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TOXIC VALUES OF SELECTED FUNGICIDES IN PLANT PESTICIDES IN RELATION TO WOOD DESTROYING FUNGI*

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Ten various fungicides applied in the plant protection against pathogenic fungi were subject to laboratory tests to determine the possibility of their use as active components of wood preservatives. The screening agar-block method was applied using the accelerated ageing test. The properties of the preparations tested were determined in relation to brown, white and soft rot fungi and mould fungi.

INTRODUCTION

The continuous progress in many fields of science makes it necessary to look for new bio-active substances, useful in wood protection against biotic factors. Many biocides, successfully used until recently, cannot be applied for various reasons. New reguirements resulted in research on the possibility of using for that purpose fungicides already verified in other fields, e.g. midicine (1a) or plant protection [13, 20, 21]. The list of compounds and fungicidal substances tested in this respect is very long. However, it should be noted that there are essential differences in demands made towards biocides intended for plant protection and those designed for wood preservation. In the first case the most important is selectivity of action, proper effectiveness minimizing the portion. The high durability of the preparation usually is not required sometimes its the action is strictly defined in time. In case of wood preservatives, the fungicide should be characterized by a wide spectrum of operation, and ability to fight against the existing injection and protect the wood against it. The major feature of all wood preservatives is their durability

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i.e. fastness to water and radioresistance including ultraviolet radiation. The last quality is particularly important in relation to impregnating and decorating agents, widely used for the protection of wood surface, aiming at the preservation of its aesthetic finish.

From the existing literature on attempts to apply new fungicides in the wood preservation, leading the way for the preparation of modern wood pesticides, the following authors should be mentioned: Gajdziński and Mroczkiewicz [2], Lutomski [7], Metzner et al. [13], Tsunoda and Nishimoto [18], Zaprutko et al. [23, 24]. The number of publications issued in relation with that problem is much bigger than the literature mentioned. It also refers to chemical compounds, finding practical application in preparation of chemical agents protecting wood against biological factors. Among those the following can be mentioned: 3-iodo-2-propynyl-butyl carbamate [4], dichlofluanide [16], furmetamide [14], tin organic compounds [12, 17, 18], triazole compounds [3, 6, 22] and many others. There are a lot of specialized companies offering the producers various types of fungicides to protect materials, including wood, against biological corrosion.

The aim of this work was to examine fungicides used for the protection of plants against pathogenic fungi. The test substances were obtained from the Chemical Works "Organika-Azot" at Jaworzno, their names are mentioned in Table 1.

SCOPE AND METHODS OF RESEARCH

The research was carried out in three stages. It started with the selection of a solvent among the following, most often used: water, ethanol, acetone, xylene, toluene, chloroform and ethyl acetate. 1% solubility (by weight) was accepted as the limit of suitability for further tests. The results are shown in Table 1. Three of the substances tested have not shown sufficient solubility in the above mentioned solvents.

The next step included eliminatory research on seven fungicides to choose the most active preparation, intended for further tests planned on a wider scale.

The eliminatory tests were carried out using disk method (for *Coniophora puteana*) and filter paper on perlite substrate method for four species of soff rot fungi and mould fungi.

The particulars concerning disk method have been described in earlier publications [8, 10].

The "filter paper" method for initial evaluation of chemical agents effectiveness towards soft rod fungi and mildew fungi was applied among other by Zaprutko et al. [23, 24] in their research on nitroimidazole derivatives. The results of eliminatory tests are shown in Table 2.

Four fungicides characterized by the low activity in the eliminatory tests, were classified for the next stage. These were the following: Curzate, Fenarimol,

Table 1

List of test fungicidal substances
Zestawienie badanych substancji grzybobójczych

Name of preparation Nazwa preparatu	Active substance Substancja czynna	Solvent Rozpuszczalnik
Curzate	1–(2–cyano–2–metoxymino–aceto)–3–ethylurea 1–(2–cyjano–2–metoksyimino–acetylo)–3–etylomocznik	Acetone Aceton
Fenarimol	Alpha–(2–chlorophenyl)–alpha–(chlorophenyl)–5–pyrimidine methanol Alfa–(2–chlorofenyl)–alfa–(chlorofenyl)–5–pirymidynometanol	Acetone, ethanol Aceton, etanol
Fenuron	2, 5–dimethyl–N–phenyl–2, 4, 5–trimethyl–N–phenyl 2, 5–dimetylo–N–fenylo–2, 4, 5–trimetylo–N-fenyl	Acetone, ethanol Aceton, etanol
Captan Kaptan	1, 2, 5, 6–tetrahydro–N–(trichloromethyltio)–phtalimide 1, 2, 5, 6–tetrahydro–N–(trichlorometyltio)–ftalimid	Ethyl acetate Octan etylu
Carboxyne Karboksyna	5, 6–dihydro–2–methyl–1, 4–oxatin–3–carboxylic acid anilide Anilid kwasu 5, 6–dihydro–2–metylo–1, 4–oksatin–3–karboksylowego	Acetone, xylene, toluene Aceton, ksylen, toluen
AZOT complex Kompleks „Azot"	Mixture of cooper 8–hydroxyquinolinolate and salicylic acid Mieszanina 8–hydroksychinolinianu miedzi i kwasu salicylowego	–
Metaxyl primex 70	(±)–N–(2–methoxyacetol)–N–N–(2.6–xylilo)–methyl alaninate (±)–N–(2–metoksyacetylo)–N–N(2, 6–ksylilo)–alaninian metylu	Acetone Aceton
Miedzian 50	Copper oxychloride Tlenochlorek miedzi	–
Nuarimol	Alpha–(2–chlorophenyl)–alpha–(4–fluorophenyl)–5–pyrimidinemethanol Alfa–(2–chlorofenyl)–alfa–(4–fluorofenyl)–5–pirymidynometanol	Acetone Aceton
Topsin	Methyl thiophanate Tiofanat metylu	–

Table 2

Preliminary evaluation of fungicidal properties in tested fungicides
Wstępna ocena grzybobójczych właściwości badanych fungicydów

Fungicide Fungicyd	Test fungus (method) Grzyb testowy (metoda)					
	Coniophora puteana		*Chaetomium globosum*	*Trichoderma viride*	*Aspergillus niger*	*Paeciliomyces varioti*
	Disk method Metoda krążkowa		Filter paper on perlite substrate Metoda bibułowa na podłożu perlitowym			
	Fungicidal boundary value Graniczna wartość grzybobójcza		Protection effectiveness (in % impregnating solution) Skuteczność zabezpieczenia (w % roztworu impregnacyjnego)			
	kg/m³	%				
Curzate	>0.489	>0.176	>0.5	0.5	0.5	0.5
Fenarimol	0.194 - 0.384	0.041 - 0.080	0.01	0.5	0.5	–
Captan Kaptan	>0.847	>0.176	>0.5	0.5	0.5	0.5
Fenuron	0.019 - 0.037	0.09 - 0.177	>0.5	0.5	>0.5	>0.5
Carboxyne Karboksyna	<0.009	<0.048	0.01	0.1	0.1	–
Metalaxyl primex 70	>0.451	>0.094	>0.5	>0.5	>0.5	>0.5
Nuarimol	>0.466	>0.097	>0.5	>0.5	>0.5	0.5

Fenuron and Carboxyne. The last mentioned, was also evaluated in the earlier research carried out by Ważny and Grzywacz [20, 21] as a very efficient biocide, giving hope for successful application in wood preservation.

Fungicidal properties of those preparations in the third stage of research were determined by screening agar-block test, used for initial evaluation of potential fungicides in the Research Institute of Forestry in Eberswalde [5]. Samples used for that test have dimensions of $40 \times 15 \times 4$ mm (the smallest size was measured along the fibres). The requirements concerning the wood quality were in accordance with the quidelines of the European Standard EN 113 [1]. Other methodical particulars of the mycological test also followed those quidelines i.e. the kind of substrate for fungi, the method of saturation and conditioning, the number of samples in flasks, the conditions of incubation, the way of determining the fungicidal boundary value. Still unpublished results of comparative research on boundary values of wood protection using the EN 113 method and the screening agar-block test [5] show high convergence. The differences observed do not exceed 1 degree in the concentration series of impregnating solutions used for sample saturation.

The similar method of initial testing of triasoles was used by Goodwine [3].

The applied method was used among other things for the evaluation of quality of some commercial impregnating and decorating agents designed for wood surface protection [11]. In this case test fungi were species of *Basidiomycetes*, and causing soft rottening. The samples were drawn from pine and beech softwood (*Pinus sylvestris* L., and *Fagus silvatica* L. respectively).

The half of thus prepared samples, saturated, saturated and conditioned, were subjected to mycological test. The remaining samples underwent the

process of accelerated ageing, consisting in washing out and exposure to ultraviolet radiation. The washing-out was carried out for two weeks, five times a week, with daily exchange of water. Samples were exposed to the UV radiation for four weeks, fourteen days at each of sample bigger surface, from the distance of about 30 cm. The applied lamp was of 30 W power and 253.7 μm wave length. Samples, aged and unaged were subjected to the attact of fungi during 6 weeks under proper for test fungi conditions of air temperature and relative humidity. The criteria of sample resistance to the attact of fungi were as follows: in case of the *Basidiomycetes* it was mass decrement (2.0% limit), whereas in case of the *Ascomycetes* fungi – the degree of mycelium growth in the 6-degree scale.

RESULTS

The solubility test of tested ten fungicides from the group of plant pesticides eliminated 3 preparations from further research. The remaining were well-soluble in acetone, ethanol, xylene, toluene or ethyl acetate (Table 1). It explicitly suggests their possible usefulness for the preparation of oil-solvent agents. Those substances showed different biological activity during initial evaluation. The determined values made it possible to establish the range of concentration of impregnating agents for the next stage of research carried out using the screening agar-block test [5].

The results of tests shown in Table 3 inform about the activity of four preparation towards brown, white and soft rot fungi. The tests performed confirmed, already observed by Ważny and Grzywacz [20, 21] the high effectiveness of carboxyne, a systemic fungicide, constituting the active component of the "Vitavax" preparation.

The results obtained also allow to make the preliminary evaluation of suitability of the test substances for the preparation of impregnating and decorating agents. Those agents are usually applied for surface preservation of wood exposed to weather. Properly selected fungicides play an important part among components of such preservatives [9]. High degree of washing out and susceptibility to UV radiation indicate that none of four test fungicides selected for final tests can be used for that purpose. They are either subject to washing out or chemical changes under the influence of various factors.

In case of carboxyne those changes can be probably the result of oxidation. They consists in hydroxylation, as well as sulfoxidation in the aromatic ring. At a certain stage of reaction among other things, a sulfoxide is generated characterized by the lack of fungicidal properties [15]. Changes in the other of pesticides subjected to preliminary evaluation, e.q. captan, consist in the hydrolytic reactions, with the simultaneous lack of oxidation reactions. Those reactions can stand for an example of complicated and differentiated behaviour of various chemical substances in the environment in which wood protection

Table 3

Fungicidal properties and artificial ageing resistance in tested fungicides, determined by screening agar-block method

Grzybobójcze właściwości i odporność na sztuczne starzenie badanych fungicydów oznaczone skróconą metodą agarowo-klockową

Fungicide Fungicyd	Test fungus Grzyb testowy	Fungicidal boundary value Graniczna wartość grzybobójcza (kg/m³)		Durability index Wskaźnik trwałości
		before ageing process przed procesem starzenia	after ageing process po procesie starzenia	
Curzate	*Coniophora puteana*	1.99	>3.92	>1.97
	Coriolus versicolor	1.65	>6.21	>3.76
	Chaetomium globosum	0.830	>6.11	>7.36
Fenarimol	*Coniophora puteana*	2.18	>4.32	>1.98
	Coriolus versicolor	0.885	>3.37	>3.83
	Chaetomium globosum	0.835	>6.19	>7.41
Fenuron	*Coniophora puteana*	3.99	>4.57	>1.15
	Coriouls versicolor	0.841	>3.17	>3.77
	Chaetomium globosum	0.830	>6.11	>7.36
Carboxyne Karboksyna	*Coniophora puteana*	0.592	>4.35	>7.35
	Coriolus versicolor	0.690	>4.49	>6.50
	Chaetomium globosum	0.864	>4.66	>5.41

also takes place. The attemptes aiming at implementation of new chemical preservatives require comprehensive and complex research, including ageing processes which cannot be omitted and should represent the important evaluation factor.

CONCLUSIONS

1. Fungicides applied for plant protection i.e. Curzate, Fenarimol, Fenuron and Carboxyne vary in toxic properties in relation to fungi causing the decay and colouring of wood. The most active is carboxyne characterized by the equal effectiveness of protection against fungi belonging to different classes.

2. Ageing processes i.e. washing out with water and exposure to UV radiation of 253.7 nm wave length cause evident drop in biological activity of the selected fungicides which in consequence cannot be taken into consideration as active components of wood surface preservatives (impregnating and decorating agents).

3. During laboratory screening tests, while determining the fungicidal properties of the potential fungicides, the attention should be also paid to the change of those features under the influence of such external factors as washing-out with water and UV radiation.

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WARTOŚCI TOKSYCZNE WYBRANYCH FUNGICYDÓW ŚRODKÓW OCHRONY ROŚLIN W STOSUNKU DO GRZYBÓW ROZKŁADAJĄCYCH DREWNO

Streszczenie

Dziesięć różnych fungicydów stosowanych w ochronie roślin przed grzybami chorobotwórczymi poddano badaniom laboratoryjnym w celu określenia możliwości wykorzystania ich jako składniki aktywne środków ochrony drewna. Posłużono się skróconą metodą agaro-klockową z zastosowaiem przyspieszonego testu starzeniowego. Właściwości badanych preparatów oznaczono w stosunku do grzybów powodujących brunatny, biały i szary rozkład oraz pleśnienia drewna. Stwierdzono wysoki stopień podatności badanych fungicydów na wymywanie wodą i działanie promieni ultrafioletowych.

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