

COPPER COMPOUNDS AS A MODIFYING FACTORS OF WOOD PRESERVATIVES BASED ON THE QUATERNARY AMMONIUM SALTS

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Preliminary trials of improving wood preservatives based on the quaternary ammonium compounds were carried out. Three copper compounds: copper chloride, copper sulfate and copper acetate in various quantitative patterns were used. The toxic values (ED₅₀, ED₁₀₀ and LD) for the *Coniophora puteana* and ED₁₀₀ for *Trichoderma viride* were determined.

Key words: QAC wood preservative, copper salts, modifying of wood preservative, screening test, *Coniophora puteana*, *Trichoderma viride*

INTRODUCTION

The quaternary ammonium compounds represent a new generation of wood preservatives. They are characterised, apart from their considerable effectiveness on a broad spectrum of wood degradation factors, by essential proecological values when proving almost a complete harmlessness for human beings, animals, plants and environment. The QAC (Quat) type wood preservatives world wide produced find broader and broader use. These are also successfully used in our country in buildings, in monuments protection, in agriculture, in mushroom growing etc. The produced Boramon, Mycetox B, Mycetox M, Mycetox 04-SL preservatives ensure the full protection against biodegradation, they get fixed in wood and are harmless for the environment.

Investigations aimed at continued improving wood preservatives based on the quaternary ammonium compounds are carried on in the Department of Wood Protection, Warsaw Agricultural University. Apart from the up to the present successfully used formulations containing the boron compounds (Ważny and Rudniewski 1995, 1996) trials have been undertaken of using various copper compounds as a supplementary component, introducing them into the recipes should not only improve the physico-chemical properties but also widen the effectiveness of using in the environments in particular disadvantageous to the work of wood, i.e. in open air in the contact with wet ground or with water. In this spirit investigations of estimating the influence of various copper compounds on the properties of wood preservatives based on the quaternary ammonium compounds have been undertaken.

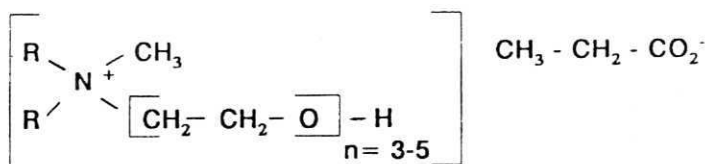
Use of the copper chloride ($\text{CuCl}_2 \times \text{H}_2\text{O}$) as a supplementary component was suggested by Butcher et al. (1979), Butcher (1980) in New Zealand and them by Ruddick (1983) in Canada and by Hedlay et al. (1995) in Japan. Copper sulphate ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$) was the subject of investigations of Butcher and Greaves (1982), of Drysdale (1983) in New Zealand and Austria and in Japan (Tsunoda and Nishimoto 1987). Copper oxide

(CuO) suggested by Wallace (1986), by Archer et al. (1993), by Preston et al. (1994) in USA as well by Ruddick (1987) in Canada is also taken into consideration. In spite of the positive results on the up to now investigated copper compounds their use as supplementary components of wood preservatives of the QAC type makes grave methodical difficulties since they are for the most part insoluble in water. In this respect application of special methods of preparation is required. At the same time the hitherto available publications contain not many information on the fungitoxic value of formulations composed of copper compounds. The existing data have been most often obtained in the effect of applying the methods of semi-technics (cellar method) or simply experimental practice. They are doubtless valuable information but they can not replace investigations with the classical laboratory methods.

Investigations undertaken by the authors are aimed at filling a gap in recognising the effectiveness of wood preservatives of the quaternary ammonium salts type supplemented with the copper compounds with the intention of modifying the preparations produced in this country.

MATERIALS AND METHODS

By way of example one quaternary ammonium compounds of the QAC type i.e. the didecylmethylpolyammonium propionate (LONZA, Basel - Switzerland), and three copper compounds:



copper chloride ($\text{CuCl}_2 \times 2\text{H}_2\text{O}$)

copper sulfate ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$)

copper acetate ($\text{Cu}/\text{CH}_3\text{COO}/_2 \times \text{H}_2\text{O}$)

have been exposed to investigations when applying them separately and in combination with the QAC expressed by the proportions QAC to the copper compounds as follows: 1:2, 1:1, 2:1, 4:1. The required proportions were obtained when using intermediate solutions in the form of the 5% QAC water solution and 0.2 mole water solution of the copper compound.

Investigations of the fungitoxic value were carried out with the agar method (screening) according to Ważny and Grzywacz (1976), and Ważny and Thornton (1986). Preparations under investigation were put into the sterile agar-maltose medium (composed of 2% agar, 2% maltose extract) in Petri dishes, in the concentrations of logarithmic grading from 0.05 to 1.25% for the copper compounds and from 0.005 to 0.5% for the QAC its mixture with the copper compounds.

The culture was centrally inoculated when applying the inoculum of 5 mm diameter of the test fungus *Coniophora puteana* (Schum. ex Fr.) Karst. BAM Ebw. 15 strain, of the main test species for the brown wood decay.

Incubation was carried out at the temperature of $22 \pm 1^\circ\text{C}$ and relative air humidity of

85±2°C without the light access. The ED₅₀, ED₁₀₀ and LD values according to the below given rules were taken as the criterion of estimating the biocide properties of investigated preparations.

The ED₅₀ value - effective dosis hampering the growth of the fungus in 50% as determined upon the measurements of the colony diameter in the relation to the diameter of the control colony (without the fungicide).

The ED₁₀₀ value - effective dosis hampering the growth of the mycelium of the fungus was determined upon the measurements of the colony diameter in relation to the diameter of the control colony (without the fungicide).

The LD value - lethal dosis causing the complete killing of the mycelium proved by test transplanting.

At the some time the test fungus *Trichoderma viride* Per. ex Fr. SGGW 118 strain, which causes, according to the environment conditions, moulding or mould decay of wood was used. For technical reasons only the ED₁₀₀ value for this fungus was determined when considering this determination as an interesting supplement of the gained results.

RESULTS

The rates of the growth of test fungus mycelium in the agar-maltose culture obtained for various concentrations of particular versions of QAC with the addition of copper compounds were graphically prepared. Figures from 1A to 1C present the exemplary reactions of the *Coniophora puteana* fungus on the activity of the selected combinations of fungicides. Summary results of the ED₅₀, ED₁₀₀, LD toxic values for *Coniophora puteana* and ED₁₀₀ for *Trichoderma viride* determined on the base of diagrams are depicted also in table 1. It was proved that the addition of copper compounds to the quaternary ammonium salts exerts an advantageous influence on the reactions of both test fungi whereat this influence depends on the type of the copper compounds and on the quantitative proportions of components. In no case worsening of the toxic reactions of the mixtures under investigation with regard to the QAC value without additions was shown. Copper chloride showed a positive reaction for both fungi in the mixture with QAC in the volumetric proportion: 1 part of QAC: 2 parts of Cu compound. With the emaining proportions of the QAC mixtures with the copper chloride no improvement of the effectiveness of reaction of the mixtures in relation to the separately reacting QAC with regards to the *Coniophora puteana* was stated.

Copper sulfate in the combination 1:2 and 1:1 exerted an advantageous influence only on the ED₁₀₀ value for the *Trichoderma viride* fungus and it did not changes the value for *Coniophora puteana*. The best effects were indicated with the use of the copper acetate. In the proportion of QAC to Cu 1:2 and 1:1 a perceptible growth of effectiveness was obtained expressed by the ED₅₀, ED₁₀₀ and LD values for *Coniophora puteana* and ED₁₀₀ for *Trichoderma viride*.

RECAPITULATION

Using of various copper compounds with the quaternary ammonium compounds pointed out in bibliography has gained a positive prove in the carried out investigations. Copper compounds, apart from the anticipated reaction on the physical properties of the

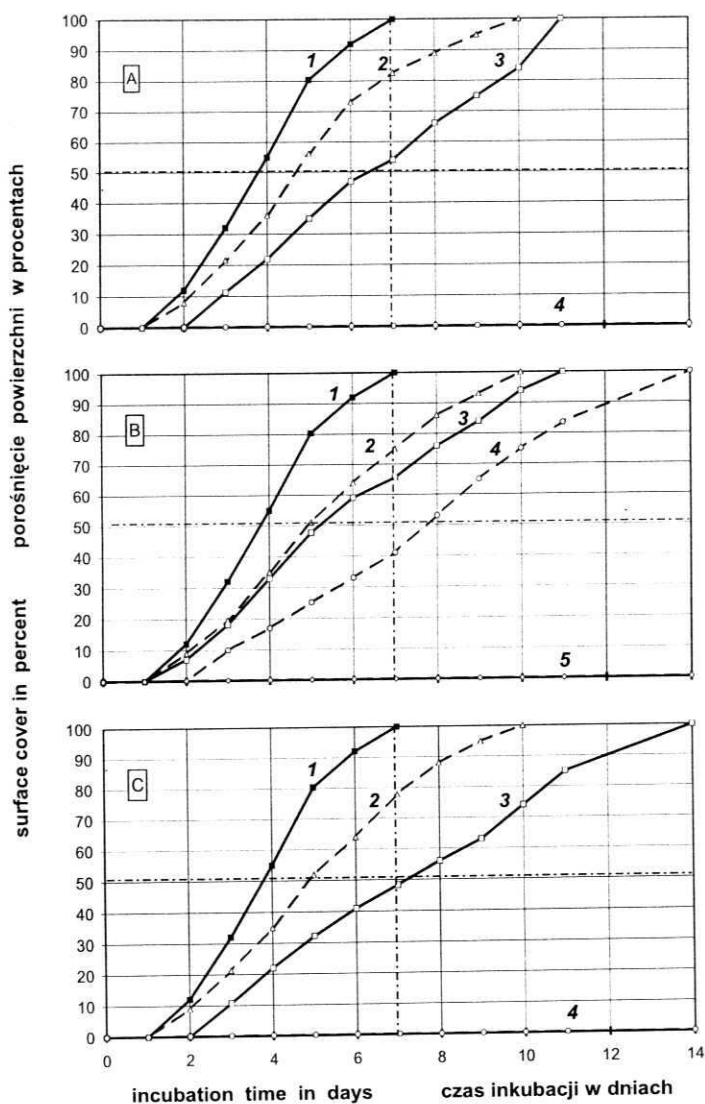


Fig. 1. Effect of the copper-modified QAC biocides on the growth of *Coniophora puteana* fungus on agar medium

A - QAC + Copper chloride (1:2)

B - QAC + Copper sulfate (1:2)

C - QAC + Copper acetate (1:2)

Concentration of fungicide:

1 - Control (0%); 2 - 0.02%; 3 - 0.05%; 4 - 0.1%; 5 - 0.2%

Rys. 1. Wpływ preparatu typu QAC modyfikowanego związkami miedzi na wzrost grzyba *Coniophora puteana*:

A - QAC - chlorek miedziowy (1:2)

B - QAC - siarczan miedziowy (1:2)

C - QAC - octan miedziowy (1:2)

Stężenie preparatu:

1 - Kontrolny (0%); 2 - 0.02%; 3 - 0.05%; 4 - 0.1%; 5 - 0.2%

Table 1

Tabela 1

Fungitoxic values of the preparation of the QAC type modified with copper compounds

Wartości toksyczne preparatu typu QAC modyfikowanego związkami miedzi

Preparation Preparat	Composition Skład	Fungitoxic values (%) Wartości toksyczne (%)			
		<i>C. puteana</i>			<i>T. viride</i>
		ED ₅₀	ED ₁₀₀	LD	ED ₁₀₀
Control - kontrolny	1	-	-	-	-
QAC	1	0.02 - 0.05	0.2	0.2	0.5
CuCl ₂	1	0.05 - 0.1	0.1	0.5	0.5
CuSO ₄	1	0.05 - 0.1	0.2	0.2	0.5
Cu(CH ₃ COO) ₂	1	0.05	0.1	0.1	0.2
QAC - CuCl ₂	1 - 2	0.05	0.1	0.1	0.1
	1 - 1	0.05	0.2	0.2	0.2
	2 - 1	0.05 - 0.1	0.2	0.2	0.2
	4 - 1	0.05 - 0.1	0.2	0.2	0.5
QAC - CuSO ₄	1 - 2	0.05 - 0.1	0.2	0.2	0.2
	1 - 1	0.1	0.2	0.2	0.2
	2 - 1	0.1	0.2	0.2	0.5
	4 - 1	0.1	0.2	0.2	0.5
QAC - Cu(CH ₃ COO) ₂	1 - 2	0.05	0.1	0.1	0.2
	1 - 1	0.05	0.1	0.1	0.5
	2 - 1	0.05 - 0.1	0.2	0.2	0.5
	4 - 1	0.05 - 0.1	0.2	0.2	0.5

preparations which were not the subject of these investigations have indicated an advantageous influence on the fungitoxic properties of the preparation of the QAC type.

From the three used copper compounds a positive reaction on both fungi has been obtained mainly for the copper acetate and to a somewhat small degree for the copper chloride whereas an improved reaction of the QAC with addition of the copper sulfate was proved only in the case of the *Trichoderma viride* fungus. The effectiveness of added copper compounds was apparent with their considerable quantitative share in the preparation of the QAC type (1:2 and 1:1). The carried out preliminary trials appear to prove the right direction of the undertaken investigations aimed at the improvement of wood preservatives based on the quaternary ammonium compounds. These investigations required further studies with regard to other test fungi as well as other copper compounds. Positive results obtained in the agar medium should be proved in investigations in which wood will be used for the protection of which the tested compounds are first of all destined.

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ZWIĄZKI MIEDZI JAKO CZYNNIKI MODYFIKUJĄCE ŚRODKI OCHRONY DREWNA OPARTE NA CZWARTORZĘDOWYCH SOLACH AMONIOWYCH

Streszczenie

Przeprowadzono wstępne próby udoskonalenia środków ochrony drewna opartych na czwartorzędowych związkach amoniowych. Zastosowano trzy związki miedzi; chlorek miedziowy, siarczan miedziowy i octan miedziowy, w różnych układach ilościowych. Oznaczono ich wartości toksyczne (ED₅₀, ED₁₀₀ i LD) dla grzyba *Coniophora puteana* i ED₁₀₀ dla *Trichoderma viride*. Uzyskano na ogół pozytywne działanie związków miedzi w zależności od stosunku ich udziału względem QAC. Największe nadzieje spośród zbadanych związków rokuje octan miedziowy.

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