



## STUDIES ON THE INTERACTION BETWEEN BIRCH VENEER AND COMPOUNDS WITH BIOCIDAL POTENTIAL ACTION

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### Abstract

This paper discusses the results of study concerning the interaction between the birch veneer and some compounds with biocidal potential action are presented. With this end in view the samples of veneer were immersed in solutions with a concentration of 5% of the following products: unmodified straw lignin or modified through hydroxymethylation, furan resin and tannins dissolved in 0.1 N ammonia solution. To make a comparison, the same combined treatments were applied, using ammonia solutions of some copper compounds ( $\text{CuCl}_2$  and copper-ammonia solution) and the above mentioned organic compounds to obtain *in situ* their complexes. The stability of the treatments was followed through successive elution with distilled water of the impregnated samples. The toxicity of the extracts was followed by germination tests of tomato seeds. The obtained results highlighted that the stability of the treatments are in agreement with the nature's products, the functionality and the complex forming degree, that determine their interaction with the veneer.

**Keywords:** biocides, birch, copper compounds veneer, furan resins, lignin, tannin

### 1. Introduction

Frequent utilization of wood in different fields and its reduced stability on the action of environment factors infer using chemical compounds for protection against biological agents attack. Dimensional instability of wood is a consequence of its hygroscopicity and absorption or desorption capacity of water vapors from atmosphere take place as to establish a permanent equilibrium between its humidity and that of the environment.

An excessive increase in humidity and temperature influence significantly the biological stability of wood. To increase the biostability of wood, diverse chemical treatments based on its chemical modification or impregnation are recommended (Malutan et al., 2008), and these determine the modification of wood properties because, sometimes new materials could be obtained.

The evaluation of the effects of wood treatments, carried out by specific procedures of bioprotection can be evidenced through separate and successive stages according to the degree of wood chemical modification, physico-mechanical properties

and durability (Dumitrescu et al., 1997; Ungureanu et al., 2008). In this respect, there are various possibilities given by a large variety of products used for wood treatment, but most of them are characterized by high toxicity (Popa et al., 1993, 2007). That is why the finding solutions based on the properties of natural compounds is now in progress. From this point of view, lignins and polyphenols have shown an increased interest and the elucidation of their action mechanism will allow to create bioprotection systems which could substitute or supplement the products used at present. (Malutan et al., 2007; Popa et al., 2007; Rowell, 1984, 2005).

At the same time the possibilities to obtain some bioprotection agents soluble in water and compatible with the environment are analyzed by a number of researchers. This paper presents a study on the interaction between birch veneer and different products with potential biocidal action (lignin and its derivatives, tannin and furan resins) obtained from renewable resource, as well as with copper compounds, as a possible combination of two categories of biostabilization agents. At the same time, the efficiency of the treatment is analyzed

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regarding its stability in the elution conditions in the presence of water, and the eluted products after different periods of time are evaluated for their toxicity, using tests on the germination of tomato seeds.

## 2. Experimental

### 2.1. Materials

In this study the following materials have been used:

- birch veneer samples with the dimensions (1x10) cm and the equilibrium relative humidity of 7.00%;
- unmodified straw lignin from Granit Recherche Development (Switzerland) and straw lignin modified through hydroxymethylation (Popa et al., 2007).
- unmodified and hydroxymethylated Pb 1000 (commercial product based on lignin)
- copper chloride;
- tetraaminocopper hydroxide (cuproxam);
- ammonia solution 0.1N;
- furan resins - from Trans Furan Chemicals (Belgium);
- tannin- from Tanin Svenica, Slovenia;

### 2.2. Methods

Using the veneer samples and the mentioned products dissolved in ammonia solution 0.1 N, at a concentration of 5 %, the following treatments have been applied:

- a) the immersion of the samples in solutions for 5 minutes followed by their drying;
- b) the immersion of the samples in solutions of the copper compounds, drying them and then treating with ammonia solutions of lignin and its derivatives followed by drying.

Then the impregnated and thermally treated samples were immersed successively in distilled water for 24, 48, 72 and 96 hours, and the elution liquids were collected after each interval of time. These samples were characterized in terms of their absorption by UV spectroscopy at 280 nm and toxicity. The absorption in UV was determined using the spectrometer V-55 Jasco, NO, CO 2951930. The evaluation of toxicity degrees was carried out by germination of tomato seeds. Thus in Petri dishes with the diameter of 10 cm a filter paper support was introduced along with 10 mL of aqueous extract. Then, 10 seeds of tomato were introduced and the percentage of germinated seeds was determined after 96 hours. As reference sample distilled water has been used.

## 3. Results and discussion

At present there are sustained preoccupations to find new solutions to increase the resistance of wooden products through acceptable

methods from the environment point of view. It is well known that the compounds of secondary metabolism - lignin and polyphenols - are included in the defense mechanism developed by plants against the pathogens and nonpathogenic microorganisms.

On the other hand the mentioned compounds could result as industrial by-products of chemical wood processing or from the technologies of biomass refining. At the same time, this renewable source of raw material was proved convenient for obtaining some derivatives with increased functionality, or some important products such as furan resins. The application of compounds based on copper in wood protection due to their antifungal properties has also been known and used for a long time. These facts were prominent in a first stage of the study of the interaction of birch veneer with some products based on modified and unmodified lignin, polyphenols (tannins) and furan resins along with copper compounds.

The possibility of complexes forming *in situ* between organic compounds and copper ions was also taken into account. The samples of veneer treated in the above mentioned conditions were analysed to establish the retention degree of bioprotection agents. With this aim, the samples were exposed to a successive extraction by distilled water for different durations (Figs. 1-3) and the mass losses were determined.

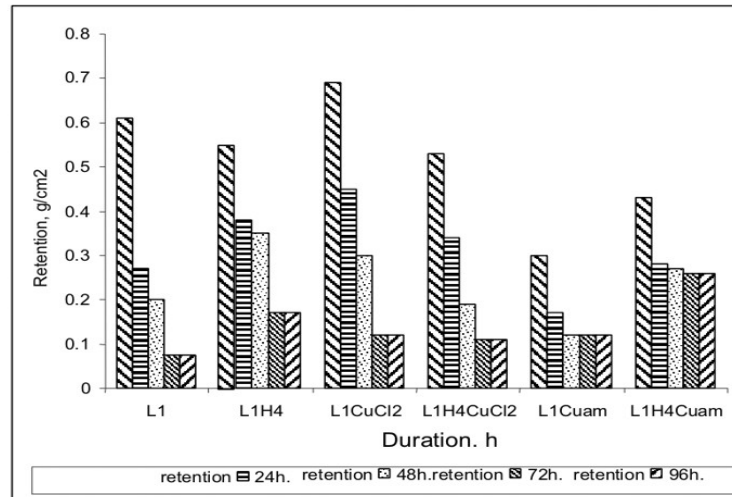
The data presented in Fig. 1 are obtained in the case of the birch veneer treated with lignin, its hydroxymethylated derivative and their complex with copper. From the analysis of these results one can identify an increased affinity of veneers for modified lignin through hydroxymethylation reaction, as well a high stability at the treatment by extraction with distilled water. At the same time preliminary impregnation of wood with solution of copper ions assure, as it was expected, a high retention degree and stability of applied treatment.

This fact is determined by the presence of functional groups in the wooden substrate, and also of those introduced into lignin, offering thus a good condition for complex forming with copper ions and therefore a better fixation of them on used support.

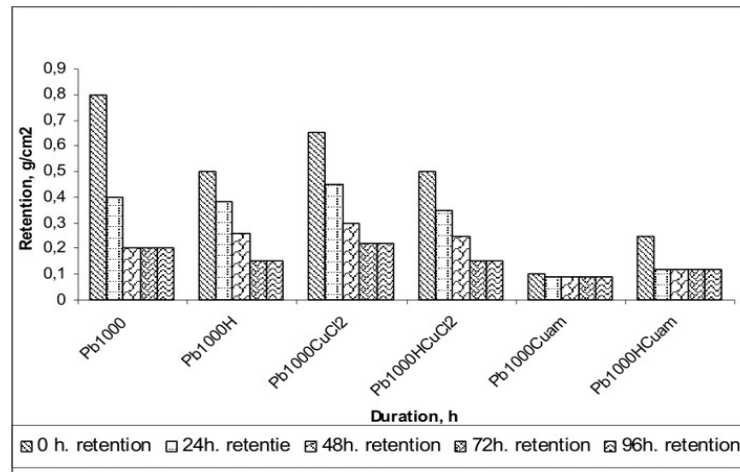
In case when the product Pb1000 and its derivative are used it can be noticed that the last one is better retained on the surface of veneer (Fig. 2) due to its increased functionality. Moreover this fact is confirmed by high stability of the complex with copper of the hydroxymethylated derivative.

The data obtained concerning furan resin and tannins are presented in Fig. 3. In this case we observed a reduced affinity against wood, as compared with lignin and its derivative. The complex forming of tannins with copper ions is favorable for the interaction with substrate, a situation similar to that reported in literature (Yamaguchi et al., 2001).

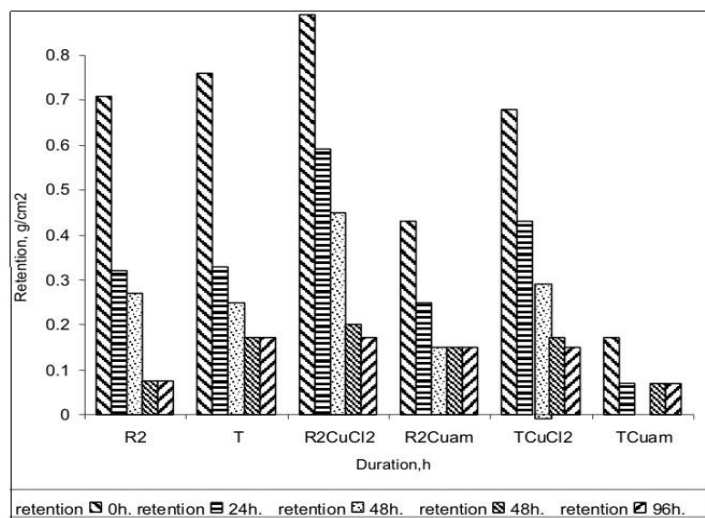
The extracts separated by water were investigated by UV spectroscopy and it was observed that there exist a correlation between absorption and degrees of retention.



**Fig. 1.** Variation of retention of lignin (L1), hydroxymethylated lignin (L1H4) and their complexes with copper ions (L1CuCl<sub>2</sub>, L1H4CuCl<sub>2</sub>, L1Cuam and L1H4Cuam) by birch veneer as a function of elution degree after extraction with distilled water for different durations



**Fig.2.** Variation of retention of Pb1000 nonmodified and modified through hydroxymethylation reaction (Pb1000H) and their complexes with copper ions (Pb1000CuCl<sub>2</sub>, Pb1000Cuam, Pb1000HCuCl<sub>2</sub>, Pb1000Hcuam) as a function of elution degree



**Fig. 3.** Variation of retention of furan resin (R2) and tannins (T) and their complex with copper ions (R2CuCl<sub>2</sub>, R2Cuam, TCuCl<sub>2</sub>, TCuam) depending on the elution duration

Thus, the values of absorption intensity are more reduced when the degree of retention is increased. At the same time, most of the products taken into consideration were eluted within the first 24 hours (Figs. 4 -6). The complex forming capacity of the studied products with copper ions assured a high stability degree of the treatment. The increasing the elution duration over 24 hours didn't remove important quantities of the compounds with biocide potential action and the values of the absorption intensities of extracts were relatively constant. Taking into account that the veneer protected with the studied products will come into contact with the environment and it will be exposed to the interaction

with water, which removes part of the used compounds, it was then necessary to obtain information concerning the toxicity of leachates. With this and in view, the elution liquids resulted after successive immersions of wood samples in water were tested from the point of view of the toxicity in the germination experiments of tomato seeds (Figs. 7-9). The data obtained in this study point out that the toxicity of the extracts was different depending on the compound or complex used, and that toxicity effect diminished with the decrease of the concentration (increase of elution time) and these are not to be considered as relevant.

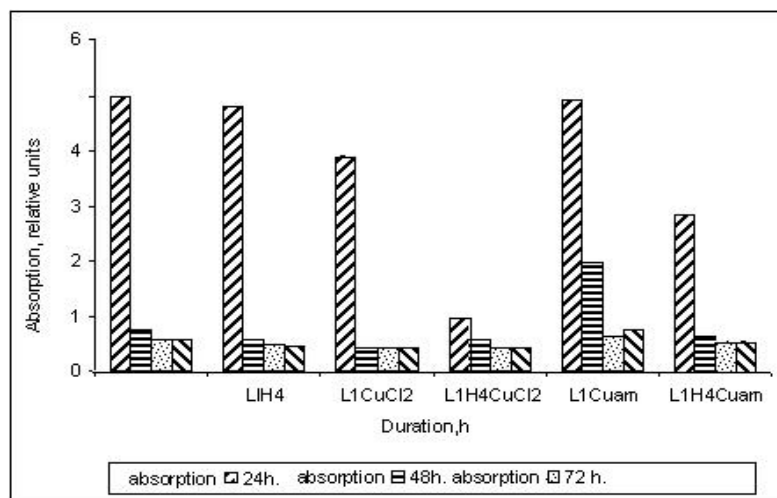


Fig. 4. Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with L1, L1H4, L1CuCl<sub>2</sub>, L1H4CuCl<sub>2</sub>, L1Cuam, L1H4Cuam

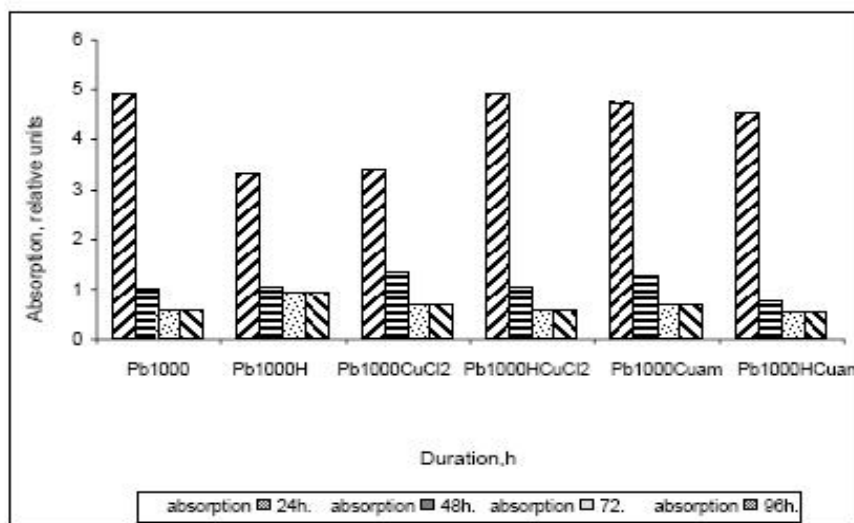


Fig. 5. Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with Pb1000, Pb1000H, Pb1000CuCl<sub>2</sub>, Pb1000HCuCl<sub>2</sub>, Pb1000Cuam, Pb1000HCuam

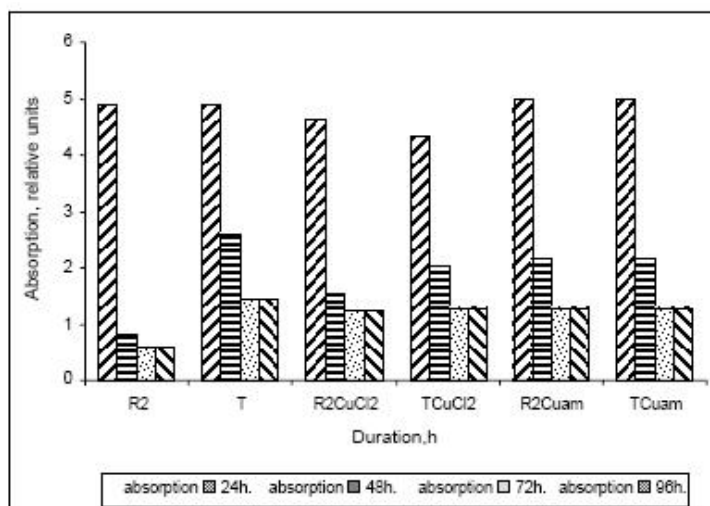


Fig. 6. Variation of absorption intensity in UV of leachates depending on elution time for the samples treated with R2, T, R2CuCl<sub>2</sub>, TCuCl<sub>2</sub>, R2Cuam, TCuam.

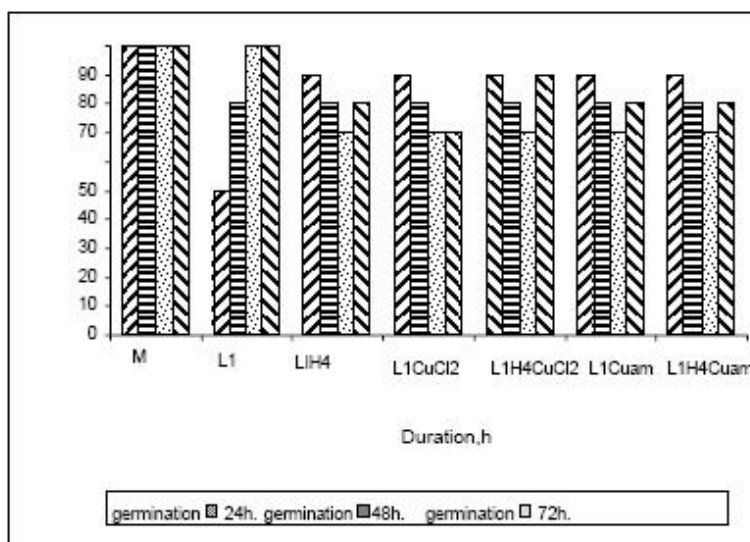


Fig.7. The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of the veneer treated with L<sub>1</sub>, L<sub>1</sub>H<sub>4</sub>, L<sub>1</sub>CuCl<sub>2</sub>, L<sub>1</sub>H<sub>4</sub> CuCl<sub>2</sub>, L<sub>1</sub>Cuam, L<sub>1</sub>H<sub>4</sub> Cuam

The information obtained in this study will be completed with biodegradability tests of birch veneer treated with the studied compounds which could have a biocide potential action.

#### 4. Conclusions

A study concerning the interaction between birch veneers was carried out using a series of products, which could have a biocide potential action, such as unmodified and modified lignin by hydroxymethylation, furan resin and tannins, along with their complex obtained *in situ* using the CuCl<sub>2</sub> and copper ammonia solution.

The stability of the treatments was followed by successive elution with water of wooden substrate impregnated with mentioned compounds. It can be

concluded that the retention degree is influenced by the nature of products, their functionality and the complex forming capacity.

UV spectroscopy led us to the conclusion that there exists a direct correlation between the absorption of extracts and the retention degree. A significant removal of treating agents was found within the first 24 hours, and that no important losses could be identified. The capacity of tomato seeds germination in the presence of solutions resulted after successive extraction with water of birch veneer treated with products with biocide potential activity didn't reveal major toxic effects. Therefore, we consider that there is a premise to obtain some environmentally friendly biocide agents.

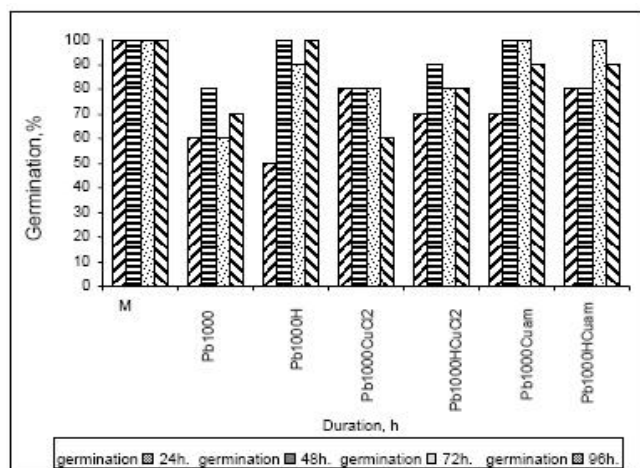


Fig. 8. The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of veneer treated with Pb1000, Pb1000H, Pb1000E<sub>2</sub>, Pb1000CuCl<sub>2</sub>, Pb1000HCuCl<sub>2</sub>, Pb1000E<sub>2</sub>CuCl<sub>2</sub>, Pb1000Cuam, Pb1000HCuam, Pb1000E<sub>2</sub> Cuam

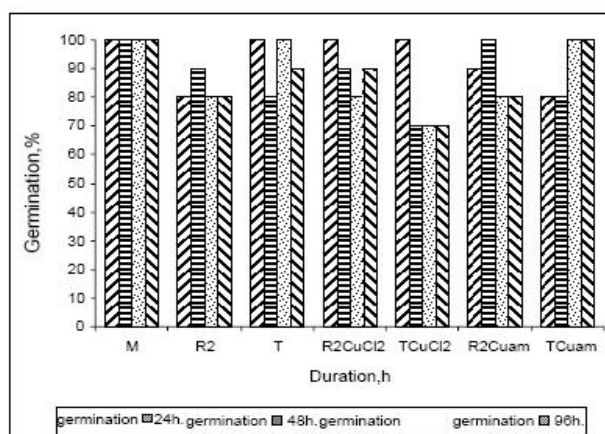


Fig. 9. The evolution of germination degree of tomato seeds in the presence of leachates resulted after the elution of veneer treated with R2, T, R<sub>2</sub>CuCl<sub>2</sub>, TCuCl<sub>2</sub>, R<sub>2</sub>Cuam, TCuam

### Acknowledgement

The authors would like to thank to the Granit Recherché Développement SA, for supplying the lignin samples, furan resins and tannin and to ECOBINDERS (SIXTH FRAMEWORK PROGRAMME, NMP2 – CT – 2005 - 011734) and CEEX-CNCSIS, LIGNOMAT, 4153/2006 for their financial support.

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