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CONDITIONS AND POSSIBILITIES OF NANOBIOCIDES FORMULATION FOR WOOD PROTECTION[1]

During development of nanobiocides for wood protection the need to identify mineral composition of wood in respect of trace elements and nourishing conditions of wood destroying fungi in relation to these elements was discussed.

Keywords: nanobiocides, wood destroying fungi, wood protection, mineral composition of wood, mineral nourishing of fungi, trace elements

Introduction

The application of nanotechnology in different industries raises great hopes of developing new methods and materials of specific technical properties. It is assumed that nanotechnology is a technology in the scale ranging from 1 to 100 nanometers which allows transformation of atomic structures [Siegel et al. 1999; Kafarski 2007]. At the beginning of the 21st century research on development of nanobiocides and possibility of their application in wood protection was also started. Despite serious procedural difficulties in respect of apparatus and technology a number of concepts of modern nanopreparations protected by patents owned by their authors or producers have already been developed [Clausen 2007]. Nanobiocides are expected to have revolutionary physical characteristics which facilitate penetration into wood as well as biotic properties for a broad spectrum of microorganisms which destroy wood in various environments. For the time being the mechanism of penetration, distribution and location of nanocomponents of preparations in wood tissue structure has been observed. Previous

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research concerned mainly preparations based on nanocopper and nanosilver and to a smaller extent it dealt with other elements [Ellis 2007; Matsunaga et al. 2007]. It is expected that nanotechnology will make it possible to improve wood resistance to biodegradation not only directly through introduction of nanometals but also indirectly as a carrier of organic biocides.

Matsunaga et al. [2007] with the use of X-ray microanalyser-aided scanning microscope conducted research on micro-distribution of metals in wood commercially treated with nanomolecules of copper and iron. These elements were found in bordered pits and in the middle layer of pine wood cell wall in the range from 10 to 100nm. At the same time they noted that copper location differed from the one obtained when treatment is done by conventional method. Meanwhile Archer [2007] detected the presence of nanocopper only in cell lumen and in bordered pits but not inside cell wall. This limits the possibility of using nanocopper for the protection of wood against soft rot and also confirms different character of the process of its penetration in comparison to classic copper soluble in combination with ACQ.

The ready publications on nanobiocides toxic value are very scant as well. Nanosilver has antibiotic effect on bacteria, yeast and moulds [Kourai 1996]. Dorau et al. [2004] demonstrated its weak inhibitory effect on fungi and moulds in laboratory tests. During a soil test Ellis et al. [2007] obtained toxic values against *Gloeophyllum trabeum* – fungus causing brown rot of wood – in the order of 100–200 ppm.

Because of fascination with nanotechnology and possibility of its application in wood protection the necessary confrontation between the nanopreparation concept and the conditions of biochemistry, physiology and toxicology of natural material like wood as well as organisms causing its degradation has not been taken into consideration yet. It seems that without information about these relations formulation of nanobiocides is acting "blindly".

This paper is an attempt to draw the attention of developers of nanotechnology to the need to find correlation between project concepts of nanobiocides and the above-mentioned values based on knowledge which has been gained so far. The following issues should be taken into account: mineral composition of wood in respect of trace elements as possible biologically active factors, mineral composition of wood destroying fungi, mineral composition of wood attacked by fungi, and mineral needs of fungi in the scope of the content of physiologically active elements and their toxic action.

Trace elements in wood

Wood as a product of natural biochemical and physiological processes of ligneous plants is created as a result of photosynthesis aided with mineral compounds taken from soil together with water. Therefore, when it comes to nanobiocide formulation it is indispensable to identify mineral composition of this material taking into consideration especially these elements which are expected to be biochemically active components. A detailed composition of wood in this scope is not well known. The published information most often gives a summary content of mineral compounds (ash) and the share of some main macroelements [Kollmann, Côté 1968]. Only few studies include numerical data on microelements, i.e. trace elements, for individual wood species. It seems that so far the most comprehensive information on the subject is found in the study by H. Ważny and J. Ważny [1964]. A spectral analysis for 34 European and extra-European wood species, after incineration, was carried out using an average dispersion quartz spectrograph by Zeiss type Q-24. The spectrograph was the most modern apparatus in those days and the results of the analysis were selectively verified using a contemporary optical emission spectroscope ICP-OES by Percin Elmer Optima 3000. Values of 13 trace elements were determined: Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Ba, Pb. Wood samples were selected if possible from trees of average age class, partially from dendrological collections. Diversity of the content of these elements in the wood of Scots pine and sessile oak was tested: 1) in different parts of stem, in branches and roots (vertical section), 2) in stem transverse section, and also 3) depending on the tree age (3 to 100 years) and 4) in beech wood of various origins. The obtained contents of particular trace elements, in ppm of dry wood mass, at different aspects are presented in fig. 1. These results were later confirmed in few and fragmentary research works. Dobrovolskaya [1975] conducted research on the content of 12 trace elements in various parts of Scots pine stem, and Mayer and Koch [2007] studied location of 5 microelements in transverse section of the stem of black cherry wood (*Pinus serotina*) from different habitats.

To put it general it may be said that trace elements occur in a quite broad range in all wood species and in all researched variants. They are permanent part of wood tissue mineral composition.

Trace elements in wood attacked by fungi

Further research was conducted on the healthy wood of Scots pine and oak and on the wood attacked by *Coniophora puteana* and *Serpula lacrymans* fungi according to the same method. The wood samples were exposed to pure cultures of these fungi *in vitro* for a period of 6 months [Ważny 1962, 1968]. The mass loss after this period ranged from 50 to 65%. Spectroscopic analysis after incineration demonstrated a considerable loss of trace elements, for example the loss in the case of copper and iron ranged from 50 to 88% of their content in healthy wood. The elements had been taken in and built into the structure of mycelium, rhizomorphs and fruiting bodies of wood destroying fungi.

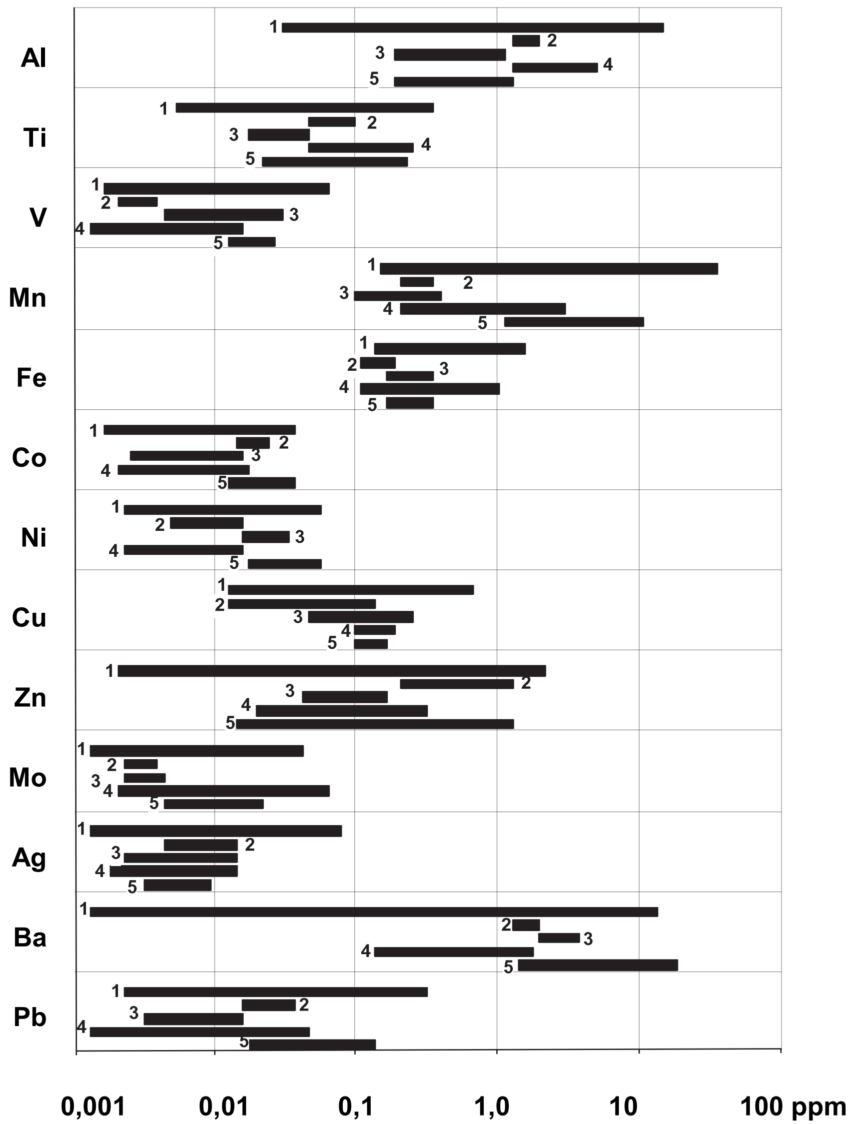

Fig. 1. Dispersion of trace elements content: 1. in different wood species; 2. in Scots pine wood on the longitudinal stem section; 3. in oak wood on the transverse stem section; 4. in Scots pine wood of various ages; 5. in beech wood of various origin

Rys. 1. Dyspersja zawartości pierwiastków śladowych: 1. w różnych gatunkach drewna; 2.w drewnie sosny zwyczajnej na podłużnym przekroju pnia; 3. w drewnie dębu na poprzecznym przekroju pnia; 4. w drewnie sosny zwyczajnej w różnym wieku; 5. w drewnie buka różnego pochodzenia

Trace elements in fungi

In the cycle of research devoted to the role of trace elements in wood protection there was also a part concerning their content at different growth stages of wood destroying fungi. Similarly to the case of wood infected by *C. puteana* and *S. lacrymans* fungi 13 trace elements in their mycelium, rhizomorphs and fruiting bodies after 6 months of „in vitro" exposure were determined [Ważny 1963]. Considerable amounts of these elements were observed in all growth stages. For instance, copper was found in mycelium and rhizomorphs of *C. puteana* fungus in the total amount of 59.30 ppm and in the not fully formed fruiting body in the amount of 45.49 ppm in relation to dry mass. In the case of *S. lacrymans* fungus these amounts were: 88.70 ppm in mycelium, 17.20 ppm in rhizomorphs, and 71.10 ppm in fruiting bodies. This data demonstrates that wood destroying fungi take in not only organic components but also considerable part of trace elements from wood during their growth on it.

The effect of trace elements on fungi growth

In order to explain the role of trace elements in wood destroying fungi growth a detailed analysis of their action was carried out. Liquid organic and mineral culture media containing glycose as energy source were prepared. The tested element was then added in logarithmic concentrations to these culture media with observance of increased purity of components and procedures. The effect of trace elements was determined for *C. puteana* and *S. lacrymans* fungi on the basis of dry mass of mycelia obtained for each of the concentrations. Figures 2 and 3 present exemplary results obtained for copper and iron. The growth curve was construed on the basis of these results. It allowed determination of fungi physiological needs in respect of these elements all the way to reaching physiological threshold concentration. On exceeding this value the under-threshold toxicity of ED_{50} and threshold toxicity (ED_{100}) were observed. At the same time research on the necessity of individual mineral elements for wood destroying fungi growth was conducted. Apart from 5 macroelements 8 trace elements (Mn, Fe, Co, Ni, Cu, Zn, Mo, Pb) in the range from 0.002 to 0.02 ppm proved to have been necessary for the fungi growth. Without these elements the growth was inhibited or very limited.

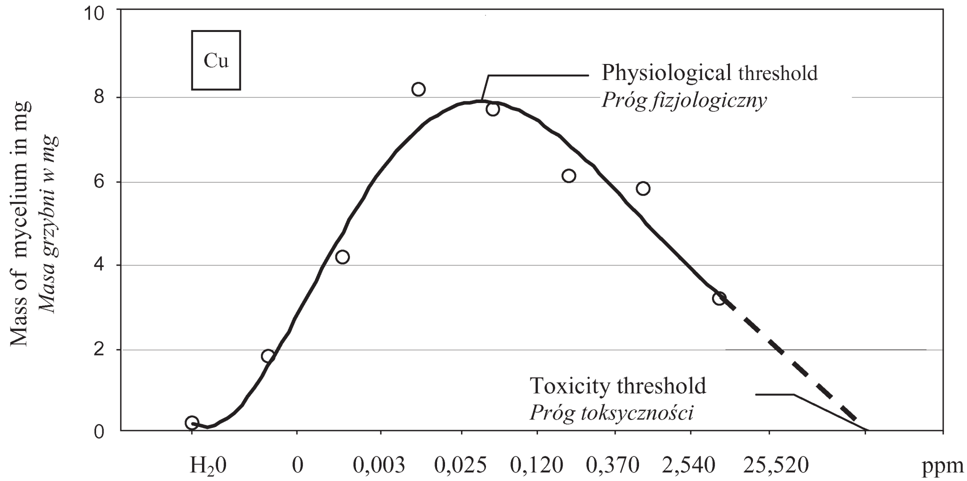

Fig. 2. The influence of Cu on the growth of mycelium *S. lacrymans*
Rys. 2. Wpływ Cu na wzrost grzybni S. lacrymans

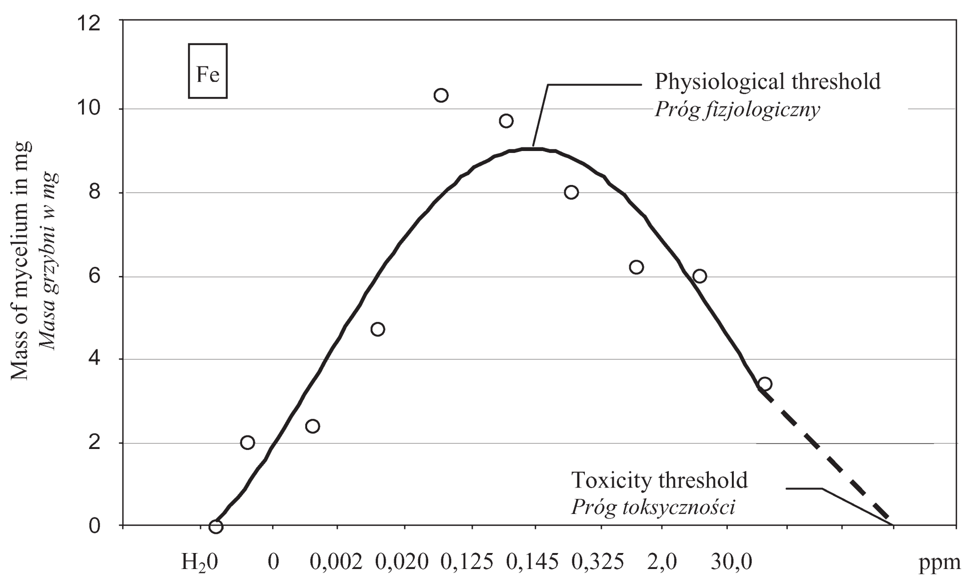

Fig. 3. The influence of Fe on the growth of mycelium *S. lacrymans*
Rys. 3. Wpływ Fe na wzrost grzybni S. lacrymans

Conclusions

Trace elements present in wood tissue play an important role in the processes of its deterioration by wood destroying fungi. These elements are built into wood cell walls during their formation. When the fungi attack wood they take in different amounts of these elements and build them into the cells of mycelium hyphae, rhizomorphs and fruiting bodies. The growth of the fungi depends on the amount of these elements contained in wood tissue. The effect of the elements ranges from positive physiological influence on the mycelium growth dependent on the available amounts to threshold physiological value on exceeding of which the elements' impact causes reduction of growth, i.e. the amount reaches under-threshold toxic values and then threshold toxic value, i.e. effective dose (ED_{50}–ED_{100}) or lethal dose (LD). Therefore the effect of nanomolecules of biocides introduced into wood tissue depends on the concentration of the elements and the order of magnitude of their nanometers. In the range of physiological under-threshold concentration of nanobiocides in wood they are not toxic but quite the contrary – they stimulate mycelium growth and deterioration processes. Only after threshold physiological value is reached the protective effect of nanobiocides is started in the under-threshold toxicity range.

The correlations between mineral structure of wood tissue and the action of nanobiocides may be interfered positively as well as negatively as a result of so-called "paradoxical effects" encountered in toxicity of low concentrations [Golubiev et al. 1972].

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WARUNKI I MOŻLIWOŚCI OPRACOWANIA NANOBIOCYDÓW DLA OCHRONY DREWNA

Streszczenie

Pierwiastki śladowe, występujące w tkance drzewnej, odgrywają istotną rolę w procesach jej deterioracji przez grzyby niszczące drewno. Są one wbudowywane w ścianki komórkowe drewna w czasie ich formowania. Grzyby, porażając materiał drzewny, pobierają z niego różne ilości tych pierwiastków, wbudowując je w komórki strzępek grzybni, sznurów i owocników. Rozwój grzybów zależy od ilości tych pierwiastków zawartych z tkance drzewnej. Występuje tu ich pozytywne działanie fizjologiczne dla wzrostu grzybni, zależne od dostępnych ilości, aż do wartości fizjologicznie progowej, po przekroczeniu, której następuje działanie w kierunku zmniejszenia wzrostu, czyli w podprogowych wartościach toksycznych, aż do osiągnięcia progowej wartości toksycznej *effective dosis* (ED_{50}–ED_{100}) lub *letal dosis*

(LD). Działanie wprowadzonych do tkanki drzewnej nanocząsteczek biocydów zależne jest zatem od koncentracji pierwiastków i rzędu wielkości ich nanometrów. W zakresie fizjologicznej podprogowej koncentracji w drewnie nanobiocydów nie będą one działać toksycznie, ale wręcz stymulująco na wzrost grzybni i procesów deterioracji. Dopiero po osiągnięciu granicznej wartości fizjologicznej, w strefie podprogowej toksyczności rozpoczyna się ochronne działanie nanobiocydów.

Słowa kluczowe: nanobiocydy, grzyby niszczące drewno, ochrona drewna, mineralny skład drewna, pobieranie minerałów przez grzyby, pierwiastki śladowe.