Studies on Wood Preservatives (V) Evaluation of Nitrostyrenes, Anti-oxidants and Miscellaneous Organobromocompounds to Prevent the Decay of Wood

Yoshiyuki INOUE*,[1] Ken-ichi KURODA*,[1] Hideaki TAKAHASHI*,[2] and Takeshi SAKAI*[3]

木材防腐剤に関する研究（第５報）

ニトロスチレン類，抗酸化剤および有機ブロム化合物の木材防腐効力試験

井上嘉幸，黒田健一，高橋英明，坂井　健

Introduction

Some wood species are resistant to biodeterioration, while most of the species are attacked by sap-staining fungi, moulds, wood decaying basidiomycetes and soft rot fungi. A great deal of attention has been given to safety control and environmental problems relating to conventional wood preservatives[1~6]. The environmental considerations are severely critical to the usage of chemicals for wood preservation through the world today. These strict social and environmental attitude have been stimulating the efforts of research to develop new, safe low-toxicity wood preservatives. Wood preservatives should afford a protective effect against the attack by fungi. This paper deals with the evaluation of nitrostyrenes, anti-oxidants and miscellaneous organobromocompounds used for the control of wood-rotting fungi. In this report, the toxicities of various compounds to two different wood-rotting fungi determined by applying the wood block method. The sand-block method recognized as the Japanese Industrial Standard (JIS A 9302) was slightly modified and applied for comparing the effectiveness and permanence of nitrostyrenes[7], anti-oxidants and miscellaneous organobromocompounds. On the other hand, decaying test for preliminary preservation was carried out by using *Fagus crenata* Bl..

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*1 Institute of Agricultural and Forestry Engineering, University of Tsukuba

*2 Course of Agricultural Sciences, Doctoral Program, University of Tsukuba

*3 Sandoz Pharmaceuticals, Ltd.

Materials and Methods

The outline of the method applied in the current investigation is as follows; Test block (20±0.5mm x 20±0.5mm in cross section and 10±0.5mm in length) consisted of sapwood of *Cryptomeria japonica* D. Don., with annual rings parallel to the 20x20mm face numbering three to five per 10mm and without visible evidence of defect.

Fungi used were mainly *Thyromyces palustris* and *Coriolus versicolor.* Culture fluid containing 0.2% peptone and 1% malt extract was used. A small portion of the mycelium growth of the sawdust slant was inoculated and incubated at 26±2°C, and above 70% relative humidity until the medium was covered by mycelium. The test blocks previously dried and weighing 0.01g were placed in a beaker and maintained in vacuum at the pressure of 50mmHg for 10 minutes.

The test solution containing the compounds at various concentrations was poured into the beaker through the top of the desicator while the vacuum was released at the atmospheric pressure and kept for 10 minutes, after allowing the solution to stand for a few minutes, the liquid on the face was removed and the test blocks were weighed. The standard amount of test solution absorbed by the block was about 200%. This test was associated with some leaching effects. After the impregnation, the weathering procedure was carried out as follows; The block was kept at 60±2°C for 23 hours and leached at 25±3°C for 1 hour with running water (2 to 3ℓ per minute). After the block was dried and weighed, it was placed with the cross-section down, on the surface of fungal growth and exposed to the attack for 90±2 days. After the end of the decay test, the mycelium was carefully brushed off on the test block, then, the block was dried at 60±2°C for 48 hours and the loss of weight caused by decay was determined. Decay test for preliminary preserve was as follows; Test block consisted of sapwood of *Fagus crenata* Bl.. The test solution was dipped for 10 seconds at 25°C. After drying, the weathering procedure was carried out as follows; The block was leached for 20 minutes. After the block was dried, Ultra violet light(15 Watt) was applied from the distances 20cm for 24 hours at the both cross section. Then, decay test was carried out using sand-block method for 2 months.

Results and Discussion

It is evident that there have been only a limited number of studies on the compounds using the wood block test. The wood block method uses small blocks of timber containing increasing concentrations of the preservative under test which are exposed to the attack of a vigorously growing pure culture of a real wood-destroying fungus. These block tests can also be used in order assess the performance of a preservative after weathering by leaching or volatilization; if a product has good weather resistance and a wide spectrum of activity against the test fungi it can be considered to be a realistic candidate. The candidate preservative is required to perform in an adequate manner in comparison. Normally a new preservative is first assessed against a single basidiomycete fungus and if it proves resistant to this, test is extended to further fungi, perhaps soft rot, then leaching, so that ultimately comprehensive information is available which clearly establishes whether the new preservative is likely to be reliable in service. The chemicals which are used extensively in Japan include organoiodine type chemicals, metallic naphthenates tributyltin oxide and ester of pentachlorophenol. Solvent type preservatives are usually applied by brushing, spraying or dipping and the absorption varies considerably in the kind of wood, the dimensions and shape of the material being treated.

Effective values of nitrostyrenes and related compounds on leached *Cryptomeria japonica* D. Don. by preliminary decay test are shown in Table 1. The results for anti-oxidants are shown in Table 2. The effective values determined by JIS A 9302 for anti-oxidants are shown in Table 3.

$$\text{Weight loss }(\%) = \frac{W_1 - W_2}{W_1} \times 100$$

W_1 : dry weight of test piece just before decaying test(g),
W_2 : dry weight of test piece after decaying test(g)

$$\text{Effective value} = \frac{\text{weight loss of untreated test piece}(\%) - \left(\text{weight loss of treated test piece}(\%) - \text{weight loss of test piece for correction}(\%)\right)}{\text{weight loss of untreated test piece}(\%)}$$

Test piece for correction: in the cases of oils and oil-borne preservatives, this test piece was placed on the same culture medium without inoculation.

The results for miscelleneous organobromocompounds are shown in Table 4. Effective values and absorbed solution of commercial wood preservatives are shown in Table 5. The determination of the effective value of wood preservative according to the JIS A 9302 method takes about 6 months if weathering test are included. However, in the case of preliminary decay test, it takes about 3 months.

Among the chemical candidates which have been tested so far their availability or potential as wood preservatives, butylated hydroxytoluene have been proved to be satisfactorily effective against *Tyromyces palustris*. Based on the results of a number of nitrostyrene derivatives and related compounds screened against decay fungus, *p*-(β-nitrovinyl) chlorobenzene, *p*-chloro-(α-chloro-β-nitro) styrene were the most effective in controlling wood decay fungus. *m*- or *o*-chloro-β-nitrostyrene, α-naphthyl-β-nitroethylene and α-thiocyano-β-nitrostyrene derivatives showed very low activity against wood rotting fungus.

In the case of preliminary decay test using anti-oxidant, SWC showed good result. Test blocks treated with anti-oxidant were covered by mycelium as same as untreated test block. Anti-oxidant did not show high level of effective value compared with commercial wood preservatives. Among organobromocompounds, dibromo indanone type compound showed good result. However, the effective value on this compound was about one half of that of dichlorofluanide.

Literature Cited

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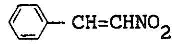
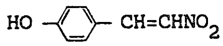
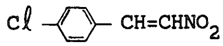
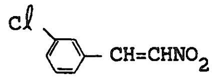
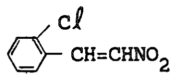
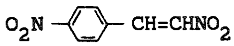
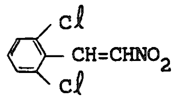
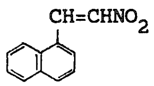
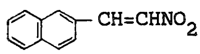
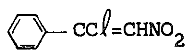
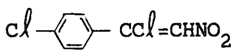
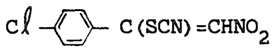
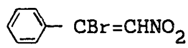
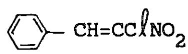
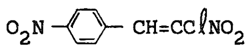
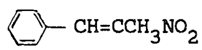
2. D.D. Nicholas; Wood and Fiber, **14**, 37 (1982)
3. J.A. Butcher; Mater. Org., **14**, 43 (1979)
4. J.A. Butcher et al; For. Prod. J., **27**, 19 (1977)
5. J.A. Butcher et al; For. Prod. J., **27**, 22 (1977)
6. M.A. Hulme and J.F. Thomas; For. Prod. J., **29**, 26 (1979)
7. M. Koremura; Nippon Nogei-Kagaku Kaishi, **36**, 473, 552, 557 (1962)

要旨

ニトロスチレン類，抗酸化剤および有機ブロム化合物を用い，ブナ材を用いる予備防腐効力試験とスギ材を用いる木材防腐効力試験（JIS A 9302を準用）を行った。用いた木材腐朽菌はオオウズラタケ（*Tyromyces palustris*）およびカワラタケ（*Coriolus versicolor*）である。ニトロスチレン類ではp－（β－ニトロビニル）クロロベンゼン，p－クロロ（α－クロロ－β－ニトロ）スチレン，抗酸化剤では2,6－ジ－tert.－ブチル－p－クレゾール，有機ブロム化合物では2,2－ジブロムインダン－3－オンに良好な防腐効力が認められた。なお，市販木材防腐剤は，油溶性および乳剤のいずれも指定濃度の1/10でも良好な防腐効力を示した。

Table 1 Preliminary decay test.

Compound	Effective value
	80.7
	79.4
	91.2
	40.5
	42.3
	80.7
	74.8
	40.1
	64.7
	76.0
	88.2
	41.2
	50.5
	72.8
	76.5
	85.3
Untreated	0

Concentration:1%

Solvent:dimethyl formamide

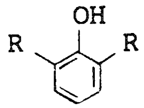
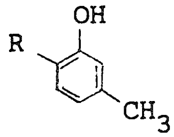
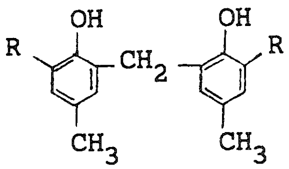
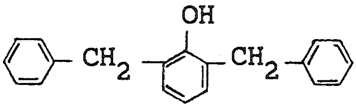
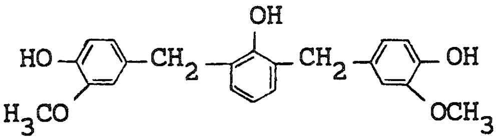
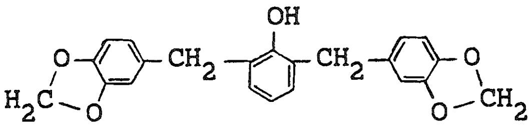
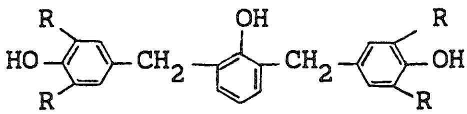
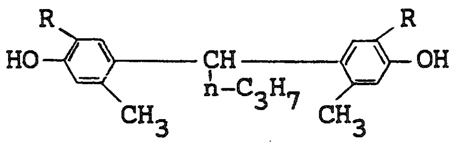
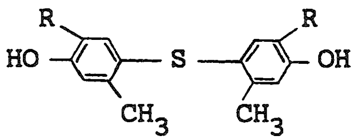
Wood block:*Fagus crenata* Bl., sapwood(20x20x10mm)

Treatment:dipping for 10 seconds

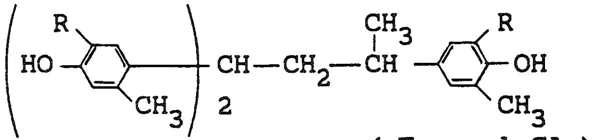
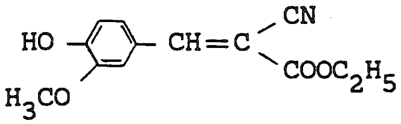
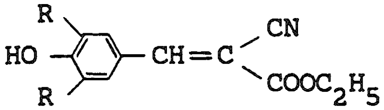
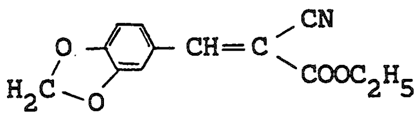
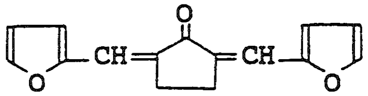
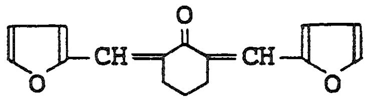
Weathering:Ultra-violet light and leaching

Test fungus:*Tyromyces palustris*

Table 2 Preliminary decay test using anti-oxidants.

Anti-oxidant	Effective value
 (BHT)	63.9
 (3M6B)	65.5
	52.6
	68.6
	65.2
	83.0
	0
 (SWP)	64.5
 (SWC)	90.8

To be continued

 (Topanol CA)	56.1
	93.8
	60.6
	63.4
	7.8
	48.4
Untreated	0

R:tert-Butyl

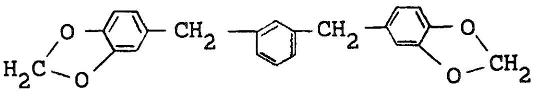
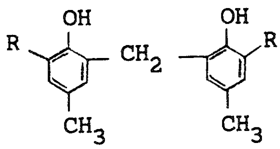
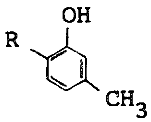
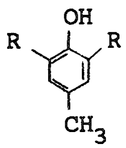
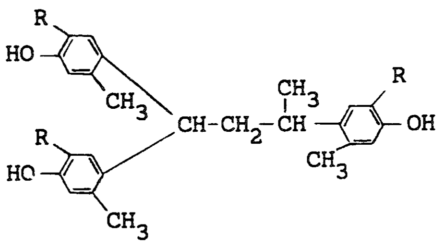
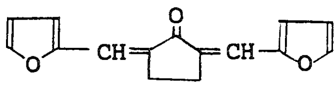
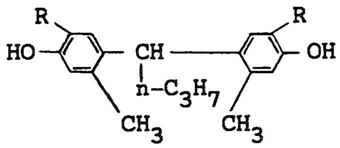
Concentration:1%

Solvent:methyl alcohol

Test fungus:*Tyromyces palustris*

Weight loss of untreated test block:28.7%

Table 3 Effective values on anti-oxidants on leached *Cryptomeria japonica* block by JIS A 9302.

Anti-oxidant	Effective value
	64.4
	0
	0
	98.3
	61.1
	71.1
	89.4
Untreated	0

R:tert-Butyl

Concentration:0.5%

Solvent:methyl alcohol

Test fungus:*Tyromyces palustris*

Table 4 Effective values of miscellaneous organobromocompounds by JIS A 9302.

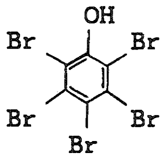
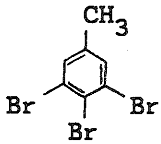
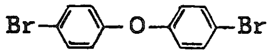
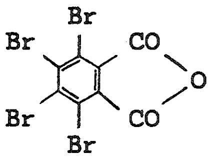
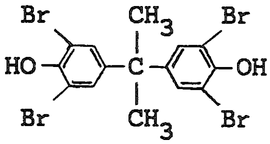
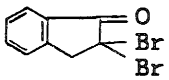
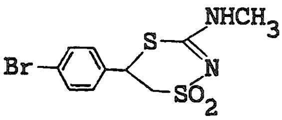
Compound	Concentration (%)	*Tyromyces palustris*	*Coriolus versicolor*
$(BrCH_2CHBrCH_2O)_3P{=}O$	0.5	0	0
	0.5	0	0
	0.5	40.8	25.9
	0.5	0	0
	0.5 0.1	45.2 32.0	10.3 0
	0.5	0	0
	0.2 0.1 0.05	100 40.5 25.9	100 95.0 0
	0.5	0	0
Untreated	0	0	0

Table 5 Effective values and absorbed solution of commercial wood preservatives.

Commercial wood preservative	Concentration	Absorbed solution (ml) after steeping for 6 hrs at 25℃		Effective value determind by JIS A 9302	
		Cryptomeria japonica D. Don.	*Fagus crenata* Bl.	Weight loss (%)	Effective value
Oil-borne type A	original liquid	1. 11	0. 68	0	100
	1/3	1. 05	0. 70	0	100
	1/10	1. 04	0. 64	0. 7	97. 2
Oil-borne type B	original liquid	1. 05	0. 57	0	100
	1/3	1. 04	0. 64	0	100
	1/10	0. 94	0. 67	24. 9	1. 6
Xylamon TR (oil-borne type)	original liquid	0. 99	0. 51	0	100
	1/3	0. 95	0. 65	0	100
	1/10	0. 98	0. 55	0	100
Woodtreat 55 (bodied mayonaise type emulsifiable concentrate)	original liquid	0. 89	0. 43	0	100
	1/3	1. 04	0. 54	0	100
	1/10	1. 09	0. 73	0	100
Emulsion type C	original liquid	1. 46	1. 23	0	100
	1/3	1. 42	1. 24	0	100
	1/10	1. 41	1. 21	0	100
Untreated	—	—	—	25. 3	0