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► **To cite this version:**

Michael Rosenthal, Claus-Thomas Bues. Longitudinal penetration of silicon dioxide nanosols in wood of . European Journal of Wood and Wood Products, 2010, 68 (3), pp.363-366. 10.1007/s00107-010-0455-5 . hal-00604413

HAL Id: hal-00604413

<https://hal.science/hal-00604413>

Submitted on 29 Jun 2011

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Longitudinal penetration of silicon dioxide nanosols in wood of *Pinus sylvestris*

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This article is dedicated to Gerd Wegener on the occasion of his retirement as professor at the Technische Universität München.

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Abstract

For purposes of wood preservation, stabilization and fire protection, the penetration ability of bio-inspired environmentally friendly Sebosil[®] nanosols in axial direction of the pine tracheids were investigated using macroscopic evaluations and EDX microanalysis.

1 Introduction

The silification of wood is an environmentally-friendly modification method inspired by examples from nature: In petrified wood, e.g. in the Petrified Forest in Chemnitz (Rößler 2001), the organic material was replaced by minerals (mostly silicate) while the original structure of the wood is still retained. The application of this natural process to wood technology is realized by functional impregnations on a basis of silicon dioxide nanosols. The hydrolysis of silicon alkoxides produces nanoparticulate silica sols, which condense to thin transparent gel films after coating and drying (Böttcher 2001).

By means of this sol-gel technique wood can be permanently silified to a specific degree. The nanosols are currently applied as consolidation agents for wooden cultural artefacts (e.g., ceiling beams in the castle Hof near Riesa/Germany) which are invisible, and make the rotted wood rigid, seal in older toxic preservatives and protect against biological attack (Eisbein et al. 2000). Mahltig et al. (2008) give an overview of the resultant changes in flame retardant, water repellent, mechanical and antimicrobial properties. The advantageous multifunctional properties of Sebosil[®] suggest extending the application possibilities. However, new applications depend on the penetration ability of the nanosols in wood. If suitable

penetration behaviour in wood could be realized, it would be possible to use silicon dioxide nanosols to protect wooden houses, bridges, and playground equipment.

The objective of this study was to scrutinize the impregnation behaviour of silicon dioxide nanosols in different wood species using immersion as a simple manual impregnation method. The penetration ability of Sebosil[®] was investigated using macroscopic evaluation and quantitative analysis with energy dispersive X-ray spectroscopy (EDX). The results for pine wood are presented.

2 Materials and Methods

Wood of *Pinus sylvestris* L. is suitable for application-oriented penetration tests because it is easily treatable and widely-used as construction timber. From air-dried pine sapwood five cubic samples (20 x 20 x 20 mm³) were formed, which were coated on five sides (cf. Rapp and Peek 1994) with a two-component epoxy resin (Loctite[®] 9481 A/B Hysol). Thereby only the cross-section of the samples remained uncoated. These samples were immersed for 20 h in a Sudan IV stained silicon dioxide nanosol dissolved in ethanol (Sebosil[®] H, Kallies Feinchemie AG). The staining was necessary to visualize the impregnation ability by the depth of penetration in axial wood direction. After impregnation, each sample was cut into three pieces in radial direction. Two surfaces per sample were investigated. For scanning and digitalization of the generated surfaces a flat bed scanner (BROTHER MFC-215C) with a resolution of 1200 dpi was used. Then the soaked area was measured applying the computer program GIMP 2.6.

Microscopic investigations of the penetration ability of silicon dioxide were carried out by means of energy dispersive X-ray spectroscopy (EDX). Thereby a scanning electron microscope (Jeol T330A) equipped with an energy dispersive SDD detector (Bruker XFlash[®] 5010) was used. Silicon was identified with the help of the peak position of K_α (Rosenthal et al. 2009). Additional to exemplary single measurements, mapping of a 3700 x 2800 μm area with a raster of 150 dots was carried out (QUANTAX ESPRIT 1.9, Bruker).

3 Results and discussion

The macroscopic measurements of the longitudinal depth of penetration considered exactly the area which can be identified by the coloration with Sudan IV. After 20 h of immersion the penetration revealed minimum values of 1.60 ± 0.25 mm and maximum values of 2.42 ± 0.31 mm. Scheithauer et al. (1998) obtained similar results after they immersed pine for 24 h.

Quantitative X-ray microanalyses showed that the silicon content varied within the Sudan IV colored area depending on anatomical structures. Many tracheids showed no Sebosil penetration. Other tracheids showed fragments of mineral deposits in the lumen, characterized by the K_{α} -peak of Si (Fig. 1, 2 a). Some parts of the deposits probably broke out of the lumina during the cutting process.

Thereby, the remaining lumen surface is almost free of silicon (Fig. 1, 2 b). This indicates that the nanosol is generally unable to penetrate the micro-pores of the cell wall (cf. Rosenthal et al. 2009) having a diameter ranging from 1 to 4 nm (Stone and Scallan 1969, Flournoy et al. 1993). Measuring of the particle size remains to be done. However, Weigenand et al. (2007) and Gosh et al. (2009) reported that silicone emulsions with an average particle size of 40 and even 120 nm displayed cell wall penetration into the sapwood of pine (*Pinus sylvestris* L.). Another conclusion, which is suggested by the coloration of the penetration agent, could be that only the colored parts of the sample are penetrated by silicon dioxide nanosols. Fig. 3 shows the results of an EDX element mapping of a 3700×2800 μm area with a raster of 150 dots. Every dot in the figure represents the median of 10 single measurements. Obviously the portion of silicon declines with increasing distance from the impregnation surface. The coloration reaches up to a depth of 2100 μm . Beyond this line, the EDX-measurements revealed a small but not negligible amount of penetrated silicon dioxide. The noticeable decrease of the silicon content at a depth of 2500 to 3500 μm could be attributed to difficult flow through the pit membranes. Pine wood predominantly consists of axial tracheids with a length of 1800 to 4500 μm with a mean of 3100 μm (Wagenführ 2007). Flow from one tracheid to another mainly occurs through bordered pits (Stamm 1967). In softwood, the pit membrane is composed of a network-like open margo and a thickened central portion called the torus. As long as the bordered pits are in the unspirated state, flow can occur relatively easily through the openings

between the cellulose fibrils of the margo (Nicholas and Siau 1973) having diameters of 0.02 to 4 μm with a mean of 0.3 μm (Siau 1984). Capillary tension forces during drying from liquids with high surface tension (e.g. water) causes pit aspiration primarily in the earlywood (Comstock and Côté 1968). Through aspirated bordered pits there are two pathways: In the first pathway, the liquid passes through the margo, then between the torus and border and out through the aperture; in the second pathway, the liquid passes directly through small openings in the torus (Fengel 1972, Nicholas and Siau 1973). These pathways merely allow limited penetration. So the impregnation of dry wood with non-pressure methods provides only superficial protection.

4 Conclusion

To open up this bio-inspired modification method to a broad field of application, improvements of the impregnation behaviour of silicon dioxide nanosols are necessary. The flow from cell to cell as well as the penetration in the cell wall could be improved by alteration of the solvent and the decrease of the SiO_2 particle size. For evaluating the improvements a macroscopic survey of the penetration of coloured impregnation agent can provide preliminary results. However, in a scientific study using a micro analytic method more detailed information on the impregnation behaviour could be obtained.

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Fig. 1 EDX spectra of *Pinus sylvestris* L. after 20 h steeping with nanodispers silicon dioxid, black: area of a mineral filled lumen (1600 µm distance from the surface, Fig. 2 a), grey: empty lumen of a tracheid (Fig. 2 b)

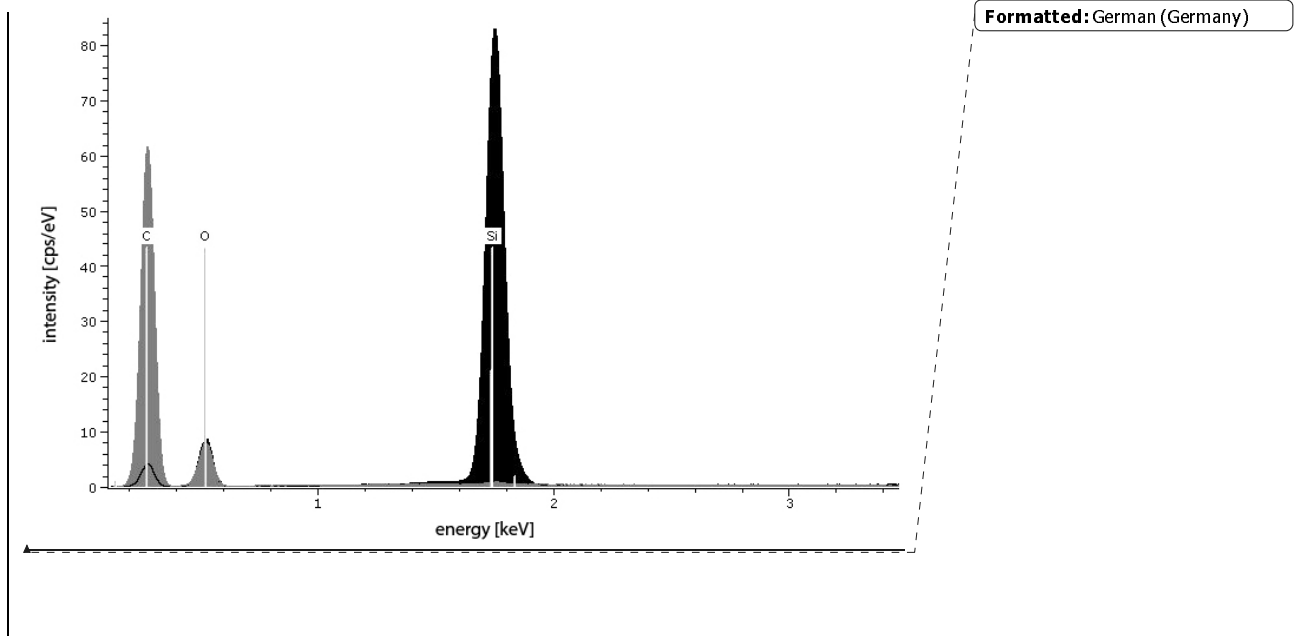
Abb. 1 EDX-Spektren von *Pinus sylvestris* L. nach 20-stündiger Tauchtränkung in nanodispersen Siliziumdioxid, schwarz: Bereich mineralischer Ablagerungen im Lumen (1600 µm entfernt von der Probenoberfläche, Abb. 2 a), grau: leeres Tracheidenlumen (Abb. 2 b)

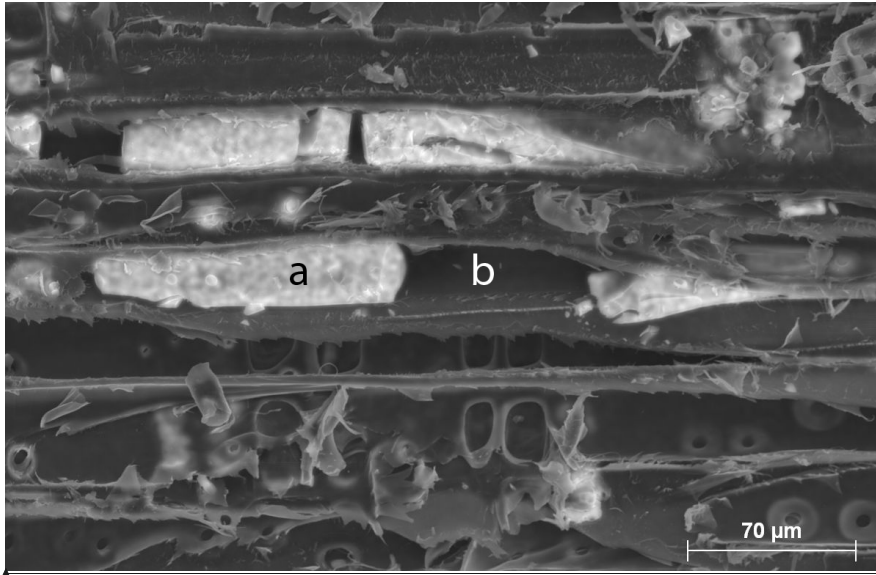
Fig. 2 *Pinus sylvestris* L. after 20 h steeping, SEM image combined with silicon element mapping: visible are fragments of the cell walls and mineral deposits (white)

Abb. 2 *Pinus sylvestris* L. nach 20-stündiger Tauchtränkung, REM-Aufnahme in Kombination mit einem Element-Mapping von Silizium: erkennbar sind Zellwandfragmente und mineralische Ablagerungen (weiß)

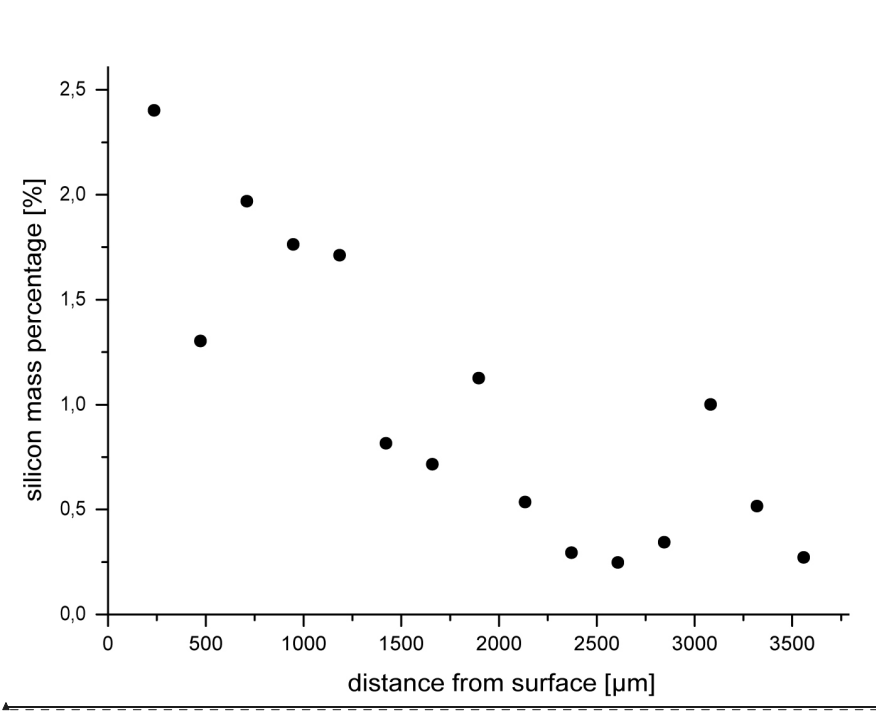
Fig. 3 Silicon content on a cutting plane (*Pinus sylvestris* L., 20 h steeping) depending on the distance from the radial/tangential sample surface

Abb. 3 Siliziumgehalt einer Schnittfläche (*Pinus sylvestris* L., 20-stündige Tauchtränkung) in Abhängigkeit von der Entfernung zur Probenoberfläche (Querschnitt)





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