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The Effect of Inorganic Preservatives in the Norway Spruce Wood on Its Wettability and Adhesion with PUR Glue

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Abstract: Recycled recovered wood, for example, from historic buildings, containing biocides, fire retardants or anti-weather paints is an attractive material for manufacturing composite wood panels which can be used for decoration as well as load-bearing walls with a typical patina. This paper investigates the effect of four inorganic wood preservatives—$CuSO_4{\cdot}5H_2O$, $ZnCl_2$, H_3BO_3 and $(NH_4)_2SO_4$—commonly used in the past, with the focus on their effect on the quality of wood bonding. The milled surfaces of Norway spruce (*Picea abies* Karst L.) wood were treated with 0.5, 1 and 2% aqueous solutions of these preservatives. The effect of preservatives in spruce wood was evaluated: (1) by its wettability with the drops of redistilled water, measuring the contact angles; (2) by the shear strength of the "spruce wood—polyurethane (PUR) Kestopur 1030 glue" interphases according to the standard EN 205; (3) by microscopic analysis of the "wood—PUR" interphases. The wettability of spruce wood worsened when using $ZnCl_2$, by a maximum of 28.2%, but on the contrary, it improved due to other preservatives mainly by using $(NH_4)_2SO_4$, at a maximum of 22.9%. In general, the shear strength of glued joints "wood—PUR" continually decreased with higher concentrations of all the preservatives. The most significant decrease of adhesion "wood—PUR", by 19.8% from 10.66 MPa to 8.55 MPa, was caused by 2% $ZnCl_2$ used for the treatment of both spruce wood specimens in interphase with the PUR glue. On the contrary, the less significant decrease of adhesion "wood—PUR", by 2.5%, was caused by 0.5% $(NH_4)_2SO_4$ applied only on one surface of the two inter-bonded spruce wood specimens. The effects of preservatives on the wood wettability and its adhesion with PUR glue were partly confirmed by microscopic analysis.

Keywords: Norway spruce wood; inorganic preservatives; wettability; adhesion strength; scanning electron microscopy

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1. Introduction

Bonding of wood is a standard technology for manufacturing construction parts used in structural engineering, as well as in the manufacture of furniture, sports equipment, musical instruments, or decorations [1]. Glued joints in wood products must be reliable and stable also in the case of weather changes. Their strength and stability depend on many factors, especially on: (1) physicochemical characteristics of a glue, i.e., its molecular weight, viscosity, surface tension, pH-value; (2) type of wood and physicochemical properties of its surface, i.e., porosity, moisture content, surface tension, pH-value; (3) technological conditions of gluing, i.e., amount of glue, open time, pressing diagram—temperature, pressure and time and (4) curing mechanism of glue, e.g., polycondensation of phenolic resins or amino resins, polyaddition of epoxy resins, polymerization of acrylates or isocyanates, separation of water or other liquid types from polyvinylacetate dispersions, etc. [2–8].

In terms of the type of glue and wood used, the strength and the quality of the glued joints can be affected by some chemical substances—usually fungicides, insecticides, fire retardants, UV-stabilizers and hydrophobizers—applied to increase the biological, fire and weather resistance of wood products [9]. Several of these substances can enter chemical reactions with structural and accompanying wood components [10,11], which subsequently result in a decrease in the mechanical and physical properties of wood [11–15]; the strength of the glued joints in the wood products is also negatively affected [16–21]. However, the mechanical properties of impregnated wood may not always decrease, for example, as supported by the studies of Keskin, Mutlu [22] dealing with the effect of impregnating beech, oak and pine woods with boron preservatives on wood strength. The results showed that the impregnation of wood with sodium tetraborate ($Na_2B_4O_7{\cdot}10H_2O$) resulted in an increase in its bending strength, whereas more mechanical properties of wood were decreased by boric acid (H_3BO_3) and other borate types. This knowledge is in accordance with the research of Colakoglu et al. [23], Toker et al. [24], Simsek et al. [25] and Simsek, Baysala [26].

Boric acid often has a negative impact on the strength of glued joints, as was observed, for example, in laminated veneer lumbers (LVLs) manufactured from beech and pine wood veneers using phenol-formaldehyde (PF) and melamine-formaldehyde (MF) glues [27]. Similarly, the experiments conducted by Wu et al. [28] mentioned the fact that the strength of glued joints in plywood made from pine wood veneers impregnated with a 6% aqueous solution of H_3BO_3 was reduced; however, the standard value for the glued joint was still met and the fire resistance of plywood improved. The negative effect of wood impregnation with the compounds of trivalent boron—boric acid or sodium tetraborate—on a decrease in strength of glued joints can be significantly affected by the type of wood and type of polymer used as adhesive or coating [29–31].

The strength of glued joints in wood products can also be negatively affected by other chemical substances used to impregnate wood or added to glue. Qin et al. [32] found out that the strength of glued joints in the specimens from pinewood impregnated with the fungicide alkaline copper quaternary (ACQ) decreased by more than 16% when 0.1% ACQ was used. However, a further decrease in the strength of glued joints when the concentration of ACQ increased to 1% was only slight. Lim et al. [33] dealt with the effect of impregnation of pinewood with a micronized copper azole-type C (MCA-C) biocide in the amount of 1.0 kg/m^3 and 2.4 kg/m^3 to manufacture cross-laminated timber (CLT). In contrast, following the experiments, the strength of the glued joints was, in the case of the specimens, with lower MCA-C (1.0 kg/m^3) significantly lower compared to the specimens with higher MCA-C (2.4 kg/m^3). Shukla and Kamdem [34,35] did not confirm a significant negative effect of the biocides copper arsenate (CA), ACQ and MCA on the strength of glued joints in LVL beams made from pine and maple wood veneers using PF or polyvinyl-acetate (PVAc) glues.

Nowadays, the attention of practice is focused on the issue of wood waste recycling and its reuse to manufacture wood-based panels [36,37]. However, many recycled wood materials can contain various chemical components providing high durability and thus, the adhesion strength of glued joints in the manufacturing of wood-based panels can be affected in a negative way [38–40]. Piao et al. [41], when investigating the presence of the preservative, chromated copper arsenate (CCA), in removed beams made from pine wood, found that there was a decrease in the CCA content in wood beams from the surfaces to the central part as a result of partial leaching by water during long term exposure to outdoor conditions. Subsequently, the studies of Piao et al. [42,43] dealt with using the mentioned wood material to manufacture bonded beams. The strength of glued joints prepared from wood specimens with CCA was lower compared to untreated ones.

Theoretically, the strength of glued joints or adhesion strength "wood—glue" depends on many factors related to the presence of wood preservatives or other chemical additives in wood: (1) the presence of the specific type and the amount of a preservative in recycled wood; (2) technological parameters related to applying the preservative to wood in the past, e.g., impregnation pressure, time, and temperatures; (3) exposure history of recycled wood, e.g., leaching, evaporating, and changes to the chemical structure of a preservative, as these factors affected the preservative distribution across the wood. The studies of Örs et al. [44], Akyüz et al. [45] dealt with the effect of an extended time of impregnation of various wood species—coniferous as well as broad-leaved—with the preservative Imersol-Aqua on the change in the strength of glued joints when using the PVAc and PUR glues. The extended time of impregnation resulted in a decrease in the strength of glued joints because of the higher preservative quantity rate in wood.

In general, it can be stated that several chemical substances—usually wood preservatives—have a negative effect on the strength of glued joints made from new and/or recycled wood. An increase in their concentration and the extended time of impregnation of wood results in noticeable negative effects, especially when linked with a specific type of wood and amount of glue. A decrease in the strength of glued joints prepared from impregnated wood is associated with a decrease in the adhesive bonding on wood surfaces owing to (1) the presence of improper, especially hydrophobic substances on wood surfaces; (2) the lower or higher penetration rate of cell lumens filed with a chemical substance used [21,46–48].

Gluing quality of recycled wood depends also on its aging history—connected either with changes in its molecular, anatomy and geometry structure [14] and for chemically treated woods as well as with changes in the amount, distribution and composition of preservatives, coatings and other additives present in the wood. For example, weathering of untreated wood in exteriors is connected with (1) the photo-oxidation and the depolymerization of lignin and hemicellulose macromolecules present in the cell walls due to the activation energy of sun rays, and (2) the rainwater leaching the polar natural substances of wood (e.g., tannins and pectins) and polar depolymerized substances created by primary photo-oxidation of wood (e.g., phenyl-propane fragments and monosaccharides) [14]. Weathering of wood treated with preservatives is usually even more complicated because several inorganic biocides and fire retardants can create inorganic acids or bases capable of degrading wood [11,15]; some organic biocides are partly volatile or their chemical structure can be modified by UV-light [14].

The aim of the article was to assess the effect of some inorganic wood preservatives on the change in wetting the surfaces of spruce wood and the change in the strength of glued joints "spruce wood—PUR glue". Preservatives used in the past or present, to protect wood against wood decaying fungi and molds (copper sulphate $CuSO_4{\cdot}5H_2O$, zinc chloride $ZnCl_2$, and boric acid H_3BO_3), against wood destroying insects (H_3BO_3), or to eliminate the wood flammability (H_3BO_3, and ammonium sulphate ($(NH_4)_2SO_4$), were used in the experiment.

2. Materials and Methods

2.1. Wood, Inorganic Preservatives, Wood Treatment with Preservatives

The spruce wood (*Picea abies* Karst. L.) without sap-zone was used in the experiment. Specimens with the dimensions of 80 mm × 20 mm × 5 mm (longitudinal × radial × tangential), with no knots and other abnormalities or defects, were sawn from one naturally dried spruce board with dimensions of 2000 mm × 300 mm × 30 mm. The board was prepared from a 96-year-old spruce tree trunk obtained from the National Forest Centrum in Zvolen. For the shear strength test, a total of 500 specimens were used (25 set types × 10 replicates in one set type × two specimens for preparing one set; see Section 2.3). For the wettability test, a total of 15 specimens were used (five types × three replicates; see Section 2.2). For the microscopy analysis of "wood—glue" interphases, a total of 10 specimens were used; see Section 2.4). During the preparation of specimens, the surfaces of the spruce board were gradually milled in a milling machine (D630-EL, Robland, Bruges, Belgium) in order to use smooth spruce wood surfaces for testing the wettability (Section 2.2) and for preparing the glued joints by EN 205 [49] (Section 2.3). Specimens before other tests were conditioned to the moisture content of 8 ± 1%.

The milled surfaces of spruce wood were treated with four types of inorganic wood preservatives—copper sulfate $CuSO_4{\cdot}5H_2O$, zinc chloride $ZnCl_2$, boric acid H_3BO_3, ammonium sulfate $(NH_4)_2SO_4$)—used in an aqueous solution with concentrations of 0.5, 1, and 2%, i.e., similarly as were they applied in practice in the past.

Copper sulfate—blue vitriol, was as “Holtz-Balsam” used already in 1718, and later in the 19th and 20th centuries for the treatment of green wood by Boucherie technology, as well as of wood products for interiors. Today, it is not used as a stand-alone for wood protection, because of its high corrosive effect on iron and steel, discoloration of wood, and poor resistance to leaching. However, copper (II) is still applied in combinations with other biocidal and fixing compounds [50].

Zinc chloride was a fungicide recommended for wood protection in 1815. In 1956 it was used also as an insecticide for wooden arts, however, with low or no efficiency. Today, zinc (II) fungicide cations are applied to wood and wood composites in the form of nano-zinc oxide [50].

Boric acid was successfully used as a fire retardant from 1851, and as a biocide for wood protection from 1877 [50]. Later, it was combined in commercial biocides with chromium and copper compounds with the aim of its fixation against leaching. Today, fixation of trivalent boron in wood against water leaching is secured by colloid silicones, animal proteins, or zinc sulfate creating insoluble zinc metaborate.

Ammonium sulfate is still one of the most effective fire retarders used for the protection of wood structures and various cellulose materials, which can be fixed with wood components and used in a humid environment [51].

The double coating process at the atmospheric pressure and a temperature of 20 °C ± 2 °C was performed on the milled surfaces of spruce wood specimens (80 mm × 20 mm), with the application rate of the preservative solution 2 × 120 ± 10 g/m^2. The coating was conducted using pipettes and brushes—i.e., first, the exact volume of drops of a preservative was applied on the milled surface using a pipette, secondly, drops were equally spread on the milled surface of the specimen. The second coating was carried out after 24-h of air conditioning of the specimen.

2.2. Wettability of Spruce Wood Specimens Treated with Inorganic Preservatives

The strength of the formed glued joints is significantly affected by the wettability of the wood surfaces [52], and therefore, this characteristic was analyzed in the experiment as well. The spruce wood specimens treated only with the highest 2% concentration of aqueous solutions of individual wood preservatives were used to test the wettability.

The wettability of spruce wood surfaces was determined by the contact angle sessile drop measurement method proposed by Liptáková, Kúdela [53]. It was associated with determining the “initial” and “equilibrium” contact angles of the redistilled water drop with a volume of 0.0018 mL at its soaking into the wood substrate. For measurements a goniometer Krüss DSA30 Standard (Krüss, Hamburg, Germany) was used. The time history of the water drop shape, from the first contact with the wood surface up to the complete soaking into the wood, was recorded with a camera—setting the scanning frequency in accordance with the wetting interval. The “initial” contact angle θ_0 was evaluated at the beginning of the wetting process, meaning the moment of the first contact between the drop of water and the wood substrate. The “equilibrium” contact angle θ_e was designed in the time moment when the acceding contact angle of the water drop changed into the receding contact angle. The time of θ_e determination was influenced by the type of inorganic preservative (from 100 s in presence of ammonium sulfate up to 168 s in presence of boric acid); however, the effect of different wood densities under the drops could not be ruled out.

2.3. PUR Glue, Preparation and Shear Strength of Glued Joints in the Control and Test Sets

One-component PUR Kestopur 1030 glue (Kiilto, Tampere, Finland) with the following parameters: viscosity 7000 mPa·s at a temperature of 20 °C, density of 1200 kg/m^3, open time of 30 min, and pressing time of 90–120 min, was used in an experiment.

Two specimens of spruce wood were bonded to create control or test sets according to the standard EN 205 [49] with a contact area of 10 mm × 20 mm (Figure 1). A control set was prepared from two untreated specimens. The first group of test sets consisted of one specimen treated with a preservative and one untreated specimen. The second group of test sets consisted of two specimens treated with the same preservative type of an identical concentration. PUR glue in an amount of 120 g ± 10 g/m^2 was applied on the contact areas of both bonded specimens of spruce wood. After bonding, the control and test sets were pressed with 1.2 MPa under standard conditions at a temperature of 20 °C ± 2 °C and relative air humidity of 65 ± 5% for 7 days.

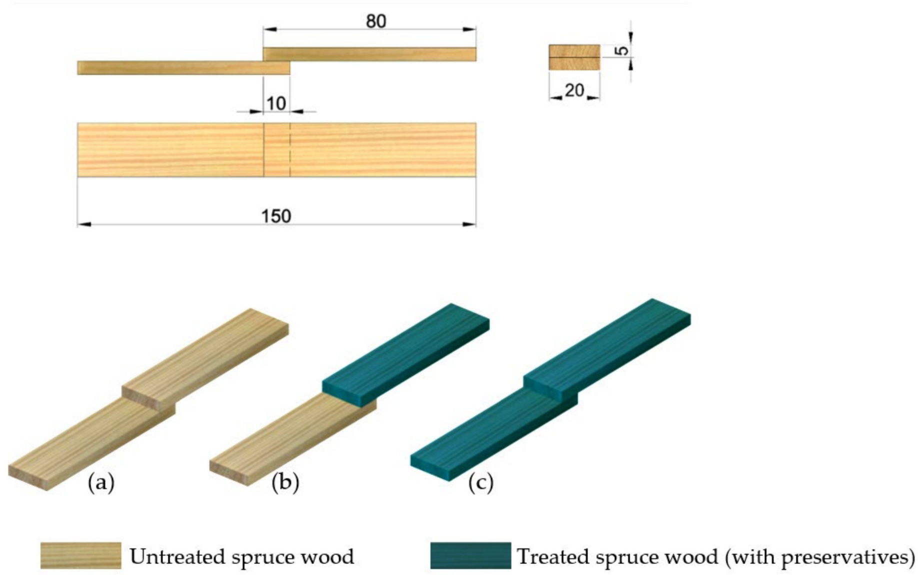

Figure 1. Dimensions of spruce wood specimens used for preparation of the control and test sets according to the standard EN 205 [49]. Dimensions are in mm. Composition of the sets is analogous with the sets prepared from themmally treated spruce woods [54]. Notes: (**a**) Control set, (**b**) First group of test set (Treated spruce and Untreated spruce), (**c**) Second group of test set (Treated spruce and Treated spruce).

The shear strength of glued joints in control and test sets (Figure 1) was tested with a LabTech 4.050 device (LaborTech s.r.o., Opava, Czech Republic), at the regular speed of loading of 50 mm/s up to the failure of the glued joints.

2.4. Microscopic Analysis of "Wood—PUR" Interphases

Microscopic analysis of the "spruce wood—PUR glue" interphases was performed on 6 mm × 5 mm × 5 mm micro-plates (longitudinal × radial × tangential), which were made successively by sawing from glued sets 80 mm × 20 mm × 10 mm (longitudinal × radial × tangential) (Figure 2). The glued sets of each type were prepared from two reference spruce specimens or from two spruce specimens treated with the highest 2% concentration of the inorganic preservative. Before microscopic analysis, the cross-sections of the micro-plates were cut with a razor blade to achieve their total smooth surface. The micro-plates were then coated with gold using a high vacuum in a VEB Hochvakuum device (Dresden, Germany) and the phase interfaces were analyzed with a Tescan Vega electron microscope (Tescan, Brno, Czech Republic) [55,56].

2.5. Statistical Analyses

The evaluations of the measured data (arithmetic means and standard deviations) and processing of the linear correlations between the preservative concentration and shear strength of glued joints were performed by the Microsoft Excel (Version 2010; Microsoft corporation, Redmond, WA, USA). The statistical software STATISTICA 12 (StatSoft Inc., Tulsa, OK, USA) was used to evaluate the Duncan tests of the contact angles, as well as the shear strength values, in comparison to reference replicates.

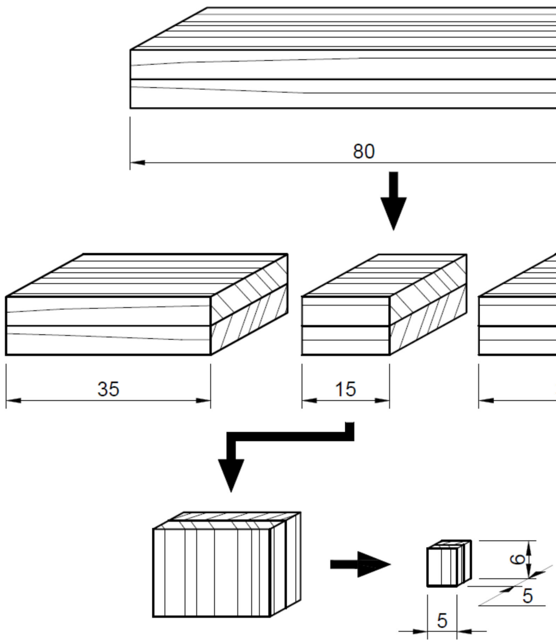

Figure 2. Preparation of the micro-plate (6 mm × 5 mm × 5 mm) for microscopic analysis of the "wood—PUR" interphase.

3. Results and Discussion

3.1. Wettability of Spruce Wood Effected by Inorganic Preservatives

The wettability of the spruce wood specimens treated with the 2% aqueous solutions of inorganic preservatives was evaluated by measuring the contact angles of the drops of redistilled water on their surface two times, i.e., θ_0—initial contact angle, and θ_e—equilibrium contact angle (Table 1). The specimens treated with $ZnCl_2$ showed a larger initial contact angle θ_0 by 28.2% than the control untreated specimens, while on the contrary, in the specimens treated with $(NH_4)_2SO_4$, the contact angle θ_0 was smaller by 22.9%. The significant differences in the initial contact angle θ_0 of the specimens ranged from 57.96° (at using $(NH_4)_2SO_4$)) to 96.43° (at using $ZnCl_2$), i.e., the difference in θ_0 was as much as 38.47°.

Table 1. Wettability of spruce wood surfaces treated with 2% inorganic wood preservatives—characterized by the θ_0 "initial contact angle" and the θ_e "equilibrium contact angle".

Spruce Wood Treated with 2% Inorganic Preservative	Contact Angle (°)	
	θ_0	θ_e
Without preservative	75.20 (8.03)	39.25 (7.58)
$CuSO_4 \cdot 5H_2O$	71.05 (9.61) d	37.32 (7.86) d
$ZnCl_2$	96.43 (9.21) a	46.45 (5.70) b
H_3BO_3	62.54 (5.98) a	40.06 (5.06) d
$(NH_4)_2SO_4$	57.96 (5.47) a	36.14 (9.61) d

Notes: Mean values are from 18 measurements (6 different measuring spots using 3 replicates). Standard deviations are in parentheses. Duncan tests are documented by the indexes (a, b, d), comparing the contact angles θ_0 and θ_e of the treated specimens to the control ones without preservative. (Significance of indexes: a—very significant change > 99.9%, b—significant change > 99%, d—insignificant change < 95%).

When determining the equilibrium contact angles θ_e, no more evident effects of individual preservatives were observed, whereby the highest value, even 18.3% higher than in the case of untreated spruce wood showed that in the wood treated with $ZnCl_2$, the angle θ_e increased from 39.25° to 46.45°. The maximal difference of an angle θ_e, i.e., between the highest value (in presence of $ZnCl_2$) and the lowest value (in presence of $(NH_4)_2SO_4$), was 10.31°.

Lower values of contact angles indicate improved wettability and better glue penetration into the wood structure [57]. Following, the results of the Duncan tests can conclude that the wood wettability was not significantly affected only by $CuSO_4 \cdot 5H_2O$. It was significantly and most apparently decreased by zinc chloride; however, such treated wood retained good wettability with polar water when θ_e did not exceed 47° (Table 1). This result also indicates, that due to the presence of $ZnCl_2$ in the wood, the strength of glued joints could be decreased (see Section 3.2). On the contrary, the wood wettability was significantly improved with ammonium sulfate (Table 1), and subsequently, the strength of the glued joints should not be more evidently worsened (see Section 3.2). Spruce wood treated with H_3BO_3 had an "initial" contact angle about 16.8% lower than the reference, and an "equilibrium" contact angle already higher about 2.1% than the reference wood. From this result, it can be concluded that H_3BO_3 with a prolonged time of application, had a worsened degree of wettability of wood surfaces, similar to findings by Aydin and Colakoglu [58]. The results of other studies dealing with the wettability of wood impregnated with various preservatives also showed certain changes in contact angles, whereby improving or eliminating the surface wettability depends upon the type of chemical substance used [59–61].

3.2. Strength of Joints "Spruce Wood—PUR Glue" Effected by Inorganic Preservatives

The greatest strength of the glued joints of 10.66 MPa was observed in the case of the control set consisting of two specimens of spruce wood not treated with chemical substances. Lower adhesive strength ranging between 10.49 and 8.55 MPa was observed in the first group of test sets in which one specimen was treated with a preservative and the second specimen was not treated with a preservative; the strength decreased by 1.59% to 19.79% (Table 2). A considerable decrease in the adhesive strength between 10.39 and 8.44 MPa was determined in the second group of test sets consisting of two specimens treated with a given preservative of an identical concentration when the strength decreased by 2.53% to 20.83% (Table 2).

Table 2. Shear strength of joints in the reference (control) set and the test sets—formed from two spruce wood specimens (untreated or treated with inorganic preservative) and PUR glue.

	Shear Strength (MPa)				
Preservative Concentration "c" (%)	**$CuSO_4 \cdot 5H_2O$**	**$ZnCl_2$**	**H_3BO_3**	**$(NH_4)_2SO_4$**	**Without Preservative**
Reference group of test set (Untreated spruce and Untreated spruce)					
0	-	-	-	-	10.66 (1.24)
First group of test sets (Treated spruce and Untreated spruce)					
0.5	9.93 (0.93) d	9.97 (0.72) d	10.49 (1.25) d	10.37 (0.68) d	-
1	9.63 (0.64) c	9.24 (0.88) b	9.56 (1.06) c	10.17 (1.04) d	-
2	9.56 (0.72) c	8.55 (0.62) a	8.80 (0.90) a	9.35 (1.06) c	-
Second group of test sets (Treated spruce and Treated spruce)					
0.5	9.36 (0.78) b	9.65 (0.85) c	9.58 (1.15) b	10.39 (1.25) d	-
1	9.04 (1.07) b	8.69 (0.55) a	9.23 (0.63) b	9.84 (1.24) d	-
2	8.78 (0.96) a	8.44 (0.68) a	8.68 (1.22) a	8.83 (1.49) b	-

Notes: Mean values are from 10 measurements. Standard deviations are in parentheses. Duncan tests are documented by the indexes (a, b, c, d), evaluating the shear strength of joint values of the first and second groups of the test sets formed from two specimens "one or both treated with preservative" in relation to the reference—control set having the strength value of 10.66 MPa (Significance of indexes: a—very significant decrease > 99.9%, b—significant decrease > 99%, c—less significant decrease > 95%, d—insignificant decrease < 95%).

With a gradual increase in the concentration of all wood preservatives used (c = 0 up to 2%), there was an evident decrease in the strength of glued joints (σ), as it was also proven with statistically significant linear dependencies "σ = /a × c/ + b", with the negative "a" values and the high coefficients of determination R^2 from 0.85 to 0.999 (Figures 3 and 4).

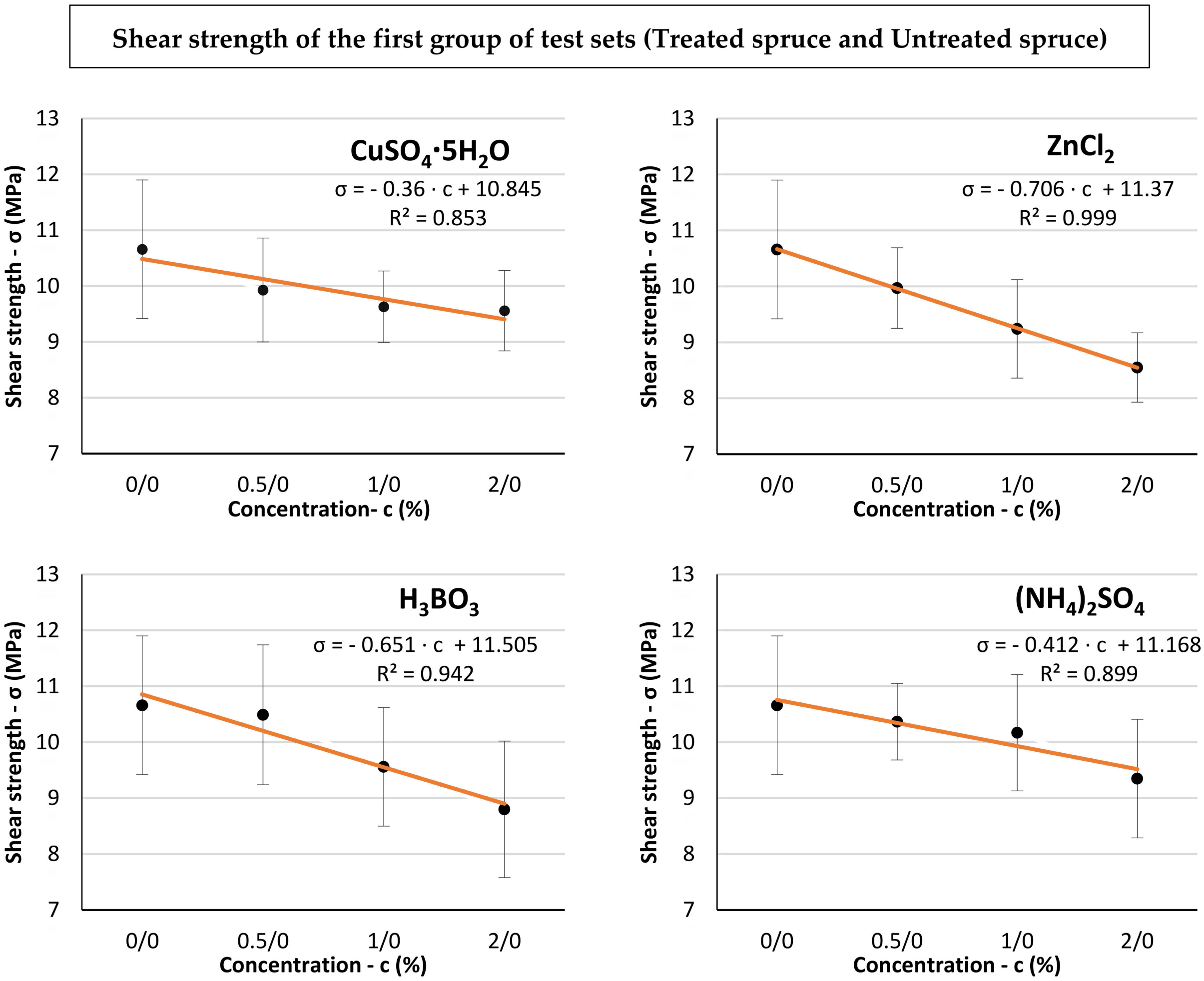

Figure 3. Linear dependencies between the shear strength of glued joints (σ) and the concentration of a preservative (c) in the first group of test sets "Treated spruce and Untreated spruce".

When evaluating the first group of test sets (created by bonding one chemically treated and one untreated spruce wood specimen), following the Duncan test, it was found that there was no significant effect of the 0.5% concentration of any of the four used wood preservatives on the strength of the glued joints. On the contrary, a 2% concentration of preservatives resulted in an apparent decrease in the shear strength of the glued joints at a level of significance of 95% to as much as 99.9% (Table 2). In the first group of test sets, the most evident decrease in the strength of glued joints by 19.79% or 17.45% was observed in the case of test sets in which a specimen treated with a 2% concentration of $ZnCl_2$ or H_3BO_3 was present.

The Duncan test for the second group of test sets (created by bonding two chemically treated spruce wood specimens) proved that the inorganic preservatives localized between the layers of PUR glue in both specimens have a statistically significant effect on a decrease in the strength of glued joints—more significantly in comparison to the first group of test sets (Table 2). Specifically, in the case of a 2% concentration of preservatives, there was a decrease in the strength of glued joints when using biocides $CuSO_4·5H_2O$, $ZnCl_2$ and H_3BO_3 at a level of significance of 99.9%; in the case of fire retardant $(NH_4)_2SO_4$ the decrease was at a level of significance of 99%. A negative effect of this fire retardant on the strength of the glued joint was apparently more modest compared to biocides, and also in the case of the use of lower 0.5 and 1% concentrations. The test sets treated with 2% $ZnCl_2$

showed the most significant decrease in the strength of the glued joint to 8.44 MPa, i.e., by 20.83%. The strength of the glued joint under 9 MPa was shown for all other test sets consisting of two spruce wood specimens treated with 2% solutions of $CuSO_4{\cdot}5H_2O$ (by 17.64%), H_3BO_3 (by 18.57%), and $(NH_4)_2SO_4$ (by 17.17%).

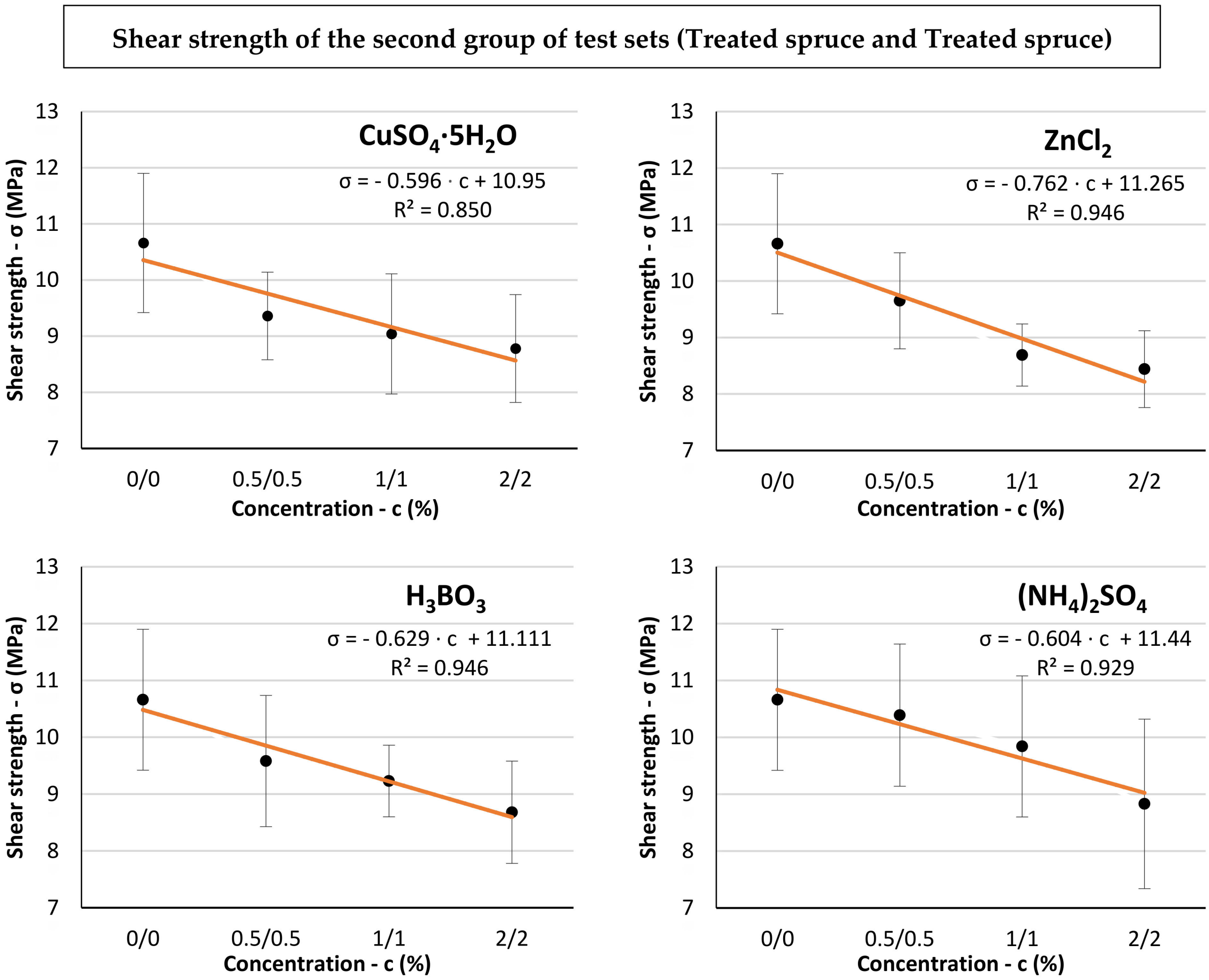

Figure 4. Linear dependencies between the shear strength of glued joints (σ) and the concentration of a preservative (c) in the second group of test sets "Treated spruce and Treated spruce".

In general, it can be stated that the quality of adhesion joints between PUR glue and spruce wood specimens was negatively influenced by the primary treatment of specimens with inorganic preservatives $CuSO_4{\cdot}5H_2O$, $ZnCl_2$, H_3BO_3, and $(NH_4)_2SO_4$. The minimum strength values given by the standard EN 204 [62] (minimum value 10 MPa) were not met in the case of most test sets prepared from the chemically treated specimens (Figures 3 and 4). Similar results were also mentioned by Atar et al. [63] and Özçifçi [30], whereby a decrease in the strength of glued joints was explained by a reduced penetration of an adhesive into the lumens and intercellular spaces in wood and reduced adhesion. Due to impregnating the wood with preservatives with a low pH-value, the lignin-saccharide matrix in wood can degrade and individual wood cells can be defibrated which results in the loss of wood mechanical properties [64,65]. Subsequently, a decrease in the mechanical properties of wood can affect the strength of glued joints. It was stated by Oezcifci, Okçu [66]. In our study, the most significant decrease in the strength of glued joints, by 17% to as much as 21%, occurred in the case when both specimens of spruce wood were treated with the highest 2% concentration of inorganic preservatives used.

3.3. Microscopic Characteristics of "Wood—PUR" Interphases Effected by Inorganic Preservatives

Microscopic analyses of the "spruce wood—PUR glue" phase interfaces are documented in Figure 5. The inorganic preservatives present on the surface of the spruce wood caused certain anomalies in the anatomical structure of the phase interfaces.

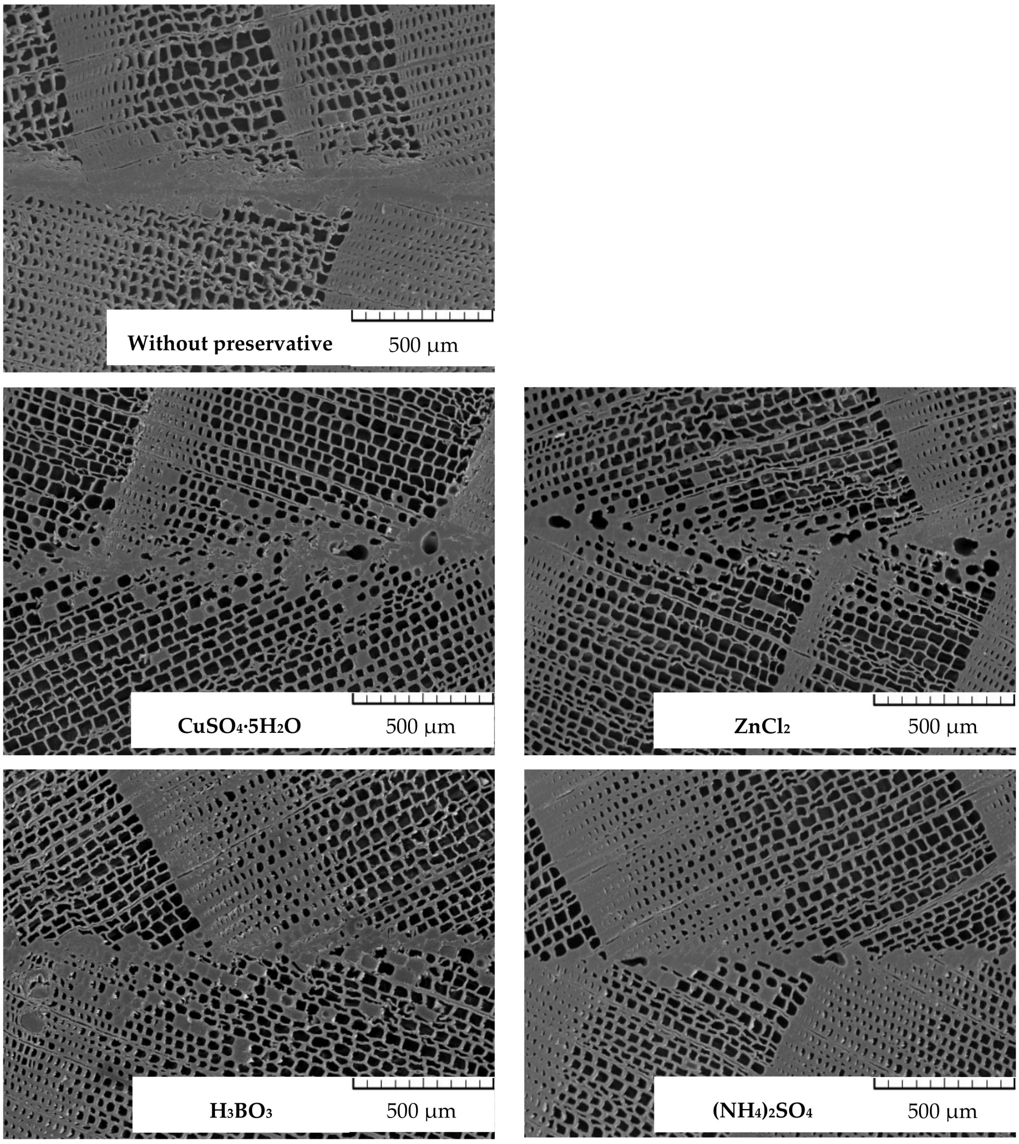

Figure 5. Microscopic analyzes of the "spruce wood—PUR glue" phase interfaces—without or with presence of inorganic preservative in the wood surface.

The glue line of the reference micro-plates was continuous, its thickness was approximately from 30 to 60 µm, with only a minimal proportion of air bubbles in the cured PUR glue, and only a weak penetration of PUR glue into the lumens of tracheids in direct contact with the glued joint (Figure 5).

The glued joints of the test micro-plates, i.e., in which the surfaces of spruce wood at the "wood—PUR" phase interface contained individual types of inorganic preservatives, were also continuous, but their thickness was usually smaller and less uniform than in the reference micro-plates. Air bubbles were relatively more common in PUR glue joints of the test micro-plates, especially when spruce wood was pretreated with $ZnCl_2$ (Figure 5). The penetration of PUR glue into the lumens of tracheids of the test micro-plates containing inorganic preservatives was usually greater than that of the reference micro-plates. The PUR glue penetrated most significantly into the lumens of specimens treated with H_3BO_3—

occasionally up to a depth of 490 μm from the glue layer (Figure 5). Because PUR glues have a lower polarity and higher viscosity, their penetration into the wood structure is usually relatively small [67]. The H_3BO_3 partially increased the initial wettability of the spruce wood surfaces (Table 1), and this phenomenon could subsequently cause an increase in the penetration of PUR glue into its structure. Due to the relatively higher and less regular penetration of PUR glue into the structure of spruce wood containing H_3BO_3, the air bubbles in the layer of PUR glue could also be formed faster and the variability of the glued joint thickness increased—with the possibility to ultimately create poorly glued joints with a lower strength (Table 2).

3.4. *Strength of Glue Joints in Sets Versus Wood Wettability*

When comparing the results of the wood wettability (evaluated by contact angles in the "initial" state θ_0 and in the "equilibrium" state θ_e) and the strength of glued joints (evaluated separately for the first group of test sets "Treated spruce and Untreated spruce" and the second group of test sets "Treated spruce and Treated spruce"), no evident links occurred between strength and wettability (Figure 6). This result can also be seen from the highest adhesion strength of the control set created from two untreated specimens of spruce wood and PUR glue (Table 2). On the contrary, the untreated spruce wood specimens did not show always the highest wettability, i.e., they did not have always the lowest contact angles θ_0 and θ_e—see a significant decrease of θ_0 in presence of H_3BO_3 and $(NH_4)_2SO_4$ (Table 1, Figure 6).

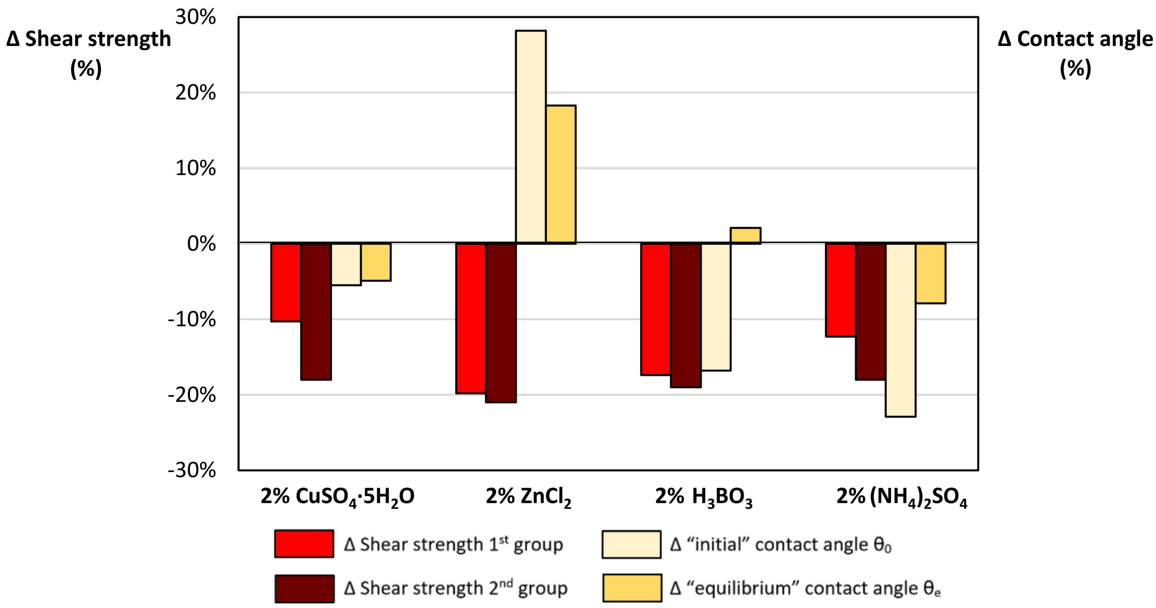

Figure 6. Comparison of the percentage change in the strength of glued joints (Δσ) for the first and second group of test sets and the percentage changes in the contact angles (Δ°) for the spruce wood specimens treated with the 2% solutions of inorganic preservatives.

The change in the contact angles of spruce wood specimens could be caused by changes in the chemical composition of the surface zone of the wood due to the selected preservatives and the filling of the lumens and intercellular spaces of the surface zone of the wood with them. Besides these factors, the wettability of the wood surface is significantly affected by its roughness [68–70]. The roughness of wood can be changed by using various chemical substances, which also can cause degradation of the lignin-polysaccharide structure of wood cells. Thus, due to the changes in roughness and molecular structure of wood, subsequently, the wettability of wood surfaces can be changed as well. Simultaneously it is necessary to mention the fact that the contact angle values can be affected also by the heterogeneous structure and different densities of wood in various parts of a specimen, in connection with the specific width of growth rings and the portion of earlywood and latewood [71,72].

From microscopic analyses of the "wood—PUR" interphases (Figure 5), it can be concluded that the reduced strength of the glued joints of test sets created from specimens containing inorganic preservatives was mainly caused by changes in the penetration of the PUR glue into the wood structure and the creation of thinner joint layers. This could be due to the irregular penetration of the PUR glue into the wood structure pretreated with preservatives and the unevenness of the glued joint as a result of the formation of a larger number of air bubbles in the cured PUR glue layer.

4. Conclusions

- The shear strength of joints, created from PUR glue and Norway spruce wood, continually decreased with increasing concentrations (0.5% to 2%) of inorganic preservatives ($CuSO_4 \cdot 5H_2O$, $ZnCl_2$, H_3BO_3, and $(NH_4)_2SO_4$) in spruce wood, and more apparently for test sets prepared from both chemically treated specimens.
- The shear strength of joints in presence of inorganic preservatives usually did not meet the minimum strength of 10 MPa by the standard EN 204, at which the lowest shear strength was achieved for the second test set when both spruce specimens were pretreated with 2% zinc chloride, while the slight losses in adhesion caused ammonium sulfate.
- Comparing the contact angles of spruce wood pretreated with preservatives and the shear strength of glued joints, only slight connections appeared between these properties, because the spruce wood specimens with lower contact angles and better wettability (using $(NH_4)_2SO_4$, but also $CuSO_4 \cdot 5H_2O$ and H_3BO_3) did not always form the test sets with a higher shear strength compared to the test sets from specimens with the worst wettability (using $ZnCl_2$).

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