.
4. Chart speed: 10 mm/minute.

The data obtained were recorded by a Shimadzu Chromatopac C-RIA, and ratio of the area of each peak was calculated.

3. Results and Discussion

3.1 Loading of fire retardants

The results by soaking method are shown in Table 1. With the progress of soaking time, the loading percent also increases, and the maximum value attained to 5.4%. The data at 48 hours show some decrease compared with that at 24 hours. This must be the dissolution of the wood components of the red lauan because of the long soaking.

The reason why the loading was not so high might be the thin surface of plywood and a disturbance by the adhesive layer. Loading of DAP was higher than that of the B-mixture, because of the easy dissolution of DAP. Then the crystallization of the B-mixture at 6% was remarkable. This phenomenon is of course not preferable.

The results by painting method are shown in Table 2. The solution at 8%

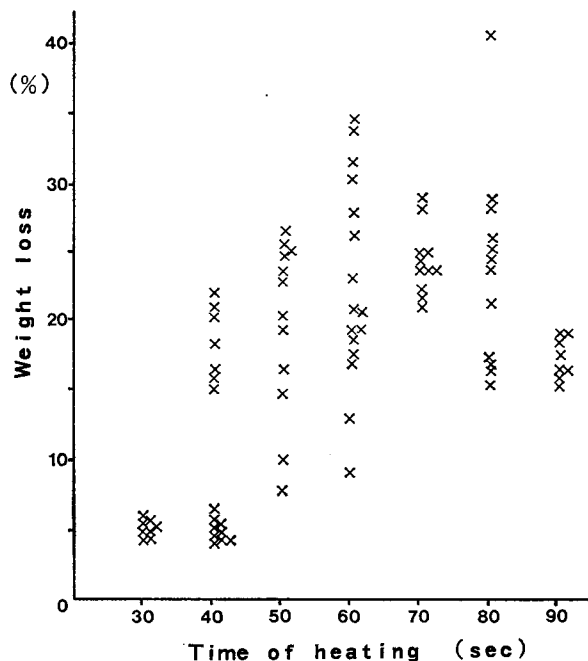


Fig. 2. Weight loss of untreated lauan plywood under various time of heating.

Table 1. Loading* of fire retardants by soaking method

Fire retardant	Time of Soaking (hr)	Concentration of fire retardant (%)				
		1	2	3	4	6
Boron-mixture	3	—	0.9	—	1.5	2.1
"	6	0.3	0.7	1.1	1.4	2.8
"	24	1.5	2.0	3.1	2.8	5.4
"	48	0.8	1.2	1.9	2.7	3.8
Diammonium phosphate (DAP)	3	0.7	1.3	1.7	1.9	2.9

* Weight percent based on air-dry plywood.

Table 2. Loading of fire retardant by painting (%)

Fire retardant	Times of painting	Concentration of fire retardant (%)			
		4	8	12	16
Boron-mixture	once	—	0.4	1.3	2.4
"	twice	0.8	1.6	4.4	6.5

Table 3. Loading of fire retardants by vacuum method (%)

Fire retardant	Time of vacuum (min)	Concentration of fire retardant (%)		
		2	4	6
Boron-mixture	30	1.0	2.8	5.2
DAP	30	1.5	2.9	4.0
B-mixture	60	1.7	3.0	4.1
DAP	60	1.3	2.5	4.1
B-mixture	30×2	3.0	5.7	8.9
DAP	30×2	2.3	4.2	6.5

or more needed hot water to dissolve the B-mixture. This painting method loads the chemicals on one side of the plywood. So, the loading percent is different from that by the soaking method. The appearance of the plywoods treated with 8% or more of the B-mixture shows remarkable crystals. Therefore, this method is thought to be unfavorable for the practical application.

The result of pressure impregnation was 4.3%, the value of which was fairly high, in spite of the short treatment time. Additionally, the crystallization of the B-mixture was not seen on surface of the plywood. However, the color of plywood changed to dark and looked unfavorable. Therefore, this method also seems unfavorable.

In case of the vacuum impregnation, in which a 4% solution of the B-mixture was used for 2 hours, the results of loading was 4.9%. The crystallization of the chemicals and also the unfavorable color change were not observed. In comparison

of the same concentration, that is 4% solution, the load showed 1.5, 1.4, 2.8 and 2.7% for 3, 6, 24 and 48 hours in the soaking time, respectively, and the pressure impregnation showed 4.3% of the loading. So, the further experiments on vacuum impregnation were progressed.

Four sheets of plywood were soaked in 2%, 4% and 6% of the fire retardants solutions for several times as shown in Table 3. And, of course, the last two lines in the Table show a duplicate treatment. The vacuum level attains 20 mmHg. The vacuum treatment for 30 minutes, air drying and the vacuum treatment for 30 minutes, that is, the duplicate vacuum one results in 9% loading of the B-mixture and 7% loading of DAP. The application of these methods showed the loading range of 1 to 9%.

ISHIHARA¹⁹ reported that a plywood treated with Boric acid-Lithium hydroxide-Methylolmelamine-condensation fire retardant got fairly excellent results in case of the 8% loading. FPL estimates that the effective loading must be 8 to 17%¹².

3.2 Combustibility

At first, the results in a case of 40-second heating are described. About a

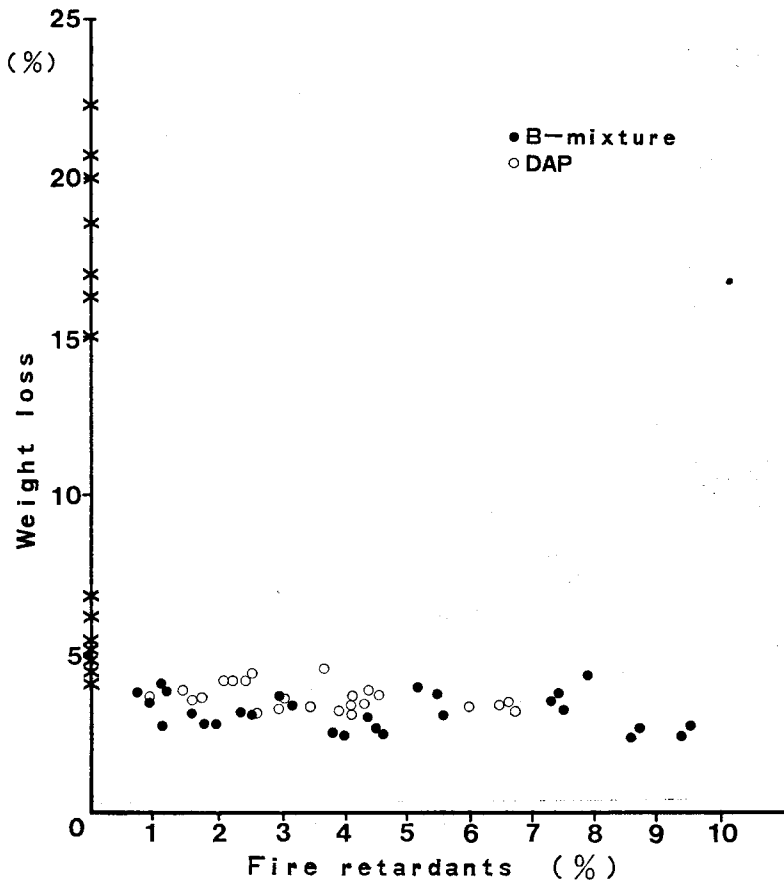


Fig. 3. Weight loss of fire-retardants-treated lauan plywood under 40-second heating.

half of untreated plywood is ignited and the weight loss attains to about 20%. The others are not ignited and the weight loss is only 5%. The loading of the B-mixture suppressed it under 4%. DAP showed a little over 4%. However, there was no remarkable difference between the B-mixture and DAP. Also, the effects of the loading percent on the weight loss were not observed. (Fig. 3).

Secondly, the results in a case of 50-second heating are described. Almost untreated plywoods are ignited, afterflame ranged from 50 to 100 seconds and the weight loss ranged from 8 to 27%. In case of the B-mixture loading of under 3%, the specimens show the afterflame of a little less than 10 seconds, and the weight loss increased to 8%. In case of DAP loading of under 3%, weight loss of over 5% is not observed. It can be said that DAP is superior to the B-mixture. (Fig. 4).

Thirdly, the results in case of 60-second heating are described. The weight loss of untreated plywood ranged from 9 to 35%. The loading of over 5% of the B-mixture shows no afterflame and the weight loss shows under 7%. The loading of under 5% of the B-mixture shows the half ignition and half inignition. The

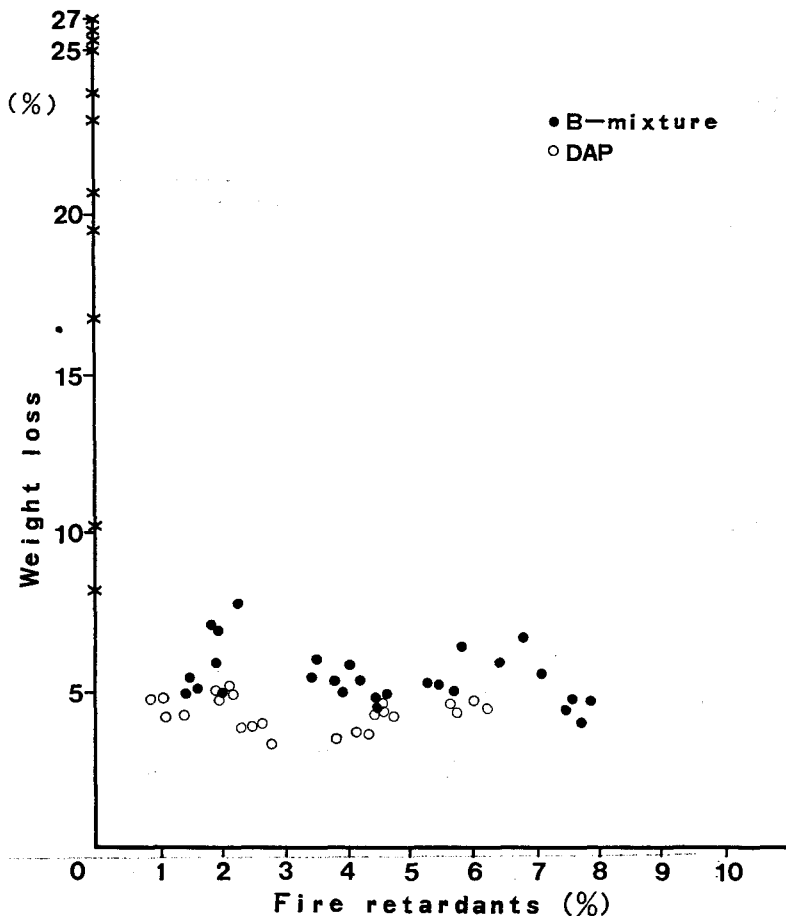


Fig. 4. Weight loss of fire-retardants-treated lauan plywood under 50-second heating.

ignited plywood shows 70- to 90-second afterflame, and the weight loss is about 20%. The loading of under 2% of DAP shows over 30 second afterflame of 2 to 3 specimens. In comparison with the loadings of under 5%, DAP shows stronger suppression than the B-mixture. But, there is not remarkable difference between two fire retardants in case of the loading of over 5%. (Fig. 5).

Fourthly, the results in case of 70-second heating are described. The weight

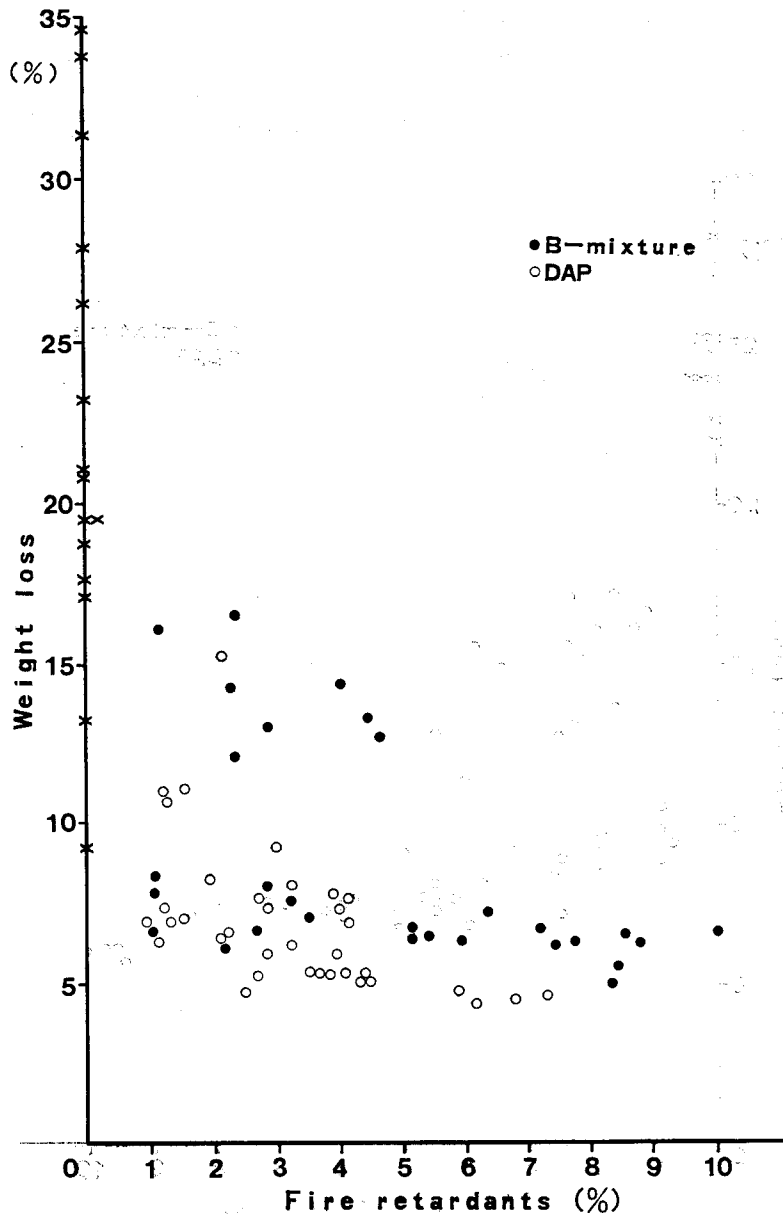


Fig. 5. Weight loss of fire-retardants-treated lauan plywood under 60-second heating.

loss of untreated plywood ranged from 20 to 30%, and the afterflame continued over 100 seconds. This seems to be the most combustible condition. B-mixture suppresses the ignition by the loading of over 5%, like the 60-second heating. The loading of under 5% afforded the 80-second afterflame for almost all plywoods. DAP suppresses the afterflame by loading of under 5%, however, the weight loss showed a slow increase with decrease of the loading. (Fig. 6).

Fifthly, the results of 80-second heating are described. Untreated plywood showed the weight loss from 15 to 40%. Fire-retardant (both the B-mixture and DAP)-treated plywood showed several cracks at the heated place along the fiber direction. This is a pre-stage of penetration caused by combustion. There were two specimens which had some longer afterflame, that were 80 and 66 seconds of

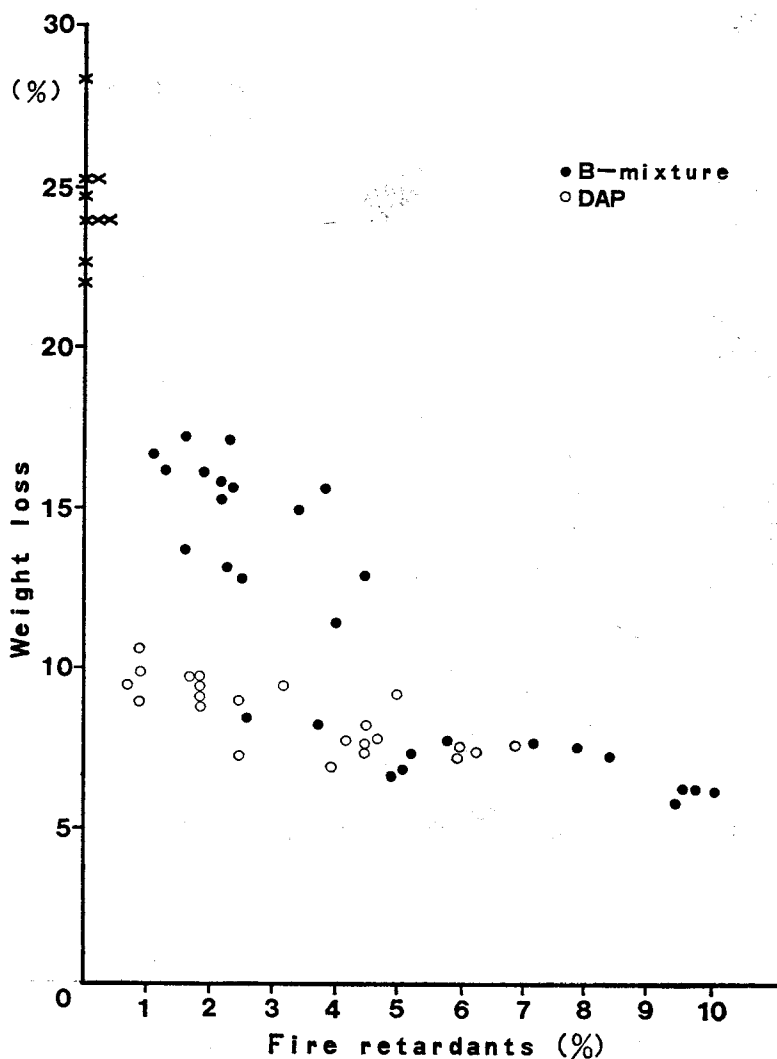


Fig. 6. Weight loss of fire-retardants-treated lauan plywood under 70-second heating.

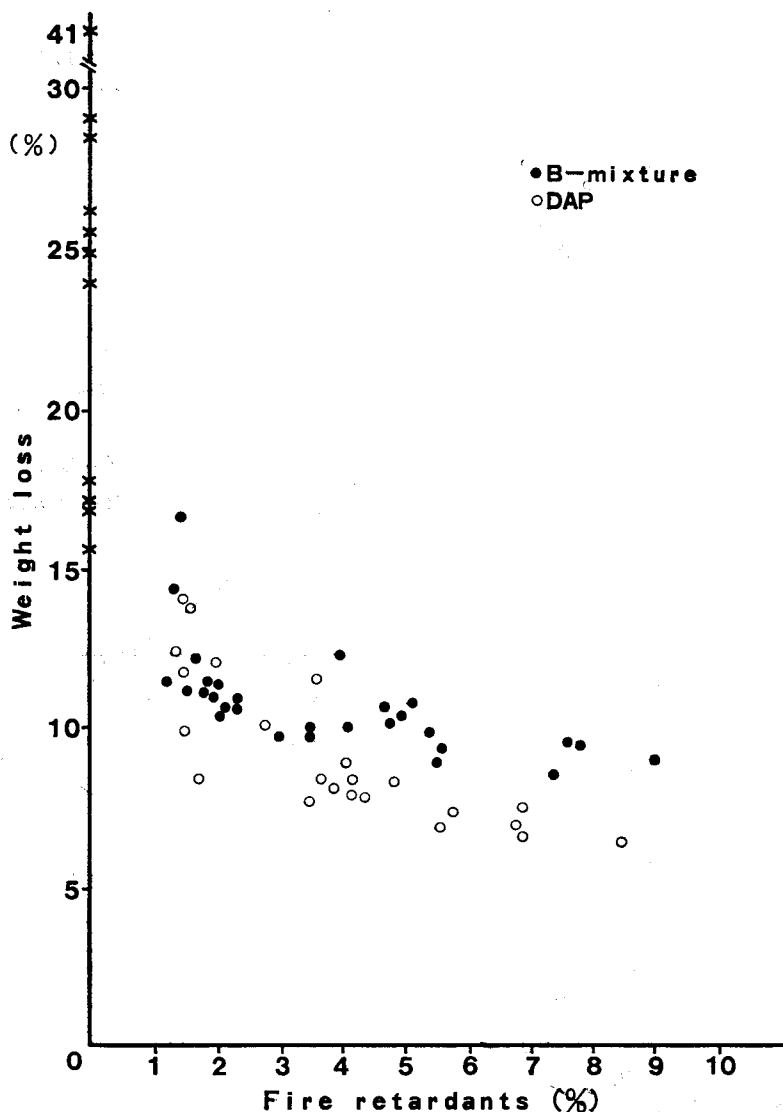


Fig. 7. Weight loss of fire-retardants-treated lauan plywood under 80-second heating.

1.4% and 1.3% loadings of the B-mixture, respectively. (Fig. 7).

Consequently, there was only some difference between the B-mixture and DAP in case of 70-second heating, however, there was no remarkable difference between two fire retardants, especially when the loading was over 5%.

3.3 Variation of gases evolved

The results of this experiment is based on non-oxygen circumstances. But, it is important to examine the properties of fire retardants under this condition. Of course, in practical fire condition, such oxygen-deficient circumstances will appear.

Total amount of gas evolved from 1 mg of wood did not vary regardless of

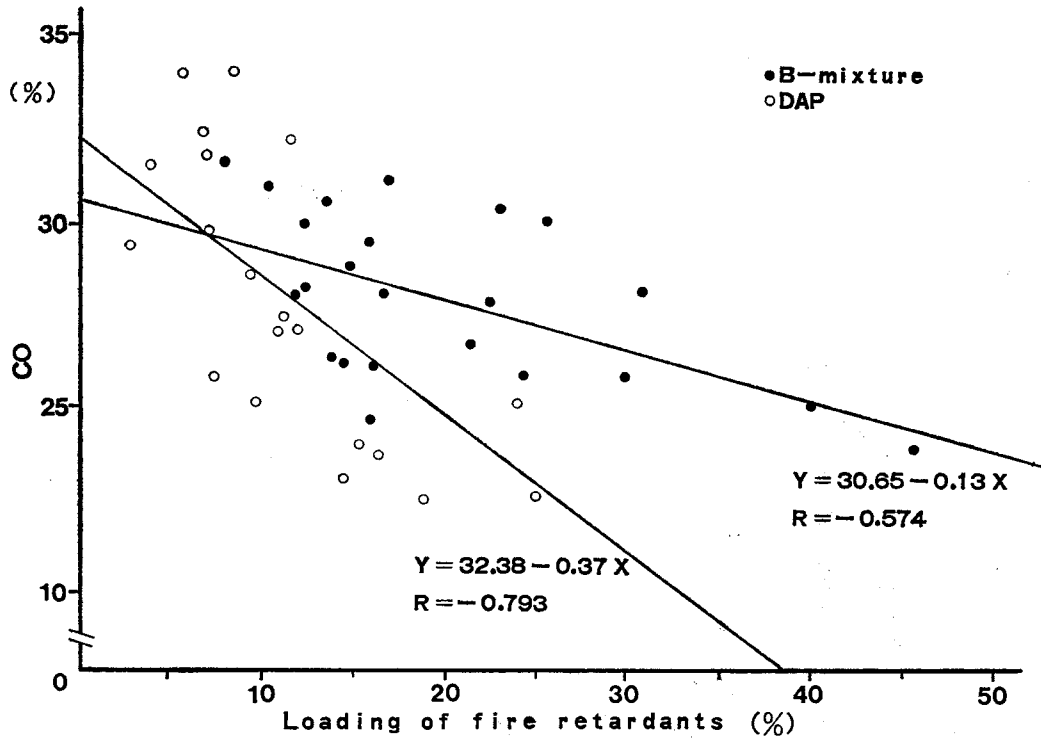


Fig. 8. Evolution of carbon monoxide during pyrolysis from the specimens loading various amounts of fire retardants.

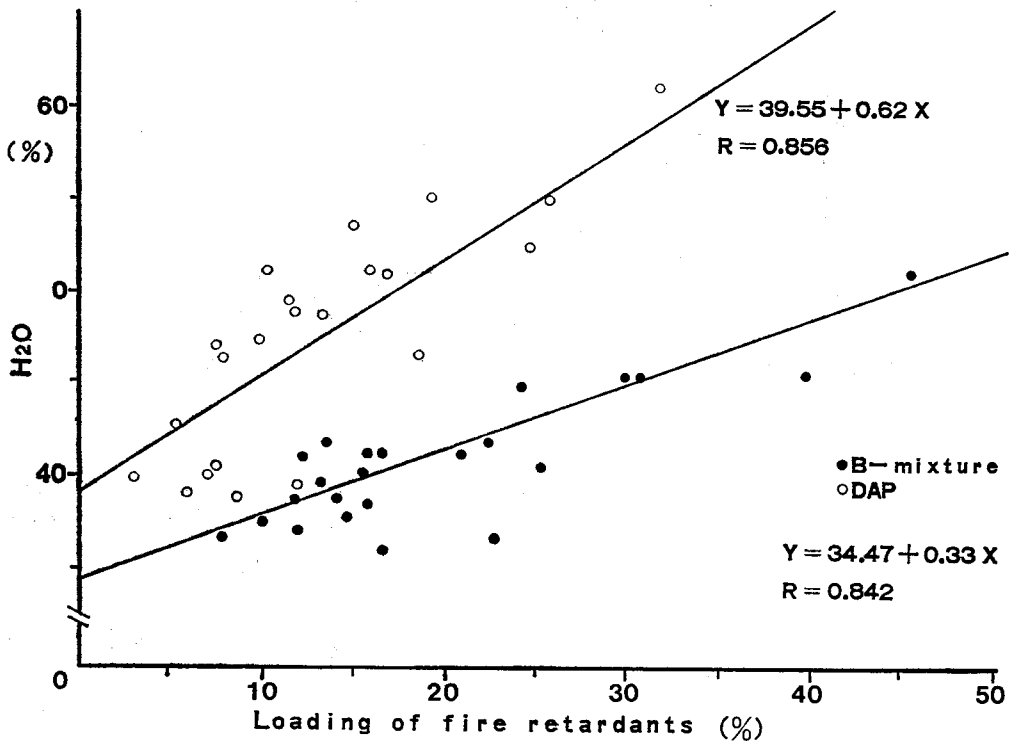


Fig. 9. Evolution of water vapor during pyrolysis from the specimens loading various amounts of fire retardants.

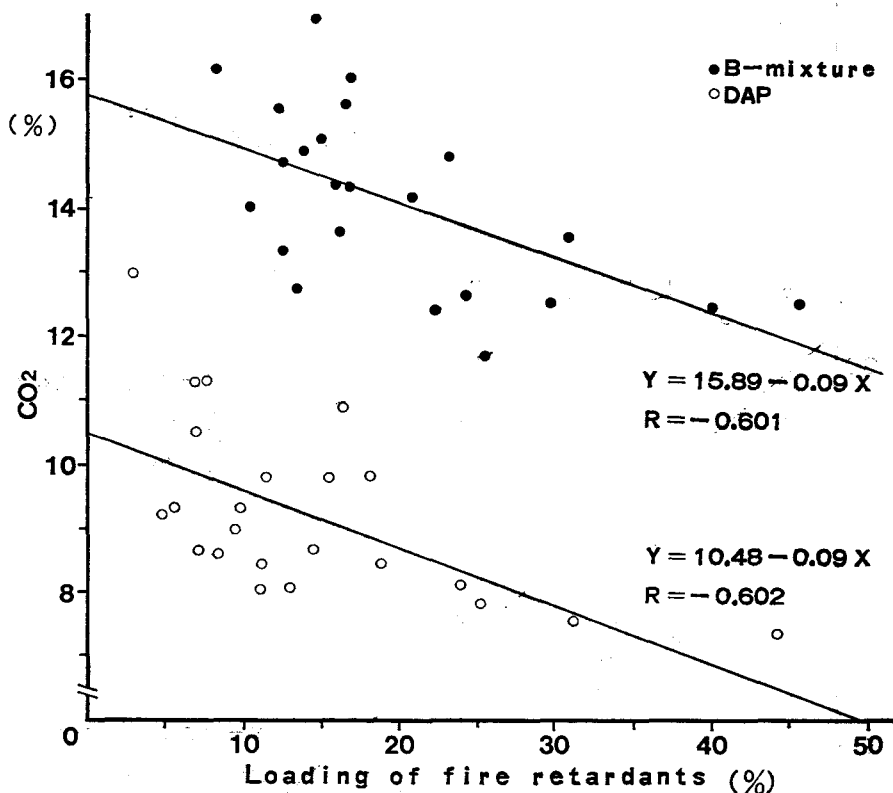


Fig. 10. Evolution of carbon dioxide during pyrolysis from the specimens loading various amounts of fire retardants.

various loadings of fire retardants. Evolution ratio of carbon monoxide decreases with increase of fire retardant. Comparing the B-mixture, DAP shows the higher inclination of regression line. (Fig. 8).

Evolution ratio of water showed the highest correlation in 6 components that were detected. The B-mixture and DAP increased water, especially the latter showed higher inclination. (Fig. 9).

Evolution of carbon dioxide, which is uncombustible, decreases with increase of fire retardants. The B-mixture reacts with plywood to evolve more carbon dioxide by 5% than DAP does. (Fig. 10).

And also, evolution of methane, which is combustible, decreases with increase of fire retardants. The B-mixture reacts with plywood to evolve more methane than DAP does. (Fig. 11).

Consequently, combustible carbon monoxide and methane decrease and uncombustible water increases, especially the water causes depression of circumstance temperature.

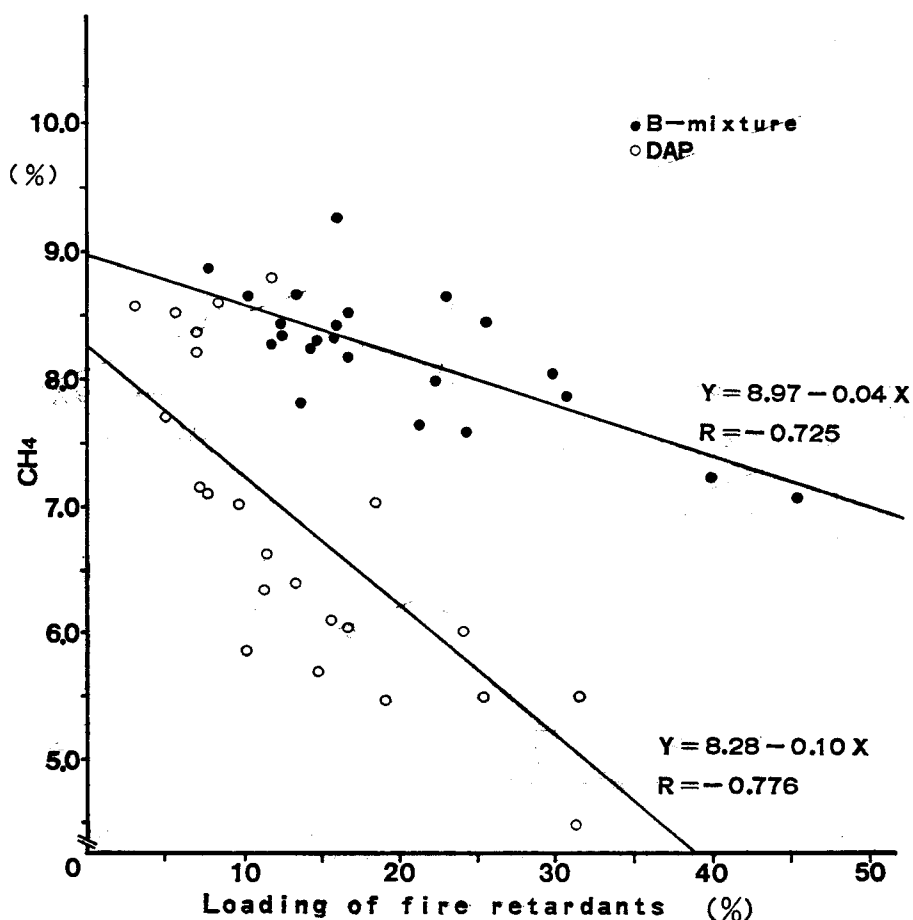


Fig. 11. Evolution of methane during pyrolysis from the specimens loading various amounts of fire retardants.

4. Conclusion

Fairly good results on the fire retardancy of plywood were observed by the vacuum impregnation of the mixture of boric acid and sodium borate, the loading of which is 5 percent or more. The following problems are the stabilization of flame used for combustion, the effects of thickness of plywood and the smoking of specimen during heating.

Summary

Wood is a very fine and beautiful interior material, however it has one weak point, that is the flammability. Fire retardation in our environment is becoming an important problem. The various fire retardants were surveyed. Boron compounds look fairly favorable chemicals. Basic experiments on paper as cellulose were already reported¹⁰. This study is summarized as follows:

1. The raw material was extended to woody material. As the practical speci-

men, a commercial lauan plywood was adopted, because of the relatively homogeneous property and the easy processing to desirable size.

2. As a most convenient combustion test, an apparatus which is used in JIS A 1322 was adopted. But the specimen size in the standard is too big to treat with fire retardants in our laboratory. So, the size was decreased from 20×30 cm to 15 cm square. And the judgement of effect of the fire retardant was changed from a length of carbonized area to the weight loss, because value of the former is not so clear.

3. Method of loading of fire retardants was studied. Several methods such as soaking, painting, pressure impregnation and vacuum one were tried. As the results, the last vacuum method showed the excellent data, especially the duplicate one resulted in 9% loading of the Boron-mixture.

4. Method of combustion test was studied. Combustion time was varied. Heating within 30 seconds did not ignite the plywood, and that of 90 seconds penetrated the plywood by combustion. Therefore, 40- to 80-second heatings are suitable ways for the purpose, and at last 70-second heating shows understandable performance of combustion, because it causes the maximum combustion of this plywood.

5. Loading of 5% or more of the B-mixture gave a fairly good result, which meant the suppression of the weight loss to 8% or less.

6. Judging from the results according JIS A 1322... Testing Method for Incombustibility of Thin Materials for Buildings, the specimens loading 5% or more of the B-mixture improved fairly the weight loss in the combustion test.

7. The effects of the B-mixture as a fire retardant on the pyrolysis-gas of treated plywood were studied. Total volume was not varied, but the toxic and combustible carbon monoxide decreased fairly with increase of the B-mixture. Combustible methane also decreased and incombustible water fairly increased with increase of the B-mixture. The water vapor will work as a depressor of temperature of the circumstances.

8. Next objects are the stabilization of flame caused by the use of town gas, the effects of thickness of plywood and the smoking of specimen during heating.

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要 約

各種難燃薬剤を検討の結果、ホウ素化合物が安全面からみて優れていると思われる。何故なら、処理材料の熱分解のさいに亜硫酸ガスとか青酸ガスのような有毒ガスを発生しないからである。

本論文は合板にたいする処理法を検討し、減圧注入がすぐれていることをあきらかにした。すなわち、30分減圧・風乾・30分減圧の二重注入法によりホウ素混合物を9%注入することができた。

ホウ素混合物で処理したラワン合板をJIS A 1322・建築用薄物材料の難燃性試験方法に準拠して燃焼試験をおこなった。なお、試験方法を簡素化し、15 cm角の小型材料を用いるようにした。5%以上のホウ素混合物を添加した試験材料は燃焼試験において重量減少率をかなり改善した。

ホウ素混合物処理合板の小片が熱分解ガスクロマトグラフィーにより分析された。その結果、防火薬剤の増加とともに有毒可燃の一酸化炭素が減少し、可燃メタンも減少し、不燃かつ火災時周辺温度を低下させる水蒸気が増大し、セルロースとはほぼ同様の結果を示した。