CZECH MYCOL. 50 (4), 1998

Loss of antifungal activity of selected fungicides in treated wood due to natural ageing
Part 1: Activity against moulds

Ladislav Reinprecht

Faculty of Wood Technology, Technical University, T. G. Masaryka 24, SK-960 53 Zvolen, Slovak Republic

Reinprecht L. (1998): Loss of antifungal activity of selected fungicides in treated wood due to natural ageing. Part 1: Activity against moulds – Czech Mycol. 50: 249–258

The activity of 2-thiocyanomethylthiobenzothiazole (TCMTB) and selected organotin compounds (OTC = TBTO, TBTS, TBTCA and TBT-DEDTK) against moulds was evaluated by means of mycological tests in which treated and subsequently naturally aged beechwood samples were exposed to the effect of a mixture of six moulds under laboratory conditions. Natural ageing of the treated samples took place under an angle of 45 °, and during periods of 0, 2 or 4 months. TCMTB was characterized as the relatively most stable fungicide with antimould activity.

Key words: 2-thiocyanomethylthiobenzothiazole, organotin fungicides, beechwood, natural ageing, moulds.

Reinprecht L. (1998): Strata protihubovej účinnosti vybratých fungicídov v impregnovanom dreve následkom starnutia. 1. časť: Účinnosť proti plesniam. – Czech Mycol. 50: 249–258

Účinnosť 2-thiocyanomethylthiobenzothiazolu (TCMTB) a vybratých organociničitých látok (OTC = TBTO, TBTS, TBTCA, TBT-DEDTK) proti plesniam sa hodnotila prostredníctvom mykologických skúšok, keď sa impregnované a následne prirodzene stárnuté vzorky buka vystavili aktivite zmesi šiestych plesní v laboratórnych podmienkach. Prirodzené stárnutie impregnovaných vzoriek sa vykonalo pod uhlom 45 °, v trvaní 0, 2 alebo 4 mesiacov. TCMTB sa prejavil ako pomerne najstabilnejší fungicíd s protiplesňovou účinnosťou.

INTRODUCTION

Wood can be colonized by various microorganisms and fungi, including moulds. Moulds often grow on relatively moist wood surfaces and deteriorate mainly the aesthetical quality of wood due to pigmentation processes. However, the ability of moulds to damage the complicated lignin-saccharidic composition of wood cells and decrease the strength of wood, wood-based materials or wooden structures is obviously very small, in spite of the fact that moulds can also produce enzymes (cellulases, xylanases, lignin peroxidases, and also others) which catalyze depolymerization and decomposition reactions of individual wood components – cellulose, hemicelluloses, lignin, or extracts (Eriksson et al. 1990, Kirk and Cowling 1984).

Protection of wood against moulds and wood-destroying fungi, with the aim of raising its natural durability, is obtained by applying various types of inorganic and

organic fungicides. The original antifungal efficacy of fungicides can be decreased due to evaporation and leaching processes, or due to chemical changes in the fungicide molecules.

Inorganic fungicides containing boron (H_3BO_3, $Na_2B_4O_7.10H_2O$), copper ($CuSO_4.5H_2O$, ...), zinc ($ZnCl_2$, ...), chromium ($Na_2Cr_2O_7$, $K_2Cr_2O_7$, ...), fluorine (NaF, $NaHF_2$, ...), or other bioactive atomes are normally water-soluble. Their chemical fixation to the wood substrate or their transformation to insoluble compounds directly in treated wood is important for such products, which must be resistant to leaching. Some of the above mentioned fungicides can be either fixed on the lignin-polysaccharidic complex individually (e.g. Cu^{2+} complexes with lignin and cellulose; $C_2O_7^{2+}$ complexes with guaiacyl lignin) and mutually (e.g. $CuCrO_4$-lignin complexes), or – in presence of wood substance – can be gradually transformed into water-insoluble complex compounds (reduction $Cr^{6+} \rightarrow Cr^{3+}$, etc.) (Nicholas and Preston 1984).

Organic compounds can be applied (Reinprecht 1994):

- as liquids (e.g. creosote);
- in organic solutions (e.g. organotin compounds [TBTO, TBTN], 1,2,4-triazole derivatives [Azaconazole, Tebuconazole, Propiconazole], carbamates:– 3-iodo-2-propanylbutyl carbamate [IPBC]);
- in water emulsions (e.g. 2-thiocyanomethyltiobenzothiazole [TCMTB]);
- in water solutions (e.g. alkyl ammonium salts, cyclohexyldiazeniumdioxy-copper [Cu-HDO] in the presence of special additives).

They usually resist better to water and to leaching processes, but some of them are more or less evaporative, or can be chemically changed into less effective compounds due to UV-radiation, oxygen, microorganisms, etc. (Plum 1982).

This work deals with the antimould resistance of wood treated with fungicides and concentrates on the stability of the tested fungicides in wood during its ageing under climatic conditions.

MATERIAL AND METHODS

Wood

Beechwood (*Fagus sylvatica* L.) samples with dimensions of 50 × 10 × 5 mm (longitudinal × radial × tangential), free from tyloses, without false red heart, knots, splits or biodefects, and with sanded surfaces.

Treatment of beechwood samples with fungicides

The beechwood samples were treated with:

a) water emulsions of the 2-thiocyanomethylthiobenzothiazole (TCMTB) fungicide in the following concentrations:
C_{TCMTB} = 0.45 %, 0.9 %, 1.8 %, and 3.6 %
[Note: In the experiments the commercial preservative product Busan 30 L – Buckman Laboratories, which contains 30 % of TCMTB, was used.]

b) ethanole solutions of selected organotin compounds (OTC), that is, with the bis-(tributyltin)oxide (TBTO), tributyltin sulfamate (TBTS), tributyltin chloroacetate (TBTCA) and tributyltin-N,N-diethyldithiocarbamate (TBT-DEDTK) fungicides, in the following concentrations:
C_{OTC} = 0.1 %, 0.33%, and 1 %
[Note: OTC were synthesized and submitted by Mr. Doc. Ing. Juraj Kizlink, CSc. – STU CHTF Bratislava. In this test only those OTC were tested, which in previous tests using the poisoned soil method (Kizlink, Fargašová and Reinprecht 1996, Reinprecht and Kizlink 1996) showed the relatively highest activity.]

Treatment of the beechwood specimens was carried out with the following two impregnation techniques:

dipping (time = 45 minutes; temperature = 20 °C; Note: only with TCMTB);

pressure impregnation (pressure = 0.6 MPa; time = 15 minutes; temperature = 20 °C)

Natural ageing of treated samples

The natural or accelerated assessment of the stability of woods, coatings and preservatives against external factors can be carried out by various methods (e.g.: Feist and Williams 1991, Hoey and Hipwood 1974, Palashev and Abrashev 1993, Podgorski et al. 1994, Reinprecht et al. 1989).

In this test the following natural ageing method of treated wood prior to mycological testing was applied:

Before natural ageing the treated beechwood samples were conditioned (4 weeks) on a moisture level of about 12 %.

Natural ageing of the samples was carried out without contact with the ground, in the industrial zone of the town of Zvolen, at an altitude of 320 m, the southern exposure, under an angle of 45 °, during periods of 0, 2 or 4 months, from 15th April to 15th August.

(Procedure: The wood samples treated with fungicides were attached onto supporting boards 300 × 100 × 20 mm large, and subsequently placed into special frames to undergo natural ageing.)

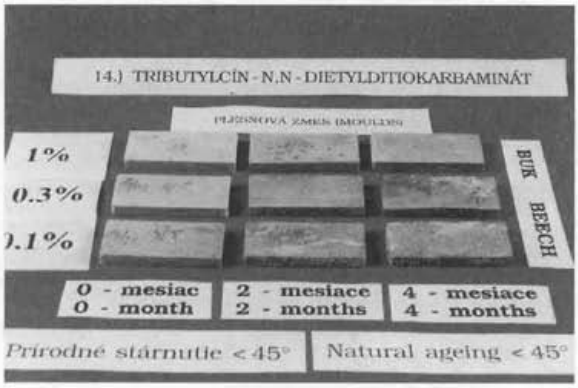

Fig. 1. The antimould resistance of treated beechwood against the tested mixture of moulds have been decreased due to ageing processes: growth of moulds on samples

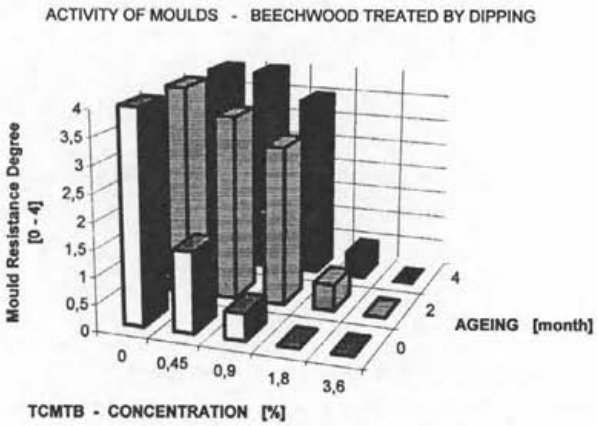

Fig. 2. Mould resistance degrees (MRD) of beechwood which was primarily treated with TCMTB using the dipping technique, and naturally aged 0, 2, or 4 months

Resistance of treated and (un)aged samples against moulds

Naturally aged surfaces 50 mm × 10 mm of the treated wood samples (50 × 10 × 5 mm), which had been aged under the influence of climatic and other open-air factors (rain, UV-radiation, emissions, etc.) during 0, 2, or 4 months, were vaccinated with a spore mixture of the following moulds:

Aspergillus amstelodami (Mangin) Thom et Church No. 2437
Aspergillus niger van Tieghem No. 1877

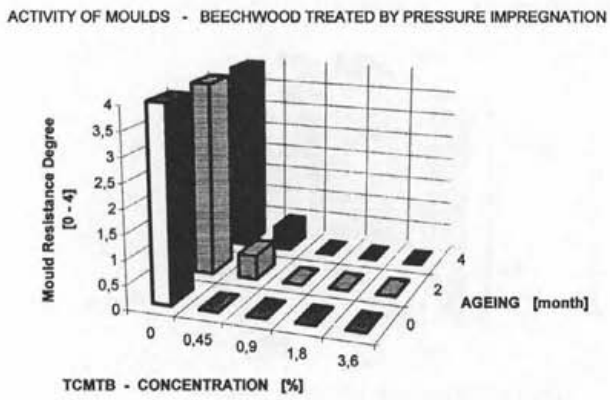

Fig. 3. Mould resistance degrees (MRD) of beechwood which was primarily treated with TCMTB by pressure impregnation, and naturally aged 0, 2, or 4 months

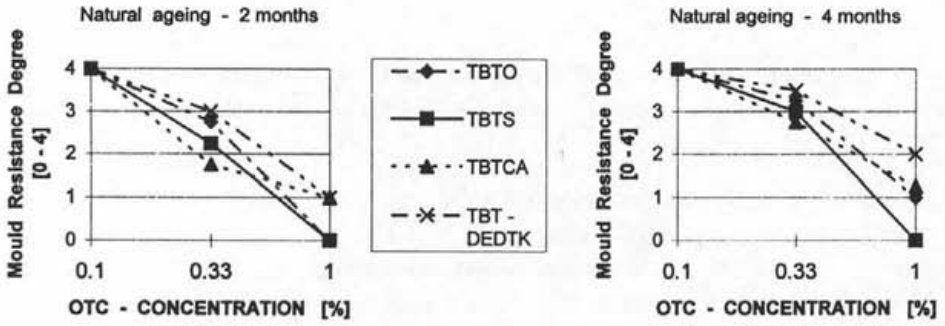

Fig. 4. Mould resistance degrees (MRD) of beechwood which was primarily treated with various organotin compounds TBTO, TBTS, TBTCA, or TBT-DEDTK by pressure impregnation, and naturally aged: 2 months (A), or 4 months (B)

Paecilomyces varioti Bainier	No. 2693
Penicillium cyclopium Westling	No. 2332
Chaetomium globosum Kunze	No. 358
Trichoderma viride Pers.: Fr.	No. 1403

The treated samples with aged and vaccinated surfaces were placed into Petri dishes on stiffened plaster and conditioned during 28 days at a temperature of $T = 29 \pm 1$ °C, and at a relative air humidity $RH = 95 \pm 3$ %.

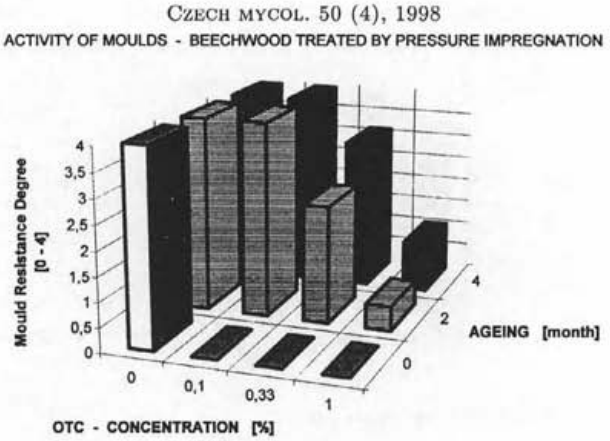

Fig. 5. Mould resistance degrees (MRD) of beechwood which was primarily treated with organotin compounds (OTC) by pressure impregnation, and naturally aged 0, 2, or 4 months (Note: MRD = mean value obtained from all tested OTC: TBTO, TBTS, TBTCA, and TBT-DEDTK)

The resistance of the treated and aged surfaces against moulds (MRD – mould resistance degree) was established after 28 days according to the following criteria (STN 49 0604 standard):

MRD	*MOULDS ON TESTED SURFACES*
0	No moulds (enlargement 50 ×)
1	< 10 % of surface covered with moulds
2	< 25 % of surface covered with moulds
3	< 50 % of surface covered with moulds
4	> 50 % of surface covered with moulds

RESULTS AND DISCUSSION

Results concerning losses of the antimould activity of the tested fungicides in treated beechwood due to its natural ageing are presented in Tables 1 and 2, Figures 1, 2, 3, 4 and 5.

For the TCMTB and organotin (OTC = TBTO, TBTS, TBTCA, TBT-DEDTK) fungicides the following critical toxic values, i.e. critical obligatory retentions of fungicide in kilograms per cubic meter of treated wood to guarantee MRD = 0, were determined:

a) apparently lower toxic values testing the antimould resistance of the treated samples which were not naturally aged:

TOXIC VALUES OF FUNGICIDES AGAINST MOULDS – WITHOUT AGEING

Fungicide	Toxic value [kg.m^{-3}]	Treatment
TCMTB	1.22–2.55	dipping
	< 2.05	pressure impregnation (p.i.)
TBTO	< 0.42	p.i.
TBTS	< 0.40	p.i.
TBTCA	< 0.40	p.i.
TBT-DEDTK	< 0.41	p.i.

b) apparently higher toxic values testing the antimould resistance of the treated samples which were naturally aged (2 or 4 months of ageing):

TOXIC VALUES OF FUNGICIDES AGAINST MOULDS – WITH AGEING

Ageing	Fungicide	Toxic value [kg.m^{-3}]	Treatment
2 months	TCMTB	2.55–4.60	dipping
		2.05–3.81	pressure impregnation (p.i)
	TBTO	1.38–4.15	p.i.
	TBTS	1.38–4.06	p.i.
	TBTCA	> 4.20	p.i.
	TBT-DEDTK	> 4.08	p.i.
4 months	TCMTB	2.55–4.60	dipping
		2.05–3.81	p.i.
	TBTO	> 4.15	p.i.
	TBTS	1.38–4.06	p.i.
	TBTCA	> 4.20	p.i.
	TBT-DEDTK	> 4.08	p.i.

In unaged samples the TCMTB fungicide had a lower antimould activity (higher toxic values) in comparison with the organotin fungicides TBTO, TBTS, TBTCA or TBT-DEDTK (Table 1 and 2).

On the other hand, the achieved results of the mycological tests with aged beechwood samples indicate indirectly, that the TCMTB fungicide (or wood treated with TCMTB) is relatively better resistant to external factors acting during natural ageing than organotin compounds – OTC (Table 1 and 2, Fig. 2, 3 and 5).

Table 1
Mould resistance degrees (MRD) of the aged surfaces of beech samples primarily treated with the 2-thiocyanomethylthiobenzothiazole (TCMTB) fungicide present in the commercial product Busan 30 L (Busan 30 L = 30 % TCMTB)
(C_{TCMTB} – concentration of TCMTB; n – number of samples; R_f – retention of TCMTB; MRD – mould resistance degree)

Moulds: *Mixture of microscopic fungi*							
C_{TCMTB}	Ageing	TCMTB application technique					
		DIPPING			PRESSURE IMPREGNATION		
[%]	[month]	n	R_f [kg.m^{-3}]	MRD [0–4]	n	R_f [kg.m^{-3}]	MRD [0–4]
0	0	6	—	4	6	—	4
	2	6	—	4	6	—	4
	4	6	—	4	6	—	4
0.45	0	6		1.5	6		0
	2	6	0.65	3.5	6	2.05	0.5
	4	6		4	6		0.5
0.9	0	6		0.5	6		0
	2	6	1.22	3	6	3.81	0
	4	6		3.5	6		0
1.8	0	6		0	6		0
	2	6	2.55	0.5	6	7.75	0
	4	6		0.5	6		0
3.6	0	6		0	6		0
	2	6	4.60	0	6	14.80	0
	4	6		0	6		0

Comparing antimould activity of the individual organotin compounds based on absolute MRD values (Table 2, Fig. 4), it is evident that, due to climatic factors, the tributyltin-N,N-diethyldithiocarbamate (TBT-DEDTK) lost antimould activity earlier in comparison with other organotin compounds (TBTO, TBTS, TBTCA).

CONCLUSIONS

Assessing the mycological tests carried out with treated and (un)aged beechwood samples, the following conclusions can be drawn:

Toxic values of both the 2-thiocyanomethylthiobenzothiazole (TCMTB) fungicide present in the commercial product Busan 30 L, and selected organotin

compounds (OTCs = TBTO, TBTS, TBTCA, TBT-DEDTK) were significantly increased due to natural ageing processes in the intervals of 0 to 4 months.

The stability of TCMTB against natural ageing factors (rain, UV radiation, etc.) was slightly higher in comparison with the tributyltin compounds, in spite of the fact that TCMTB is less effective – having higher toxic values in unaged wood.

Tributyltin-N,N-diethyldithiocarbamate (TBT-DEDTK), which was considered as a prospective organotin compound from efficacy tests on poisoned soils (Kizlink et al. 1996), had a lower weather stability compared to other tributyltin compounds (TBTO, TBTS or TBTCA).

Table 2
Mould resistance degrees (MRD) of the aged surfaces of beech samples primarily treated with organotin (OTC = TBTO, TBTS, TBTCA, TBT-DEDTK) fungicides applying the pressure impregnation technique
(C_{OTC} – concentration of the used OTC-fungicide; n – number of samples in each series [n = 4]; R_f – retention of the fungicide; MRD – mould resistance degree)

Moulds: *Mixture of microscopic fungi*									
C_{OTC}	Ageing	OTC-fungicide application technique PRESSURE IMPREGNATION							
		TBTO		TBTS		TBTCA		TBT-DEDTK	
		R_f	MRD	R_f	MRD	R_f	MRD	R_f	MRD
[%]	[month]	[kg.m^{-3}]	[0–4]	[kg.m^{-3}]	[0–4]	[kg.m^{-3}]	[0–4]	[kg.m^{-3}]	[0–4]
0.1	0		0		0		0		0
	2	0.42	4	0.40	4	0.40	4	0.41	4
	4		4		4		4		4
0.33	0		0		0		0		0
	2	1.38	2.75	1.38	2.25	1.32	1.75	1.35	3
	4		3.25		3		2.75		3.5
1.0	0		0		0		0		0
	2	4.15	0	4.06	0	4.20	1	4.08	1
	4		1		0		1.25		2

TBTO = tributyltin oxide;
TBTS = tributyltin sulfamate;
TBTCA = tributyltin chloroacetate;
TBT-DEDTK = tributyltin-N,N-diethyldithiocarbamate

Mean toxic values of fungicides against moulds [$kg.m^{-3}$]

"Pressure impregnation"	TCMTB	OTCs
unaged – 0 month	< 2.05	< 0.42
aged – 2 months	2.05–3.81	$1.38 \geq 4.20$
aged – 4 months	2.05–3.81	$1.38 \geq 4.20$

REFERENCES

ERIKSSON K. E. L., BLANCHETTE R. A. and ANDER P. (1990): Microbial and enzymatic degradation of wood and wood components. Springer Series in Wood Science, Berlin Heidelberg, 407 pp.

FEIST W. C. and WILLIAMS R. S. (1991): Weathering durability of chromium-treated southern pine. – For. Prod. J. 41, (1): 8–14.

HOEY C. E. and HIPWOOD H. A. (1974): An appraisal of artificial weathering methods for assessment of the durability of paint films. – J. Oil. Col. Chem. Assoc. 57: 151–160.

KIRK T. K. and COWLING E. B. (1984): Biological decomposition of wood. In: Rowell R. M. (ed.) The Chemistry of Solid Wood, Adv. Chem. Ser., 207, Am. Chem. Soc., pp. 455–487.

KIZLINK J., FARGAŠOVÁ A. and REINPRECHT L. (1996): Evolutional organotin compounds for biocidal wood protection suitable for small tonnage production. – Drev. Výsk. 41, (2): 19–29.

NICHOLAS D. D. and PRESTON A. F. (1984): Interaction of preservatives with wood. In: Rowell R. M. (ed.) The Chemistry of Solid Wood, Adv. Chem. Ser., 207, Am. Chem. Soc., pp. 307–320.

PALASHEV Y. and ABRASHEV G. (1993): Accelerated assessment of wood stability towards external factors. In: Proceedings of the symposium Wood Modification '93, Agricultural University Poznaň, Poland, pp. 169–172.

PLUM H. (1982): Organo-tin compounds and their influence on the environment. – Internat. Environ. Safety. 12, 4 pp.

PODGORSKI L., MERLIN A. and SAITER J. M. (1994): Natural and artificial ageing of alkyd based wood finish – calorimetric investigation. – J. Thermal Anal. 41: 1319–1324.

REINPRECHT L., HORSKÝ D. and RÍČINOVÁ K. (1989): Vplyv expozičných zaťažení na vlastnosti náterových systémov s obsahom fungicídov. (Influence of exposure rate on properties of coating systems containing fungicides). In: Zb. Ved. Prác DF Zvolen 1989/1, Alfa Bratislava, pp. 139–153.

REINPRECHT L. (1994): Ochrana dreva a kompozitov. (Preservation of wood and composites), Technical University Zvolen, 1994, 198 pp.

REINPRECHT L. and KIZLINK J. (1996): Efficiency of organotin dithiocarbamate derivatives against wood destroying fungi. In: Acta Facultatis Xylologiae TU Zvolen 1996/2, pp. 75–87.

STN 49 0604: Ochrana dreva – Metódy stanovenia biocídnych vlastností ochranných prostriedkov na drevo. (Wood protection – Methods for the determination of biocidal properties of wood preservatives.), (Standard)