Drewno 2019, Vol. 62, No. 203
DOI: 10.12841/wood.1644-3985.D04.05

Joanna Siuda, Bartłomiej Mazela, Waldemar Perdoch

WATERLOGGED ARCHAEOLOGICAL WOOD SILANIZATION WITH MTMOS

A wooden object that has survived in a wet environment is characterised by water saturation and is called waterlogged wood. The subject of the study was elm piles, dating back to the 10th and11th century, excavated from Lednica lake archaeological site. Wooden piles showed a high degree of degradation. This was evidenced by their spongy and fragile structure. As a result of the biotic and abiotic degradation of the wood cell wall, a significant change in its chemical composition was observed. The weakening of the wood structure and its increase in porosity were as a result of cellulose degradation. The archaeological wood conservation method used until now is polyethylene glycol (PEG). However, this method has some drawbacks such as high-density wood after treatment, the colour of the wood and it is a long-term process. It has already been found that alkoxysilanes are potential alternatives to the commonly used PEG. The purpose of the study was to determine the optimum concentration of methyltrimethoxysilane (MTMOS) for the medieval elm wood conservation. The general aim of the study was to develop an effective waterlogged wood dimensional stabilization through its silanization with MTMOS. After long-term dehydration (replacement of water for ethanol, during an ethanol bath) wood samples were saturated with MTMOS solutions of various concentrations. Wood samples were treated through the oscillating vacuum-pressure method. Dimensional stabilization of the sililated wood was estimated through the anti-shrink efficiency (ASE) calculation. The ASE value for PEG and MTMOS treated wood samples was 88.6% and 96.8% respectively. It was found that an ethanol solution of 20% MTMOS is the optimum concentration for waterlogged elm wood dimensional stabilization treatment (ASE = 94.1 %). The other advantage of this method includes a short impregnation time and low density of the preserved wood.

Keywords: methyltrimethoxysilane, silanization, waterlogged archaeological wood

Introduction

Wood saturated with water which has remained under high humidity for a long period is called "waterlogged wood" [Grattan 1987; Zborowska et al. 2004]. Despite the fact that it survived, it had been exposed to destructive factors for a long time. Water soluble substances such as simple sugars, mineral salts and

Joanna Siuda✉ (*joanna.siuda@up.poznan.pl*), Bartłomiej Mazela (*bartlomiej.mazela@up.poznan.pl*), Waldemar Perdoch (*waldemar.perdoch@up.poznan.pl*), Poznań University of Life Sciences, Faculty of Wood Technology, Poznań, Poland

tannins are washed out of the wood. Waterlogged wood under anaerobic conditions could be degraded by microorganisms such as erosive bacteria. Those microorganisms are able to survive and develop under anaerobic conditions which leads to wood degradation [Nilsson and Björdal 2002]. Due to biotic and abiotic factors, damage to the cell wall in wood tissue can be observed, as well as changes in the chemical composition of the wood object. Wood decomposition is a complex process, depending on the factors that cause it. Based on a number of studies, a decomposition scheme has been established: polysaccharides are decomposed first, but lignin is more resistant to degrading agents and it remains undisturbed for a long time [Ważny 1976; Hoffmann 1981; Hedges 1990; Sakai 2001]. As a consequence of this, waterlogged archaeological wood is often characterized by a significant reduction in physical and mechanical properties [Unger et al. 2001].

Waterlogged archaeological wood requires special conservation processes, as being left unprotected it dries quickly leading to irreversible shrinkage of the wood tissue and then it cracks. The drying process can even cause its complete destruction. In most cases, carbohydrates (i.e. cellulose) are degraded and the remaining lignin creates a "skeleton" [Nilsson and Björdal 2002].

Nowadays, the most popular method of preserving archaeological wood is impregnation using a polyethylene glycol (PEG) [Stamm 1956; Stamm 1959; Cook and Grattan 1985; Ambrose 1990; Jensen and Schnell 2005; Babiński 2012]. The idea of using PEG is to fill the gaps in the degraded wood in order to prevent a collapse. The most commonly used impregnation process consists of two steps. The process begins with impregnation with a lower molecular weight compound (e.g. PEG 200, PEG 400) in an increasing concentration gradient. The next step is impregnation with a high molecular weight PEG (e.g. PEG 4000) [Babiński and Poskrobko 2005; Babiński 2012]. The low molecular weight compound is readily penetrated by both strongly degraded outer layers and a well-preserved inner part. In order to ensure good stability of the most degraded wood parts, either PEG 3000 or PEG 4000 is used. However, this method has significant drawbacks. Polyethylene glycol, which is highly hygroscopic, is able to absorb water from the environment [Olek et al. 2016]. Moreover, wood after PEG impregnation is heavy and it's colour changes. [Unger et al. 2001].

Because of the disadvantages of PEG application, this research aims to explore new impregnation methods. A potential alternative could be organosilicon compounds, such as silanes [Smith and Hamilton 2001]. In view of their chemical structure and properties, silanes have mainly been used to hydrophobize surfaces e.g. of glass or contemporary wood surfaces [Tshabalala and Gangstad 2003; Hill et al. 2004]. From the chemical point of view, wood is made of biopolymers. These biopolymers have hydroxyl groups which are reactive for different compounds e.g. alkoxysilanes. Organosilicon compounds are characterized by the ability to form Si-O-C and Si-O-Si bonds with wood surfaces [Sebe and Brook 2001]. This reactivity allows for the chemical bonding of silanes with wood, which prevents them from leaching, therefore, the protection of archaeological wood against breakage, shrinkage and decay can be sustainable and effective [Smith and Hamilton 2001]. MTMOS was used in the re-conservation process of the wood samples from the Vasa ship and the results were promising. During the re-conservation process, the dimensional stabilization of the wood was retained [Tejedor 2010]. Broda and Mazela [2017] and elm wood samples were treated with a 50% MTMOS solution. Depending on the layer of wood (from the outer to the inner part) ASE was comprised of between 69.5% and 94.6%.

The purpose of the study was to determine the optimum concentration of methyltrimethoxysilane (MTMOS) for elm wood conservation. The general aim of the study was to achieve an effective waterlogged wood dimensional stabilization through its silanization with MTMOS.

Materials and methods

Object

The subject of the study was waterlogged archaeological elm wood from the waters of Lednica Lake. Elm piles were cut into smaller samples with diameters of 20 × 20 × 10 mm (tangential x radial x longitudinal directions).

Evaluation of waterlogged wood degradation

In order to evaluate the state of degradation of the waterlogged elm wood, chemical and physical analysis were done. The percentage content of the main wood components (cellulose [C], holocellulose [H], lignin [L], extractives and inorganic deposits [Koch et al. 2018] [Ex]) was determined by chemical analysis. Cellulose content was measured according to the Seifert procedure. Holocellulose content was determined according to the procedure described by Browning [1967], lignin and extractives content was measured according to the TAPPI 2006 and TAPPI 2007a standard, respectively. Maximum moisture content (MC_{max}) was determined for wood samples saturated with water under reduced pressure and then oven-dried at 105°C for 24h, compared to dry mass (m_0). MC_{max} was calculated according to Equation 1:

$$MC_{max} = \frac{m_{max} - m_0}{m_0} \times 100\% \quad (1)$$

Conventional density (ρ) was calculated according to Equation 2 as the ratio of the mass of absolutely dry wood samples (m_0) and sample volumes of water-saturated wood maximum (V_{max}):

$$\rho = \frac{m_0}{V_{max}} \tag{2}$$

PEG treatment

For the traditional method of impregnation PEG 400 and PEG 4000 was used. First, samples were saturated with PEG 400 solution in a gradient of concentrations (10%, 20%, 30%, 40%, each concentration for one week). After that, the wood was placed in 40% PEG 4000 solution for one week. Samples were dried under laboratory conditions and ASE was calculated. The number of repetitions was 5.

MTMOS treatment

MTMOS treatment was carried out in two steps. First, samples were dehydrated through their long-term immersion in ethanol (4 weeks). Next, they were subjected to the oscillating vacuum-pressure treatment with MTMOS ethanol solution at the following concentrations: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100%. The treatment consisted of 6 cycles: (at a pressure reduced by 0.1 MPa for 0.5 h and 1 MPa for 6 h)/cycle. After the treatment, the samples were cured at ambient pressure and room temperature for 1 week. The number of repetitions was 5.

Control samples

Control samples (untreated) were cured at ambient pressure and room temperature for 1 week. The number of repetitions was 5.

Anti-shrink efficiency calculation

The degree of shrinkage of the wood was determined in tangential, radial and longitudinal directions, using Equation 3:

$$\beta = \frac{l_0 - l_1}{l_0} \tag{3}$$

where: β – degree of shrinkage in a linear direction, %; l_0 – initial dimension of wood, mm; l_1 – final dimension of wood (obtained after drying), mm.

The degree of shrinkage of the cross-section of wood (β_{CS}) was calculated based on the average degree of shrinkage of wood in tangential and radial directions, according to Equation 4:

$$\beta_{CS} = \beta_T + \beta_R - \frac{\beta_T \beta_R}{100} \tag{4}$$

where: β_{CS} degree of shrinkage of the wood in the – tangential (β_T) and radial (β_R) direction.

The effectiveness of the conservation treatment was assessed on the basis of the ASE, calculated according to Equation 5:

$$ASE = \frac{\beta_0 - \beta_1}{\beta_0} \times 100\,\% \tag{5}$$

where β_0 – degree of shrinkage of the cross-section direction of untreated wood and β_1 – treated wood.

Absorption (A_m) of MTMOS or PEG

A_m was calculated according to Equation 6:

$$A_m = \frac{m_{\text{mod}} - m_{\text{unmod}}}{m_{\text{unmod}}} \times 100\,\% \tag{6}$$

where m_{mod} is the mass of the treated wood sample and m_{unmod} is the mass of the untreated sample.

Retention (R) of MTMOS or PEG

R was calculated according to Equation 7:

$$R = \frac{m_m - m_{um}}{V} \times 1000 \tag{7}$$

where R is the retention of the protecting agent (kg/m^3), m_m is the mass of the dry treated wood sample (g), m_{um} is the mass of dry the untreated sample (g) and V is the volume of the sample (cm^3).

Results and discussion

The aim of this study was to predict the optimal concentration of methyltrimethoxysilane solution (MTMOS) for dimensional stabilization of waterlogged archaeological wood. The determination of the wood stabilization coefficient (ASE) for the ethanol MTMOS solution was an additional aim.

The first step of the research was to determine the degree of wood degradation. Depending on the result, the physical characteristics were estimated [Jensen and Gregory 2006] and the chemical analysis was done. The results of this analysis are shown in table 1.

The conventional density of waterlogged archaeological elm wood (165 kg · m^{-3}) was appreciably lower than contemporary elm wood (390 kg · m^{-3}), which provided evidence of significant wood tissue degradation. MC_{max} was approximately 425% which confirmed a high degree of tissue degradation. The results clearly showed that elm wood required protection and conservation. The chemical analysis of the basic wood components was a useful tool for the evaluation of the degree of wood degradation.

Table 1. Selected physical and chemical characteristics of waterlogged elm wood

	Mc_{max} [%]	ρ [kg/m^3]	*C* [%]	*H* [%]	*L* [%]	*H/L* [%]	Ex [%]
Sample	425	165	14	10.1	72.4	0.14	1.8

C- cellulose; H- holocellulose; L-Lignin.

In the case of the waterlogged elm samples, cellulose content was significantly reduced in comparison with contemporary wood. According to Unger et al. [2001], the content of cellulose for contemporary wood is 50% whereas in waterlogged elm wood it was 14%, which confirmed the extensive decay of the basic wood component. H/L ratio is the coefficient of wood degradation [Pizzo et al. 2010] and the lower the value, the more degraded the wood tissue is. The elm wood was highly degraded (*H/L* = 0.14) where for the elm, the wood ratio was 3.3 [Unger et al. 2001].

The degree of shrinkage in a cross-section was calculated according to formula 4. As expected, the highest shrinkage (72.5%) was observed for archaeological samples (control). Depending on the concentration of MTMOS solution β_{CS} varied between 32.3% and 2.3%. The lowest shrinkage was observed at the concentration of 50% MTMOS and it was 2.3%. While the reference samples shrank at 8.2%. MTMOS and PEG treatment resulted in a significant increase in the wood's dimensional stability, with a particularly spectacular stabilizing effect observed for samples treated with 50% MTMOS.

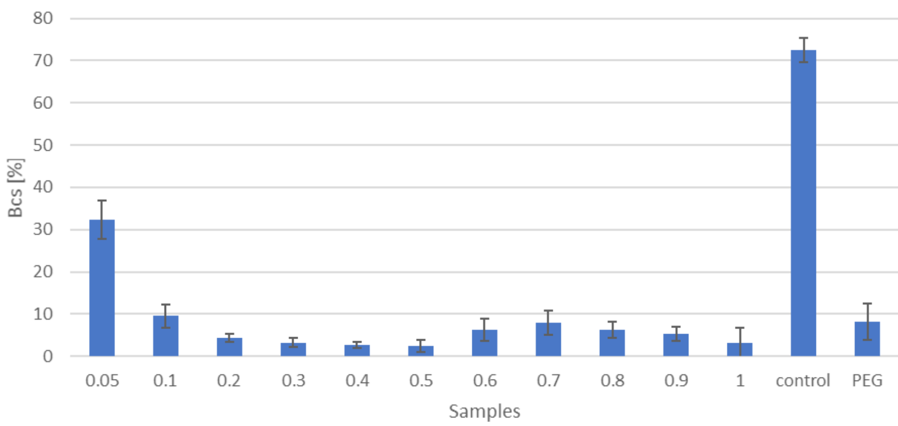

Fig. 1. Shrinkage in cross-section (β_{CS}) for wood treated with different concentrations of MTMOS

The highly degraded waterlogged elm wood required impregnation with a proper concentration of stabilizing agent. Figure 2 shows the relation between the concentration of the working solution and the ASE of the treated wood. It appears that 20% is an optimum concentration for an effective dimensional stabilization, where ASE was equal to 94.1%. However, the highest value of ASE was obtained for wood treated with MTMOS solution at a concentration of 50% (ASE = 96.1%).

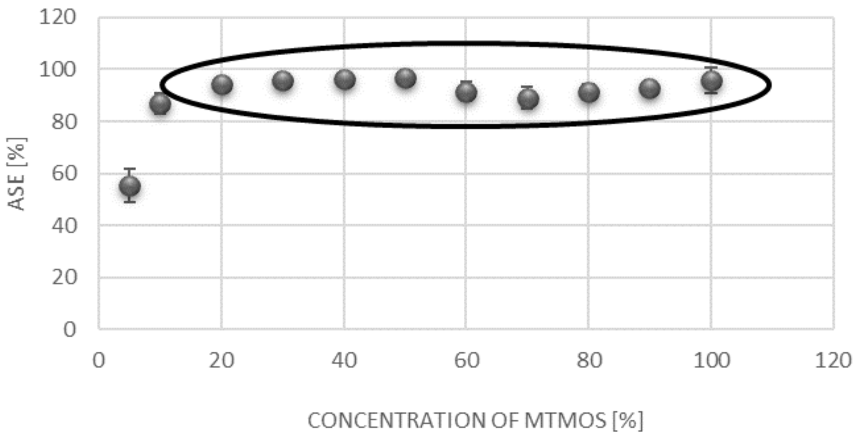

Fig. 2. ASE of wood treated with MTMOS

The research clearly shows that oscillating vacuum-pressure treatment with MTMOS provides a high dimensional stability of the treated wood. As a result of the conventional method application (i.e. soaking with PEG 400 and PEG 4000 consecutively), an average ASE for wood samples was equal to 88.6% (RSD = 5.9). It is also evident that for highly degraded elm wood, the MTMOS treatment proved to be a much more efficient method than the PEG treatment (fig. 3).

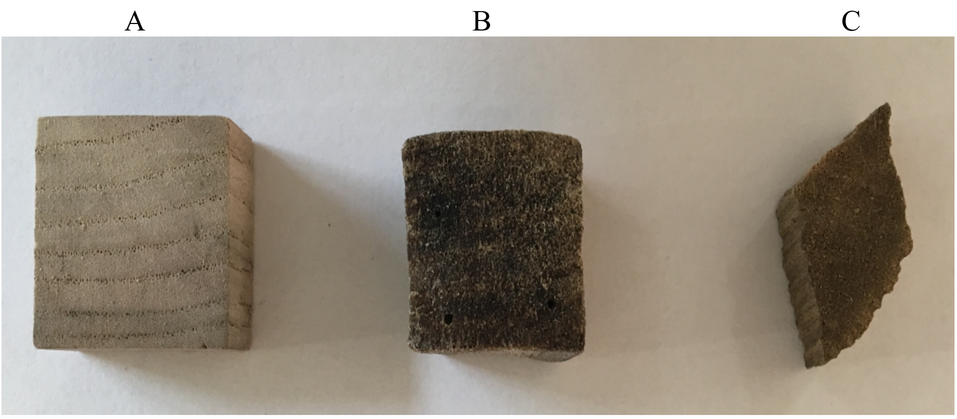

Fig. 3. Waterlogged elm wood treated samples: 20% MTMOS (A), PEG 400 and PEG 4000 (B), untreated samples (C)

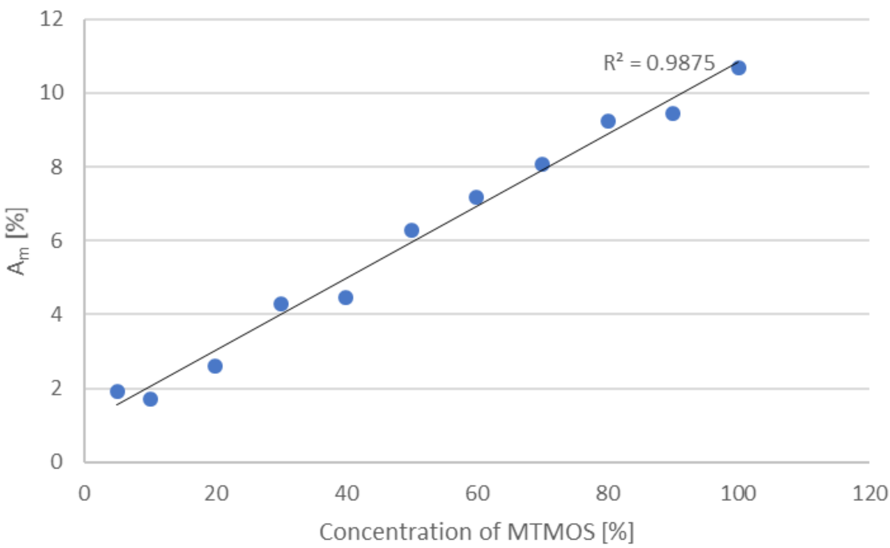

Fig. 4. A direct relation between A_m and solutions of MTMOS

The absorption of MTMOS was directly related to the concentration of MTMOS, where the correlation coefficient was equal to 0.9875. The absorption of MTMOS at the optimum concentration was much lower than for PEG treatment (9.6 ± 0.6%). This phenomenon directly influences the wood density reduction, which is the main advantage in comparison to the PEG treatment (fig. 4). The retention for MTMOS treatment was 67.9 kg/m^3 (RSD = 1.6%) and 140.7 kg/m^3 (RSD = 12.4%) for 20 and 50% concentration solution respectively. The retention of PEG (R = 419.0, RSD = 4.0%) was obviously much higher than MTMOS (acc. to equation 7).

Conclusions

The main purpose of waterlogged wooden object conservation process is to prevent shrinkage during drying and to limit eventual dimensional changes during exposing. Wood treatment with MTMOS seems to be a useful method for wood conservation. The main advantage of this method is the relatively high dimensional stabilization of wood. The oscillating vacuum–pressure method with the use of MTMOS at different concentrations of working solution was proved to be effective. Within the wide range of concentration solutions (5-100%), the optimal concentration was estimated at 20%. There are the other subsequent advantages resulting from this fact: high wood penetrability, short duration of the treatment process, easy drying process after wood treatment (doesn't require freeze-drying), low cost of the whole conservation process.

References

Ambrose W.R. [1990]: Application of freeze-drying to archaeological wood. In: Rowell R.M., Barbour R.J. (eds.), Archaeological Wood: Properties, Chemistry and Preservation. Advances in Chemistry, Series 225, American Chemical Society, Washington DC: 235--263

Babiński L. [2012]: Research on dimensional stability in waterlogged archaeological wood dried in non-cooled vacuum chamber connected to a laboratory freeze-dryer. Drewno 55 [187]: 5-19

Babiński L., Poskrobko J. [2005]: Badanie wchłonięcia poliglikoli etylenowych do mokrego drewna archeologicznego. In: Prądzyński W. (ed.), Badania i konserwacja drewna archeologicznego: 93-103

Broda M., Mazela B. [2017]: Application of methyltrimethoxysilane to increase dimensional stability of waterlogged wood. Journal of Cultural Heritage 25: 149-156

Browning B.L. [1967]: The chemistry of wood. Interscience Publisher, USA

Cook C., Grattan D.W. [1985]: A practical comparative study of treatments for waterlogged wood: part III: pretreatment solutions for freeze drying. Waterlogged wood: study and conservation. Proceedings of: the 2nd ICOM Waterlogged Wood Working Group Conference, Grenoble

Grattan D.W. [1987]: Waterlogged wood. In: Pearson C. (ed.), Conservation of marine archeological objects. Butterworth, Boston: 55-67

Hedges J. [1990]: The chemistry of archeological wood. In: Rowell R., Barbour R.J. (eds.), Archeological wood properties, chemistry and preservation. Advances in Chemistry Series 225. Washington

Hill C.A.S., Farahani M.R.M., Hale M.D.C. [2004]: The use of organo alkoxysilane coupling agents for wood preservation. Holzforschung, 58: 316-325

Hoffmann P. [1981]: Chemical wood analysis as a means of characterizing archeological wood. Proceedings of: the ICOM Waterlogged Wood Working Group Conference, Ottawa: 73-83

Koch G., Melcher E., Lenz M.T., Bauch J. [2018]: Biological and topochemical studies on the resistance of excavated oak piles (*Quercus* sp.) from a historical bridge in Bavaria. Holzforschung 72 [2]: 133-141

Jensen P., Schnell U. [2005]: The implications of using low molecular weight PEG for impregnation of waterlogged archaeological wood prior to freeze drying. In: Hoffmann P., Strætkvern K., Spriggs J.A., Gregory D. (eds.), Proceedings of the 9th ICOM Group on Wet Organic Archaeological Materials Conference

Jensen P., Gregory D.J. [2006]: Selected physical parameters to characterize the state of preservation of waterlogged archaeological wood: a practical guide for their determination. Journal of Archaeological Science 33: 551-559

Nilsson T., Björdal Ch. [2002]: Microbial degradation on waterlogged archaeological wood. Proceedings of: IAWS 2002 Beijing Conference

Olek W., Majka J., Stempin A., Sikora M., Zborowska M. [2016]: Hygroscopic properties of PEG treated archaeological wood from the rampart of the 10th century stronghold as exposed in the Archaeological Reserve *Genius loci* in Poznań (Poland). Journal of Cultural Heritage 18: 299-305

Pizzo B., Giachi G., Fiorentino L. [2010]: Evaluation of the applicability of conventional methods for the chemical characterization of waterlogged archaeological wood. Archaeometry 52 [4]: 656-667

Sakai H. [2001]: Analysis of degradation observed on ancient wooden objects buried underground. IRG/WP 01-10403

Sebe G., Brook M.A. [2001]: Hydrophobization of wood surfaces: covalent grafting silicone polymers. Wood Science and Technology 35: 269-282

Smith C.W., Hamilton D.L. [2001]: Treatment of waterlogged wood using hydrolyzable multi-functional alkoxysilane polymers. Proceedings of: the 8th ICOM group on Wet Organic Archaeological Materials conference, Stockholm: 614-615

Stamm A.J. [1956]: Dimensional stabilization of wood with carbowaxes. Forest Products Journal 6 [5]: 201-204

Stamm A.J. [1959]: Effect of polyethylene glycol on the dimensional stability of wood. Forest Products Journal 9 [10]: 375-381

Tejedor C.C. [2010]: Re-conservation of wood from the seventeenth-century Swedish warship the vasa with alkoxysilanes: A Re-treatment Study Applying Thermosetting Elastomers

Tshabalala M.A., Gangstad J.E. [2003]: Accelerated weathering of wood surfaces coated with multifunctional alkoxysilanes by sol-gel deposition. Journal of Coatings Technology. DOI: https://doi.org/10.1007/BF02730098

Unger A., Schniewind A.P., Unger W. [2001]: Conservation of wood artifacts. A handbook. Springer-Verlag Berlin Heidelberg

Ważny J. [1976]: Deterioration of ancient wood in Biskupin archeological excavations. Material und Organismen (Berlin) 3: 53-62

Zborowska M., Spek- Dźwigała A., Waliszewska B., Prądzyński W. [2004]: Ocena stopnia degradacji drewnianych obiektów archeologicznych z najcenniejszych znalezisk wielkopolskich (The estimation of degradation of wooden archeological objectives from most valuable excavation from wielkopolska). Acta Scientiarum Polonorum Silvarum Colendarum Ratio et Industria Lignaria 3 [2]: 139-151

List of standards

TAPPI (US technical association of pulp and paper industry) 2006 Acid insoluble lignin in wood and pulp T 222 om-06

TAPPI (US technical association of pulp and paper industry) 2007a Solvent extractives of wood and pulp T 204 cm-07

Acknowledgements

The work was financially supported by the Ministry of Science and Higher Education as the 2bH 15 0037 83 “Cultural heritage-research into innovative solutions and methods for historic wood conservation”.Research Grant as well as by the Ministry of Science and Higher Education as the 507.423.43. with subsidies for maintaining the research capacity.

The authors would like to express their thanks to the Directorate of the Museum of the First Piasts at Lednica for sharing the waterlogged elm logs, and Dr. Krzysztof Radka (Institute of Archaeology, Nicolaus Copernicus University in Toruń) for excavating them from the bottom of the lake.

The research was carried out within the framework of the doctoral thesis: Chemical interactions of trialkoxysilanes with lignocellulosic material (*Quercus* spp.) depending on the variable reaction conditions.

Submission date: 4.09.2017

Online publication date: 7.12.2018