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Research on the influence of the chemical composition of wood preservatives on functional properties

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Abstract: *Research on the influence of the chemical composition of wood preservatives on functional properties*
The study presents the results of tests of corrosive aggressiveness, the penetration depth, the fungicidal value and the influence on wood flammability of agents with diverse chemical composition. A favourable effect of a 10% addition of didecyldimethylammonium nitrate(III) on the corrosive aggressiveness of the preservative containing didecyldimethylammonium nitrate(V) was proved. The tests of the penetration depth proved a 1.6-fold increase in the penetration depth into wood of the mixture of 15% of tebuconazole and 85% of [DDA][NO_3], compared to pure ionic liquid. The addition of 15% of tebuconazole to didecyldimethylammonium nitrate(V) decreased the fungicidal value to a level of <0.73 kg m^{-3}.

Keywords: penetration depth, corrosivity, fungicidal value, wood flammability

INTRODUCTION

For ages wood has been used as a building material. Although this material has many advantages such as mechanical strength, good heat insulation properties, sound-absorbance, and also is characterised by easy machining and joining technique, and distinguished by high aesthetics, it can prove to be a very impermanent material, if unprotected. Already in antiquity people made attempts to protect this valuable raw material from both biological decomposition and fire, using agents found in nature [1,2]. At the beginning of the 19th century researchers developed first chemical wood preservatives characterised by a high effectiveness of protection and a broad range of applications; however, they were a serious threat to human and animal health and life.

Nowadays, the list of biocidal products admitted to trading is much limited in Europe, mainly for the sake of environmental protection [3].

Innovative wood preservatives are mostly mixtures of various organic and inorganic components, selected so as to achieve an optimum effect of the preservative. The following compounds are used as inorganic components: copper compounds (especially copper oxides, basic copper carbonate, copper di-azonium), dichromates and boric acid. Amongst the organic components there are: triazole derivatives, carbamates, tiabendazol, quaternary ammonium salts, creosote and other. Salt preservatives for impregnation against fire also contain phosphates, bromides, and sulphates (predominantly ammonium sulphates), as well as urea and borax.

The presently growing requirements regarding the durability of wooden structures, as well as fire safety and ecological safety, are the reason why new generations of agents increasing the resistance of wood to fire and microorganisms are put into use. In Poland, wood preservatives used for the protection of wood against biotic degradation factors should meet the requirements of PN-C-04906:2000 standard ”Wood preservatives. General requirements and tests”. This document indicates inter alia parameters such as penetration depth, the effect on wood flammability, corrosive aggressiveness or fungicidal value, as tests necessary for the chemical agents protecting wood against microorganisms.

The article is an attempt to define the effect of the chemical composition of wood preservatives on their functional properties such as corrosivity, the penetration depth, the fungicidal value, and the influence on wood flammability.

MATERIALS AND METHODS

Determination of the penetration depth

Tests of the penetration depth were carried out on 4 biocidal agents, i.e.: 1 – didecyldimethylammonium nitrate(V) [DDA][NO_3]; 2 – [DDA][NO_3] + tebuconazole; 3 – didecyldimethylammonium propionate [DDA][C_2H_5COO] + tebuconazole; 4 – FNW; 4 – the experimental agent FNW containing: $CuCO_3$ x $Cu(OH)_2$, H_3BO_3, N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate, and propiconazole.

The tests of the penetration depth of wood preservatives were carried out based on the guidelines of PN-75/C-04901. 0.5 g of the solutions of tested preservatives were applied on the surface of sapwood samples of Scots pine (*Pinus sylvestris* L.) of the dimensions of 50 x 50 x 20 mm and a relative moisture content of 12±1%. After 7 days of conditioning, the depth of penetration of the compounds was measured on the cross-sections.

Determination of corrosivity

Seven biocidal agents were analysed:
1 – the experimental agent FNW, 2 – the experimental copper-chromium-boron agent VP-B; 3 – a mixture of 85% of [DDA][C_2H_5COO] + 15% of tebuconazole; 4 – [DDA][NO_3]; 5 – a mixture of 80% of [DDA][NO_3], 5% of [DDA][NO_2] and 15% of tebuconazole; 6 – a mixture of 75% of [DDA][NO_3], 10% of [DDA][NO_2] and 15% of tebuconazole.

The tests were conducted by the direct method in accordance with PN-87/04910 standard. Plates of steel sheet of the dimensions of 1 x 35 x 75 mm were placed in 1% solutions of wood preservatives for the period of 10 and 20 days. After a specified time the plates were removed from the solutions, then the corrosion product was removed, the plates were dried and then weighed. The corrosive aggressiveness and the dynamics of corrosion were determined.

Determination of the fungicidal value

The fungicidal value was determined, according to the guidelines of PN-EN 113:2000 standard, on three preservatives: [DDA][NO_3], [DDA][NO_3] (15% T), and [DDA][NO_2]. Samples of pine (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.), dried to a constant mass, were impregnated in the solutions of tested wood preservatives. After a conditioning period and sterilisation, the samples were subjected to the activity of wood-decaying fungi for a period of 16 weeks in a temperature of 22 ±1ºC and a relative humidity of 70 ±5%. Once the assumed exposure period ended, the loss of mass of the samples was determined according to the procedure described in the standard.

Determination of the effect on flammability of wood

Studies of the effect of three selected preservatives (i.e. the experimental agent NFW, didecyldimethylammonium dicyanimide [DDA]DCI], didecyldimethylammonium dihydrogen phosphate [DDA][H_2PO_4]) on wood flammability were conducted using a conical calorimeter and by the methods described in PN-C-04914 standard. A preservative in an amount of 200 g cm^{-2} was applied on wood samples of the dimensions of 100 x 100 x 10 mm and a relative moisture content of 12%. Then, the samples were conditioned in a temperature of 20ºC and a relative humidity of 65±5%, until they reached a constant mass. So prepared samples were tested according to the guidelines described in the standard.

RESULTS

Table 1 compares the results of the tests of corrosive aggressiveness towards steel. The ionic liquid [DDA][NO_3], whose anion is the acidic rest of a strong acid, turned out to have been the most corrosion-causing agent. An average velocity of corrosion after 20 days was

0.2826 $g \cdot m^{-2} \cdot day$, and the depth of corrosion was at a level of 0.0139 $mm \cdot year^{-1}$. On the other hand, the mixture of this salt with didecyldimethylammonium nitrate(III) and tebuconazole was characterised by a low corrosive aggressiveness – the greater the addition of nitrate(III), the lower corrosive aggressiveness. A 10% share of [DDA][NO_2] allowed obtainment of an agent, which caused less mass loss of the steel plates immersed in it for the time of the experiment, than the mass loss of control plates. These results prove that corrosive aggressiveness depends mainly on the anion structure. Such conclusions are also confirmed by the results published by Uerdingena et al. [2005]. The copper-chromium-boron agent VP-B also demonstrated the activity inhibiting the corrosion of carbon steel. After 20 days of the test, average velocity of corrosion was -0.0484 $g \cdot m^{-2} \cdot day$, but in this case the dynamics of corrosion demonstrated an upward trend. On the other hand, the experimental agent NFW, containing ammonium propionate, was characterised by a low velocity of corrosion (0.0282 $g \cdot m^{-2} \cdot day$ after 20 days) and decreasing dynamics of corrosion.

Table 1. Aggressiveness and dynamics of corrosion of ionic liquids for carbon steel

Wood preservative	Average corrosion rate after		Depth of the corrosion after		Corrosive aggressiveness	Dynamics of corrosion
	10 days	20days	10 days	20days		
	g/m^2 x day		mm / year			
FNW	0.0295	0.0282	0.00137	0.00131	small	decreasing
VP-B	-0.2437	-0.0484	-0.0117	-0.0024	small	increase
[DDA][C_2H_5COO] 85% + tebuconazole 15%	0.1279	0.2019	0.0061	0.0100	small	increase
[DDA][NO_3]	0.3398	0.2826	0.0167	0.0139	average	decreasing
[DDA][NO_3] 80% + [DDA][NO_2] 5% + tebuconazole 15%	-0.1278	0.1189	-0.0061	0.0066	small	increase
[DDA][NO_3] 75% + [DDA][NO_2] 10% + tebuconazole 15%	-0.1609	-0.0826	-0.0082	-0.0041	small	decreasing

Fig. 1 presents the results of the penetration depth test for pine wood characterised by a moisture content of 12%. The penetration depth of ionic liquid [DDA][NO_3] was 3.8 mm and was deeper than that of the control agent NaF. Once 15 weight percent of tebuconazole was dissolved in this ionic liquid, the penetration properties of didecyldimethylammonium nitrate(V) were improved – the penetration depth was 6.2 mm. This difference was due to a lower viscosity of the mixture of this ionic liquid and a derivative of 1,2,4-triazole, compared to pure [DDA][NO_3]. In the case of the mixture of [DDA][C_2H_5COO] and tebuconazole, the penetration depth was at a level of 3.7 mm, which proved the influence of the anion structure on the penetration properties of ionic liquids. The experimental agent FNW was characterised by weak penetration properties at a level of 2.3 mm, thus below the level of the reference substance.

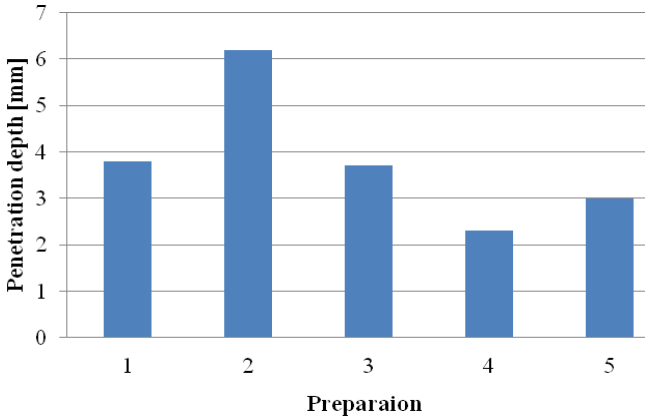

Figure 1. Depth of penetration into Scots pine wood of: 1 – [DDA][NO_3]; 2 – [DDA][NO_3]+15%T; 3 – [DDA][C_2H_5COO]+15%T; 4 – FNW; 5 – NaF

The fungicidal values against the white rot fungi and the brown rot fungi are compared in table 2. The tests were carried out for two ionic liquids with didecyldimethylammonium cation, i.e. nitrate(V) and nitrate(III). The biocidal activity of nitrate(V) was 3.95-6.78 kg·m^{-3}, determined on pine wood for *Coniophora puteana* fungus; whilst the ionic liquid with nitrate(III) anion demonstrated much weaker fungicidal properties (>6.84 kg·m^{-3}). The biocidal activity of the mixture of didecyldimethylammonium nitrate(V), containing 15% of tebuconazole, increased significantly and equalled <0.73 kg·m^{-3}. The experimental agent FNW was also characterised by good biocidal parameters, i.e. its fungicidal values were at a level of 4.54-7.15 kg m^{-3} for *Coniophora puteana* and 6.09-10.05 kg m^{-3} for *Trametes versicolor.*

Table 2. Fungicidal value of wood preservatives against *C. puteana* and *T. versicolor*, determined on Scots pine and beech wood

Wood preservative	Fungus species	Species of wood	Impregnation solution concentration	Fungicidal value according to PN-EN 113
			%	kg m^{-3}
FNW	*Coniophora puteana*	Scots pine	0.63 -1.0	4.54 – 7.15
	Trametes versicolor	Beech	1.0 – 1.6	6.09 – 10.05
[DDA][NO_3]	*Coniophora puteana*	Scots pine	0.63 - 1.0	3.95 - 6.78
[DDA][NO_3] (15%T)	*Coniophora puteana*	Scots pine	< 0.1	< 0.73
	Trametes versicolor	Beech	0.1 – 0.25	0,67 -1,67
[DDA][NO_2]	*Coniophora puteana*	Scots pine	>1.0	>6.84
	Trametes versicolor	Beech	1.0-1.6	6.37-10.07

The results of the studies on the influence of two ionic liquids with didecyldimethylammonium cation and the experimental agent FNW on wood flammability are presented in table 3. In the

case of wood protected with the ionic liquid containing dihydrogen phosphate anion [DDA][H_2PO_4], the following indices, i.e. the time to ignition, average rate of mass loss and average heat release rate after 180 s, were at a level of unprotected wood. The indices describing the influence of the compound containing dicyanimide anion [DDA][DCI] on the flammability of natural wood were at a similar level. The tests of wood protected with the experimental agent FNW resulted in the time to ignition at a level of 50.1%, and average rate of mass loss equalling 60.5% in relation to unprotected wood. All three agents met the criteria for neutral agents in terms of natural wood flammability, according to the classification criteria.

Table 3. Results of flammability tests of protected wood

Tested properties	FNW	[DDA]DCI]	[DDA][H_2PO_4]
Time to ignition	50.1 %	107.1	101.5
Average heat release rate after 180 sec	103.8 %	113.1	102.7
Maximum heat release rate	92.2 %	111.9	114.1
Average rate of mass loss per area unit	60.5%	98.5	99.2
Effective heat of combustion	69.1%	100.7	108.0
Classification	neutral	neutral	neutral

CONCLUSIONS

The corrosive aggressiveness of [DDA][NO_3], defined as average corrosive aggressiveness with decreasing corrosion dynamics, may be completely neutralised through adding 10% of corrosion inhibitor, i.e. didecyldimethylammonium nitrate(III).

Dissolution of 15% weight percent of tebuconazole in didecyldimethylammonium nitrate allowed obtainment of an agent with a high effectiveness against wood-decaying fungi and simultaneously characterised by a deep penetration into pine wood.

The tested ionic liquids containing didecyldimethylammonium cation and the experimental agent FNW met the criteria for neutral agents in terms of wood flammability.

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Streszczenie: *Badania wpływu składu chemicznego preparatów ochrony drewna na właściwości użytkowe.* Przedstawiono wyniki badań agresywności korozyjnej, głębokości wnikania, wartości grzybobójczej oraz wpływu na zapalność drewna preparatów o zróżnicowanym składzie chemicznym. Wykazano dodatni wpływ 10 procentowego dodatku azotanu(III) didecylodimetyloamoniowego na agresywność korozyjną preparatu zawierającego azotan(V)didecylodimetyloamoniowy. Badania głębokości wnikania udowodniły 1,6 krotny wzrost penetracji w drewno mieszaniny 15% tebukonazolu i 85%[DDA][NO_3] w stosunku do czystej cieczy jonowej. Dodanie 15% tebukonazolu do azotanu(V) didecylodimetyloamoniowego obniżyło wartość grzybobójczą do poziomu <0,73 kg m^{-3}.

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