Original

Laboratory Evaluation of Chemicals as Wood Preservatives

(1) 2-(Thiocyanomethylthio)benzothiazole (TCMTB)

Kunio TSUNODA*1

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Abstract——The chemical, 2-(thiocyanomethylthio) benzothiazole (TCMTB) gave promising results as a wood preservative in laboratory tests. TCMTB proved effective against decay fungi and subterranean termites at retentions of 2.5 and 2.2 kg/m^3, respectively when that was applied to the treatment of wood by vacuum/soak impregnation. Superficial treatment could protect wood from any decay fungus at a treating concentration of 1.5% as demonstrated in the decay test according to Japan Wood Preserving Association Standard-1 (1979).

Key words: 2-(thiocyanomethylthio)benzothiazole, decay test, termite test, vacuum/soak impregnation, wood preservative

1. Introduction

The candidate chemical, 2-(thiocyanomethylthio) benzothiazole (TCMTB) has been tested for its efficacy as an active ingredient of anti-sapstain formulations in various parts of the world[1~7]. The fungicide, when tested as a single chemical or a mixture with methylene-bis-thiocyanate, proved as effective as sodium pentachlorophenate in North America[1,2], whereas TCMTB was not so effective in controlling molds and staining fungi in Australasia[5,6]. Some commercial TCMTB-based formulations are now available for the treatment of freshly sawn timber, and analytical method of the chemical with HPLC has been developed in order to guarantee the quality of treated products[8,9].

On the other hand, the data is rather scattered as for the effectiveness against decay fungi. Laboratory screening tests showed the potential inhibition against soft-rotting fungi[10] and wood-decaying fungi[11 12]. More recently, TCMTB in an oil solvent gave the disappointing performance of weathered wood blocks against basidiomycetes possibly because of leaching and low retentions selected for testing. A retention of 2 kg/m^3 failed in protecting wood blocks from decay fungi in most cases[13]. When applied superficially, the chemical performed well in controlling decay fungi at treating concentrations of 1.5% or above[14].

In the present investigation TCMTB was tested for its effectiveness against

*1 Research Section of High Performance Wood Products.

decay fungi and termites in the laboratory when the fungicide was employed for vacuum/soak impregnation of wood blocks. Supplemental experiment was planned to reconfirm the fungicidal efficacy of TCMTB in surface treatment use.

2. Materials and Methods

2.1 Test chemical

Emulsifiable concentrate which contained 30% of TCMTB was employed in the present investigation. Treating solutions containing 0.1, 0.3 and 0.5% TCMTB respectively were prepared with distilled water. Supplier's information on some properties of TCMTB are shown in Table 1.

Table 1. Properties of 2-(thiocyanomethylthio)benzothiazole [TCMTB]*

Density of 30% concentrate at 25°C	1.05 g/ml
Flashpoint by Taglibue open-cup method	66°C
Toxicity	
Acute oral LD_{50}	1,590 mg/kg (rats)
Acute dermal LD_{50}	ca. 10,000 mg/kg (rabbits)

* Supplier's information

2.2 Japanese Industrial Standard (JIS) decay test

Sound sapwood blocks of *Cryptomeria japonica* D. Don measuring 20(T) × 20(R) × 10(L) mm were treated with aqueous slutions (0.1, 0.3 or 0.5% w/w) by vacuum/soak impregnation as prescribed in JIS A 9301 (1976) to obtain 6 replicates each for various test conditions. Retentions of TCMTB are given in Table 2 together with the results of decay tests.

Decay test was conducted according to JIS A 9302 (1976), provided that the additional decay fungi and weathering cycles were taken to read the results more comprehensively.

Apart from the weathering cycles designated in JIS A 9302 (JIS weathering), leaching procedure of ASTM Standard D 1413 (1976) for water-borne preservatives (ASTM weathering) and wet-dry cycles (W-D weathering) [blocks water-saturated under vacuum, kept at room temperature for 96 hrs, oven-dried at 60°C for 24 hrs and the cycle repeated twice].

Two decay fungi, *Gloeophyllum trabeum* (Pers. ex Fr.) Murrill and *Polyporous tulipiferae* (Schw.) Fries were additionally employed besides standardized decay fungi [*Tyromyces palustris* (Berk. et Curt.) Murr. and *Coriolus versicolor* (Linn. ex Fr.) Quélet] this time. The former is a brown-rot fungus commonly used for the soil block test, and the latter is known as a copper tolerant white-rot fungus[15].

2.3 Simulated above ground decay tests

Wood specimens were prepared in the same manner as described in 2.2. Using two decay fungi (*T. palustris* and *C. versicolor*), weathered or unweathered wood blocks were subjected to either NZFRI*[1] above ground test[16] or feeder-board test[17].

Details of the test methods should be referred to the previous papers.

2.4 Japan Wood Preserving Association (JWPA) decay test

Decay tests were done with brush-treated wood specimens at a rate of 110 ± 10 g/m^2 by JWPA Standard 1 (1979) and the amended Standard-1 (1989). The biggest amendment is concerned with weathering procedure. Formerly, treated wood specimens were immersed in non-running water for 30 sec, kept in a dessicator with water at the bottom for 4 hr at 26 ± 2°C, then transferred into an oven for 20 hr at 40 ± 2°C and the cycle repeated 9 times. In the amended method the blocks were subjected to immersion in non-running water for 5 hr at 25 ± 3°C followed by drying for 19 hr at 40 ± 2°C and the cycle repeated 29 times. Other techniques should be referred to the standard.

2.5 Termite test

Sapwood blocks of *Pinus densiflora* Sieb. et Zucc. measuring $10(T)\times10(R)\times20$ (L) mm were treated with aqueous solutions by vacuum/soak impregnation according to JIS A 9301. Treating strengths were 0.2, 0.3 and 0.5% of TCMTB. The treated blocks were dried at room temperature for three weeks before termite test or JIS weathering. Termite bioassay was carried out with weathered or unweathered wood blocks according to JWPA Standard-11(1) (1981). Weight loss and termite mortality were measured after three weeks' exposure to the attacks of *Coptotermes formosamus* Shiraki.

3. Results and Discussion

3.1 Fungicidal effectiveness in JIS decay test

As untreated controls were not decayed well by *G. trabeum* and *P. tulipiferae* in JIS decay test, the data with the two fungi was discarded. Summarized results are given in Table 2.

Over 30% weight loss was recorded with untreated controls regardless of weathering procedures. At the lowest test retention of 0.8 kg/m^3, JIS weathered blocks sustained 24.7% and 5.5% weight losses by *C. versicolor* and *T. palustris*, respectively. *T. palustris* failed in attacking unweathered blocks treated at a retention of 0.8 kg/m^3, whereas *C. versicolor* could degrade wood blocks of the same treatment.

At retentions of 2.5 kg/m^3 or higher both unweathered and weathered blocks

*[1] New Zealand Forest Research Institute

Table 2. Fungicidal effectiveness of TCMTB in JIS decay test

Weathering procedure	Retention [kg/m³ (mg/g)]	Mean % weight loss and standard deviation*1	
		Tyromyces palustris	*Coriolus versicolor*
JIS*2	0 (0)	32.6 (11.5)	33.0 (3.61)
	0.8 (2.5)	5.5 (6.83)	24.7 (9.27)
	2.5 (7.3)	0 (0)	0 (0)
	4.2 (12.1)	0 (0)	0 (0)
ASTM*3	0 (0)	31.1 (7.81)	37.5 (7.12)
	2.5 (7.3)	0 (0)	0 (0)
Wet-dry*4	0 (0)	29.4 (8.46)	39.5 (3.43)
	2.5 (7.3)	0 (0)	0 (0)
Unweathered	0 (0)	33.2 (7.54)	33.7 (10.4)
	0.8 (2.5)	0 (0)	18.8 (14.1)
	2 5 (7.3)	0 (0)	0 (0)
	4.2 (12.1)	0 (0)	0 (0)

*1 Standard deviation in the brackets *2 JIS weathering, *3 ASTM weathering, *4 Wet and dry cycles

were well protected from decay fungi after any weathering scheme. Toxic threshold value of TCMTB, therefore, was estimated to lie in the range between 0.8 and 2.5 kg/m³. On the basis of the values determined by the test method, TCMTB proved more effective than other preservatives such as alkylammonium compounds and copper chrome arsenate (Celkure K33) in controlling wood-decaying basidiomycetes[18]. Comparing the fungicidal efficacy of TCMTB with that of practically used oilborne organoiodine compounds, however, indicated that TCMTB was inferior to them in terms of restraining decay of pressure-treated wood[19 20].

3.2 Fungicidal effectiveness in the simulated above-ground decay tests

Results are shown in Table 3. In NZFRI above ground decay test commonly called toast rack test, TCMTB performed satisfactorily against *T. palustris* sustaining only 0~1.1% weight losses as shown in the table. Against *C. versicolor* the candidate chemical seemed less effective as the same in JIS decay test, although weight loss of the wood blocks treated at a retention of 0.8 kg/m³ was less than 4% even after weathering.

Similar results were obtained with TCMTB-treated wood blocks in feeder-board decay test. The figures here suggested that TCMTB was superior to alkylammonium compounds and CCA in the simulated above-ground decay tests[17].

3.3 Fungicidal effectiveness in JWPA decay test

As previoysly demonstrated[14], TCMTB was efficacious against *C. versicolor, T.*

Table 3. Fungicidal effectiveness of TCMTB in the simulated above-ground decay tests

Weathering procedure	Retention (kg/m³)	Mean % weight loss and standard deviation*1			
		NZFRI test		feeder-board test	
		T. palustris	*C. versicolor*	*T. palustris*	*C. versicolor*
JIS*2	0	23.9 (1.41)	19.1 (1.75)	19.6 (2.25)	15.6 (1.71)
	0.8	0.6 (0.787)	4.0 (1.46)	0.9 (0.680)	4.4 (0.715)
	2.5	0 (0)	0 (0)	0 (0)	0.2 (0.449)
ASTM*3	0	25.4 (1.58)	16.4 (1.39)	23.0 (2.58)	12.5 (1.14)
	0.8	1.0 (0.862)	3.4 (1.24)	1.0 (0.705)	4.0 (1.01)
	2.5	0 (0)	0 (0)	0 (0)	0 (0)
Wet-dry*4	0	23.6 (1.26)	7.8 (2.19)	24.2 (2.35)	13.4 (2.23)
	0.8	1.0 (0.712)	2.9 (1.47)	1.1 (1.22)	4.2 (1.24)
	2.5	0 (0)	0 (0)	0 (0)	0 (0)
Unweathered	0	23.3 (1.39)	12.2 (2.21)	24.0 (1.19)	13.4 (1.99)
	0.8	0 (0)	3.3 (1.59)	0 (0)	2.4 (1.26)
	2.5	0 (0)	0 (0)	0 (0)	0 (0)

*1～*4 Footnotes are the same as in Table 2

Table 4 Fungicidal effectiveness of TCMTB in JWPA Standard-1 (1979) decay test

Treatment conc. (%)	Mean % weight loss and value of efficiency*1					
	C. versicolor-*Fagus crenate* Blume		*T. palustris*-*C. japonica*		*S. lacrymans*-*P. densiflora*	
	Unweathered	Weathered	Unweathered	Weathered	Unweathered	Weathered
0.5	NT*2	NT	5.1 (82)	5.2 (82)	17.0 (46)	12.4 (60)
1.0	13.8 (63)	16.2 (57)	1.6 (94)	5.2 (82)	0.8 (97)	0.8 (97)
1.5	3.6 (90)	6.4 (83)	NT	NT	NT	NT
2.0	2.9 (92)	4.3 (89)	NT	NT	NT	NT
3.0	0 (100)	0.5 (99)	NT	NT	NT	NT
% weight loss of Untreated controls	37.7		28.1		31.4	

*1 Value of efficiency in the brackets
Value of efficiency=$[(W_1-W_2)/W_1]\times 100$, where W_1: mean % weight loss of untreated wood blocks and W_2: mean % weight loss of treated blocks.

*2 Not tested

palustris and *Serpula lacrymans* (Wulf. ex Fr.) Schroet. at treatment concentrations of 1.5, 1.0 and 1.0%, respectively when the chemical was applied superficially. Supplemental experiments showed that *T. palustris* could be controlled even at 0.5% as shown in Table 4. After the severer weathering cycles prescirbed in the newly

amended JWPA Standard-1 (1989), treatment strengths which could succeed in controlling the three test decay fungi with less than 3 % weight loss were not determined by the test concentrations up to 2 %.

3.4 Termiticidal effectiveness

Termiticidal effectiveness of TCMTB is given in Table 5 together with treating concentrations and retentions. Weathered specimens were unexceptionally attacked more than unweathered ones at any test retention. At 1.5 kg/m^3 weathered wood blocks sustained 4.5% weight loss and 12.8% mortality, and weight losses of less than 3% (the upper limit for a good termiticide) were achieved with wood blocks treated at retentions of 2.2 kg/m^3 or above regardless of weathering. Consequently, the efficient termiticidal effectivess of TCMTB was obtained at the similar range of retentions which were required for the inhibition of decay fungi.

Table 5 Termiticidal effectiveness of TCMTB

Treating conc. (%)	Retention (kg/m^3)	Weathering	Mortality (%)		Weight loss (%)	
			min.···max.	mean	min.···max.	mean
0.2	1.5	No	22.0···39.3	32.1	0.4··· 3.1	1.7
		Yes	8.0···19.3	12.8	3.5··· 6.2	4.5
0.3	2.2	No	15.3···30.0	21.9	0.6··· 1.0	0.8
		Yes	15.3···27.3	20.5	1.7··· 2.9	2.2
0.5	3.7	No	19.3···25.3	22.4	0····· 1.1	0.2
		Yes	13.3···26.0	18.2	1.4··· 2.1	1.8
Untreated controls			4.7··· 9.3	7.3	16.8···27.2	22.5

4. Conclusions

Satisfactory effectiveness of TCMTB in protecting timber from decay fungi and suterranean termites was attained at a retention of 2.5 kg/m^3 when the chemical was applied to vacuum/soak impregnation of wood. No marked difference in retention levels was noticed for controlling two major wood-attacking organisms. It, therefore, is interesting to investigate the applicability of TCMTB in both emulsifiable and oil solvent forms because the persistence of preservative effect could be varied with chemical forms, although the chemical seems unsuitable for glue-line treatment of plywoods[21] possibly due to the relatively low flashpoint of TCMTB (see Table 1).

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