

**Treatment of Waterlogged Wood Using Hydrolyzable, Multi-Functional Alkoxysilane Polymers**

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*Abstract - In this study, methyltrimethoxysilane (MTMS), a hydrolyzable, multi-functional alkoxysilane polymer, and Q9-1315, a MTMS alkoxysilane polymer diluted with methanol, were used in conjunction with acetone dehydration to conserve waterlogged wood. Three groups of wood were used for study. Waterlogged tongue depressors (Group 1 samples) were treated using acetone dehydration followed by immersion in MTMS. After preservation using the acetone / MTMS displacement method, images obtained using Environmental Scanning Electron. Magnified images of the treated wood were compared to similar images of non-waterlogged samples of the same wood samples, providing data on the ability of the polymer to preserve the micro-structure of the wood. A waterlogged plank from a 17th-century architectural feature was divided into four sections to form Group 2 samples. Two sections of this plank were preserved using MTMS and Q9-1315. The remaining pieces of wood were used to calculate the water content of the wood. Group 3 samples consisted of 18 waterlogged treenails extracted from the frames of La Salle's vessel, La Belle, which sank off the coast of Texas in 1686. Eight of the Group 3 wood was preserved using MTMS immersion after dehydration in acetone. Eight other Group 3 pieces of wood were treated using acetone dehydration followed by immersion in Q9-1315. Nuclear magnetic resonance spectra of samples from these sample groups indicate that when waterlogged timbers are immersed in MTMS, resins are formed through self-condensation. These polymers are sufficient to preserve the diagnostic attributes of wooden artifacts. Waterlogged wood treated in the Q9-1315 solution shrank more than MTMS-treated wood, with appreciable warping and weight loss, indicating that this solution does not contain sufficient alkoxysilane polymers to preserve badly waterlogged wood.*

**Background and Introduction**

In his address to the Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa, 1981, Colin Pearson outlined the history, structure and evolution of the ICOM Committee for Conservation Working Groups. As outlined in his historical perspective of the Waterlogged Wood Working Group, he noted that a list of 14 areas of research were outlined at the Zagreb 1978 conference. [1] Included in the program of activities were the use of organic polymers, use of tetraethyl ortho silicate, irradiation techniques and acetone / rosin techniques. In spite of the rather broad perspective

outlined for research, however, most research has focused on preservation of waterlogged wood using PEG, freeze-drying strategies and sucrose. But are many accepted treatment strategies truly reversible? Research in the fields of material scientists and botany suggest not. Irradiation, freeze-drying, acetone / rosin and even the use of PEG have all proven to be less than totally reversible. The Zagreb list however is an excellent indicator that the science of waterlogged wood conservation has advanced, and that wood conservators have been industrious in their pursuit of better treatment strategies.

In just a few years, several areas of research blossomed, due to the hard work of dedicated conservators. Cliff McCawley, David Grattan and Clifford Cook advance research into the effects of PEG / freeze-drying waterlogged wood [2][3]. Per Hoffman conducted some invaluable studies pointing to the fact that wood structures do not degrade at uniform rates, leading to his development of a highly effective, two-phase PEG treatment strategy [4]. ARC-Nucleart has advanced studies in the preservation of waterlogged wood by impregnating wood with resins, which are then hardened using radiation [5]. Alternatively, they have worked successfully in treating larger artifacts using PEG impregnation followed by freeze-drying.

Although contributions to the discipline of wood conservation continue, some of the long-term problems of waterlogged wood treatments using PEG are being realized. In his address at the Ottawa ICOM Conference, Dr. Allen Bronstein, a senior chemist at Union Carbide Company, addressed the complexities of conserving waterlogged wood and numerous factors related to the degradation of PEG [6]. During the discussion, Cliff McCawley touched on the topic of the effects of metal salts on the degradation of PEG. In retrospect, this has become a topic of great concern. In recent years, the problem of PEG decomposition, the formation of chemical complexes including aldehydes, ferrous, ferric and cupric salts has become a pressing issue. Indeed, some of our finest examples of conserved waterlogged wood are developing potential problems due to our inability to control oxidation, miscibility and the chemical reactivity of PEG with oxides and compounds found naturally in waterlogged timbers. Perhaps Bronstein was correct in stating that 'PEG treatments may not be the perfect solution to difficult problems.' Indeed, there are no ideal treatment strategies for the preservation of organic artifacts.

Treatment of Waterlogged Wood Using Hydrolyzable, Multi-Functional Alkoxysilane Polymers is an experiment to study the use of trifunctional polyols to both stabilize and maintain the physical attributes of waterlogged wood samples, as suggested by Bronstein. Instead of just creating a 'very hard and durable finish,' as he suggested, experimentation is directed at also impregnating a variety of waterlogged wood samples with a self-condensing polymer, to form a stable resin throughout the pore structure of the wood. There are some benefits to this type of resin-forming chemical reaction. Displacement of water with the chemicals used for these experiments do not appear to distress waterlogged wood, resulting in thorough impregnation of the wood. Using trace amounts of water, the alkoxysilane appears to condense without causing distortion of cell walls or appreciable shrinkage. Post-treatment microscopic and NMR evaluation of the treated wood indicates complex resins are formed throughout the wood. These resins are bound to the cell wall structures of the wood. Visually, the wood is aesthetically pleasing

without the somewhat waxy and dark coloration associated with PEG-treated wood. Most importantly, resins formed appear to prevent chemical reactivity due to the presence of ferric oxides in the wood. Considerably more research is needed to verify this observation.

At present, the alkoxysilane polymer methyltrimethoxysilane (MTMS) is expensive and therefore, only practical for use in the preservation of small artifacts. Industrial grade alkoxysilane polymers however, are available at somewhat lower prices. These products make the cost of treatment with polymers more affordable. The broad scope of application for archaeological conservation using polymers has not yet been explored since the aim of our initial research has been to evaluate the effectiveness of the resin-forming mechanism to preserve waterlogged wood. The use of functional polymers for the preservation of waterlogged wood may hold many advantages not shared by less functional polymers such as PEG. Because PEG remains partially miscible once integrated into the cell structure of wood, long-term chemical reactivity is an issue. Recent findings indicate that the slow degradation of PEG combined with a host of oxides and other deleterious materials may cause rapid degradation of treated wood. In contrast, polymerization of functional polymers produces a more stable and less chemically reactive bulking agent. Polymerization is a natural process. Chemically, the use of functional polymers for the preservation of wood is worth serious consideration since many of the components of wood are natural polymers. Lignin is a natural polymer comprised of coniferyl alcohols and other compounds. Cellulose, the most abundant of all organic compounds is a linear polymer.

Notably, wood treatment strategies outlined in this experiment are not reversible. This however may hold the answer to reducing or eliminating problems of chemical reactivity. When any bulking agent is introduced into the cell structure of wood, some degree of chemical bonding and potential polymerization process takes place. Accordingly, the stable nature of materials being introduced into waterlogged wood and other organic materials should be of concern. Compared to hydrolyzable, multi-functional alkoxysilane polymers, PEG is chemically reactive and, therefore, potentially more unpredictable. As prescribed by the ICOM Waterlogged Wood Working Group activities committee in 1978, experimentation using alkoxysilane polymers and other organic polymers is an essential phase of development in the discipline of organic artifact conservation.

Data for pre and post treatment dimensions of wood samples is noted as absolute values instead of anti-shrink efficiency (ASE) values. ASE expresses a percentage of the shrinkage of the untreated wood that has been suppressed by the stabilizing treatment. Accordingly, a portion of each samples must be left untreated ( $\beta_0$ ) and allowed to shrink or comparison against a treated sample ( $\beta_i$ ). Since all samples of wood were treated as whole objects, no untreated sections of wood were available to create ASE computations. The general equation for computing ASE is:

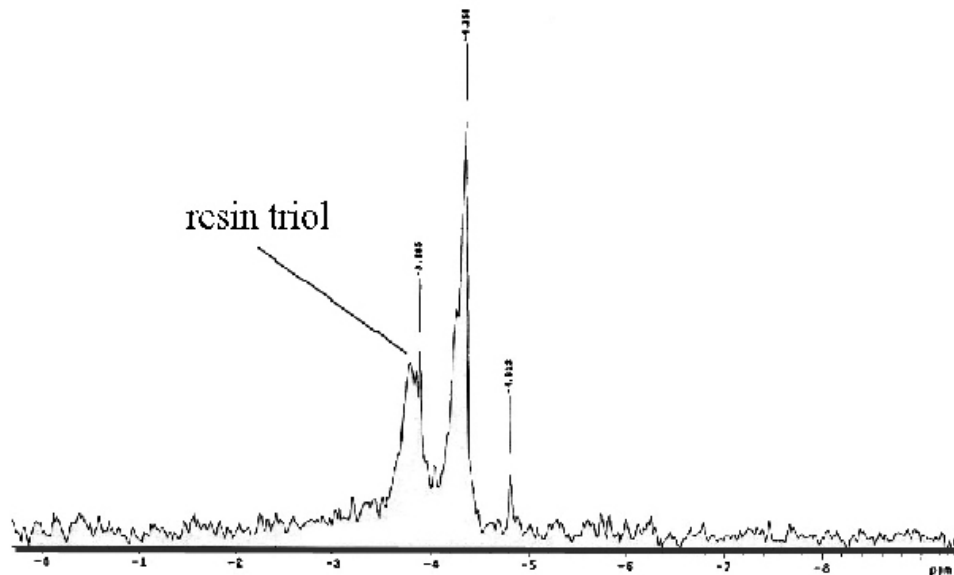
$$ASE = \frac{\beta_0 - \beta_i}{\beta_0} \times 100 (\%)$$

While expressing data as percentage changes in length, width and thickness is more cumbersome, the reader is presented with individual computations that may be helpful for replication of this experiment or for comparative analysis.

Three groups of waterlogged wood samples were utilized for this experiment. Group 1 wood samples consisted of waterlogged tongue depressors that had been immersed in tap water and sealed in glass jars for eight years. Group 2 waterlogged wood samples were sectioned from a large piece of archaeological wood from marine excavations of the 1692 provenance of Port Royal, Jamaica. Group 3 wood consisted of 18 treenails (wooden dowels) that had been extracted from the frames and large timbers of a 17th-century shipwreck. Each of these hand carved lengths of wood were similar in circumference (26.66 mm average) and, for the most part, similar in length (128.70 mm average). Many of their surfaces bore diagnostic tool marks.

Nuclear magnetic resonance (NMR) spectra of waterlogged wood treated with alkoxy silane polymers indicates that in an aqueous environment, MTMS hydrolyzes to form a triol. This triol self-condenses to form a range of polymers in the  $^{29}\text{Si}$  spectra. The primary silicon has a methyl group and three siloxy bonds (i.e.,  $\text{Si} - \text{O} - \text{Si}$ ). The second silicon environment has only two bonds. The third is formed to the methyl group while the fourth bond is to the hydroxy group as in the  $^1\text{H}$  spectrum (Figure 1). One goal of this experiment therefore, was to determine whether these polymers were sufficient to maintain the physical attributes, cell structure, and aesthetics of Group 1, Group 2 and Group 3 wood samples.

NMR analysis was also conducted to determine whether the waterlogged tongue depressors were sufficiently degraded to provide a valid substitute for archaeological wood in such an experiment. Spectra of the Group 1, 2 and 3 wood samples were nearly identical to spectra reported by Michael Wilson et al in 'The Degradation of Wood in Old Indian Ocean Shipwrecks.'<sup>[7]</sup> To determine the physical integrity of the Group 1 wood samples, control samples were oven-dried over a 24-hour period. In all cases, the degree of warping and shrinkage indicates that they respond similarly to waterlogged archaeological wood. Classroom conservation experimentation has shown waterlogged tongue depressors to be good indicators of the effectiveness of traditional treatment methods such as polyethylene glycol, acetone rosin and sucrose. This same type of waterlogged wood appears to work equally well as an indicator of the effectiveness of polymer preservation treatment strategies.

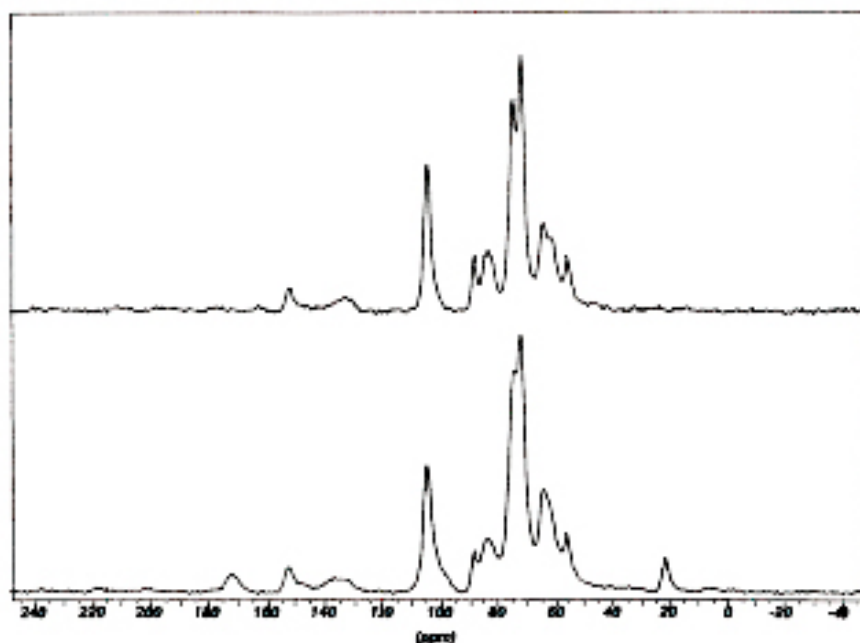


**Figure 1:**  $^1\text{H}$  spectrum of the solid polymer formed from the MTMS. It is the formation of these polymers that preserves the structure and overall shape of the artifact.

### Materials - Group 1 Waterlogged Tongue Depressors

Waterlogged tongue depressors were chosen for use in this experiment because they are easily obtained and relatively uniform in dimension, grain and color. To create a supply of waterlogged wood, thousands of white birch (*Betula papyrifera*) tongue depressors were placed into one-gallon glass jars filled with tap water. The jars were then sealed and stored in a cabinet. Hundreds of these tongue depressors, which had been immersed in tap water since June 2, 1992, were emptied into a plastic vat and rinsed in running tap water for two hours. Ten tongue depressors were selected randomly from the rinse vat and designated as air-dry samples, used to determine the average water content of the Group 1 wood. Eighteen additional Group 1 tongue depressors were randomly selected for treatment using acetone dehydration followed by acetone / MTMS displacement.

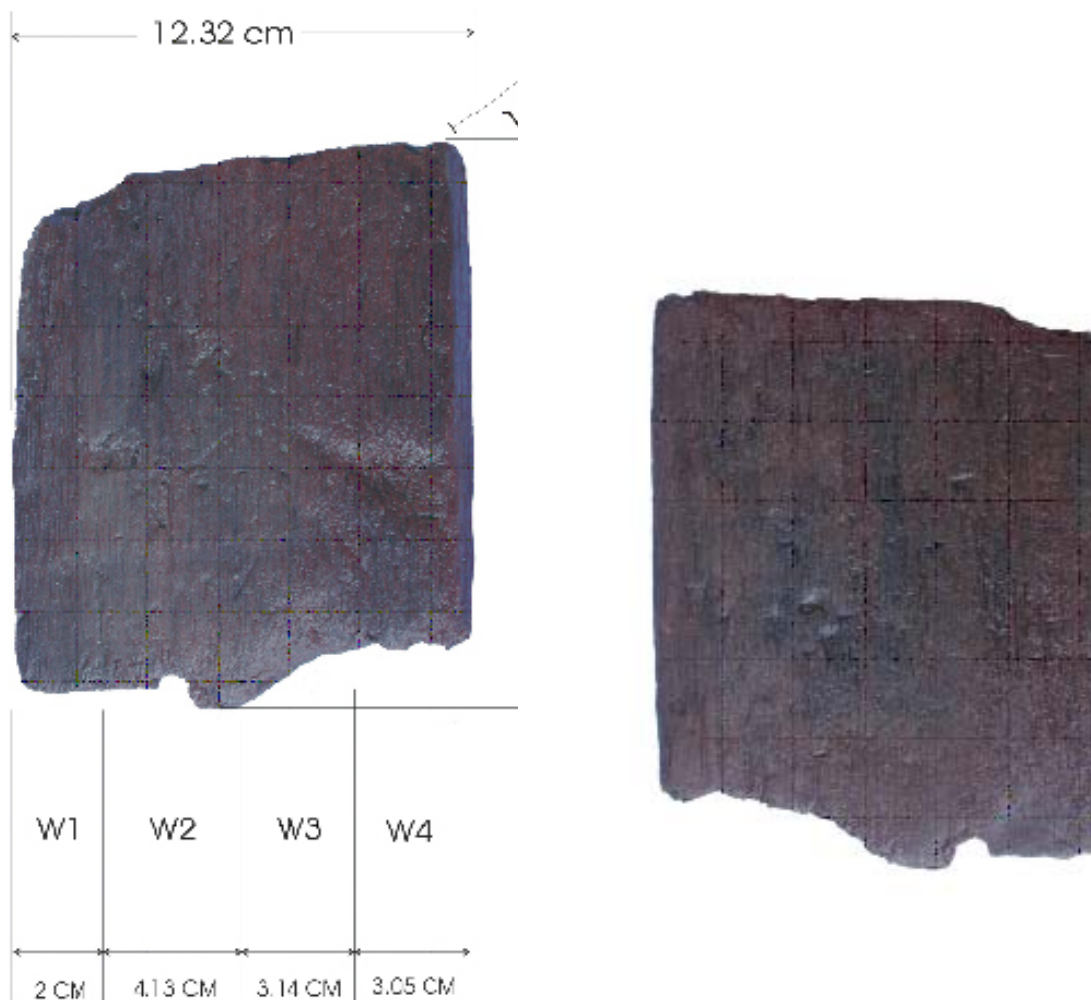
The  $^{13}\text{C}$  CP/MAS spectrum for a Group 1 sample is illustrated at the top of Figure 2. Long-term saturation in tap water has altered the chemical structure of the wood, as apparent in the loss of the acetate resonances at 22 and 174 ppm in comparison to the spectrum of a control tongue depressor that had not been waterlogged (Figure 2). The changes in these  $^{13}\text{C}$  spectra for birch tongue depressors are quite similar to those reported by Wilson et al [7] for oak from shipwrecks. The  $^{13}\text{C}$  spectral signature and macroscopic observation of extensive warping and shrinkage following air-drying suggest that these samples provide a suitable model for the analysis of waterlogged wood.



**Figure 2:**  $^{13}\text{C}$  CP/MAS spectra of an untreated, non-waterlogged control tongue depressor (bottom) and an untreated, waterlogged tongue depressor (top).

### **Materials - Group 2 Waterlogged Archaeological Wood**

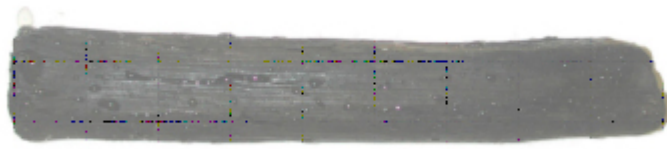
A small plank of wood recovered during archaeological excavations at the submerged site of 17th-century Port Royal, Jamaica, was selected for Group 2 wood samples. This plank has been stored in frequently changed baths of fresh water since 1989. Based on cross-section microscopic analysis, the wood has been identified as *Pinus caribaea*, commonly known as slash pine or British Honduras pitch pine. Typically, this wood has a straight fine grain that is very uniform in texture. Since excavation from the 1692 provenance at Port Royal, the plank, which measures 12.32 cm wide, 14.73 cm long and 1.87 cm thick, has been stored in fresh tap water. For this experiment, the plank was divided into four sections. Due to its waterlogged state, the wood was very fragile. Sectioning was therefore accomplished using a long scalpel blade. Figure 3 illustrates the dimensions of the Group 2 samples.



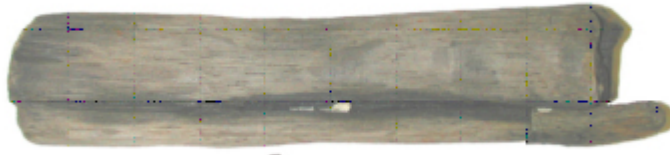
**Figure 3:** Surface characteristics, sections and dimensions of the waterlogged plank used for the Group 2 waterlogged wood samples. Top surface of the plank (left); obverse surface (right).

### **Materials - Group 3 Waterlogged Treenails**

Group 3 artifacts were treenails extracted from the timbers of a seventeenth-century shipwreck, *La Belle*. Each piece of wood was roughly carved and slightly tapered in shape. Following desalinization in freshwater baths for 24 months, 18 treenails were surface-dried with paper towels and then weighed, measured and photographed (Figures 4 and 5). Sixteen of the treenails were then placed into a series of four ethanol baths, followed by a series of four acetone baths, each lasting two weeks. Eight of the treenails were randomly picked and immersed in MTMS. Eight were immersed in Q9-1315. The remaining two treenails were air-dried for 48 hours in a vented warming oven to determine percentage water content.



**Figure 4** Waterlogged treenail before air-drying.



**Figure 5** Treenail following air-drying. Note that this treenail splintered into three sections.

### **Materials - Chemicals**

Methyltrimethoxysilane (MTMS) is a chemical monomer that reacts with water to form silane triol and methanol. The silane in turn condenses with available hydroxyl groups or other silanol monomers to form siloxane resins. The chemical formula for MTMS is  $(\text{CH}_3\text{O})_3\text{SiCH}_3$ . Typically, MTMS is a solution of 97% methyltrimethoxysilane with 2% methyl alcohol, and 1% dimethyldimethoxysilane added. The condensation product of MTMS is a resin with a molecular weight of 226. Like MTMS, Q9-1315 is generally a clear liquid. However, because of the lower percentage of MTMS and higher percentage of alcohol, evaporation during treatment is greater and there are fewer hydroxyl groups and other silanol monomers available to form resins.

The Q9-1315 solution is complex, and consists of 44% MTMS (by weight), mixed with 50% methyl alcohol, 4% isopropyl alcohol, 1% ethyl alcohol, and 1% dimethyldimethoxysilane.

Industrial-grade acetone, certified to be 99.78% free of water, was used for all dehydration processes.

### **Water Content of Group 1, 2 and 3 Wood Samples**

Percentage water content was calculated for each group of samples using the formula illustrated in Figure 6.

$$\% \text{H}_2\text{O} = \frac{\text{Weight of wet wood} - \text{Weight of oven dried wood}}{\text{Weight of oven dried wood}} \times 100$$

**Figure 6:** Formula used to calculate water content of tongue depressors and archaeological wood samples. [8]

### Group 1 Wood

Ten Group 1 waterlogged wood samples were placed in a ventilated warming oven, set at 400C, for 24 hours. The average water content of the Group 1 oven dried samples was 215.96%.

### Group 2 Wood

Following 24 hours in a vented warming oven, set at 400 C, wood section W1 weighed 4.4gm, representing a weight loss of 88.75%. In this environment, rapid dehydration was encouraged due to elevated temperatures and constant air flow. Water content was calculated to be 788.64%. Because of the uniform thickness and condition of the wood, the water content calculation for W1 was assumed to reflect the general state of degradation of the other sections of wood.

Prior to air-drying, W4, the second air dried archaeological wood sample had a mass of 104.3 gm. W4 was placed in a fume hood and allowed to air-dry for 36 hours at ambient pressure and a constant room temperature of 760F (24.40C). W4 air-dried more slowly in this lower constant temperature environment. Following drying, the sample weighed 10.3 g, representing a weight loss of 90.12%, representing 912.62% water content.

### Group 3 Samples

Two waterlogged trenails, weighing 82.1 g and 68.2 g wet weight, were allowed to air-dry in a well vented warming oven for 48 hours. After air-drying, the trenails weighed 34.48 g and 34.65 g, representing weight loss of 58% (138.11% water) and 49.2% (38.62% water) respectively.

## Treatment Methods

### Group 1 Wood

Eighteen Group 1 waterlogged tongue depressors were surface-dried with paper towels and labeled incrementally with a felt-tip pen. Length, width, thickness and weight measurements were then recorded for each sample.

The wood samples were placed in a large beaker containing one liter of fresh, industrial-grade acetone. After 24 hours, they were transferred to a second beaker containing one liter of fresh acetone and dehydrated for an additional 24 hours. After 48 hours of dehydration, the Group 1 wood was transferred into a beaker containing one liter of methyltrimethoxysilane (MTMS). The beaker was placed into a desiccator vacuum chamber where the wood was held in a reduced pressure environment of 5333.33 Pa (40 torr) for 6 hours. After 6 hours of acetone/MTMS displacement, the wood was allowed to sit in the solution at ambient pressure and room temperature for an additional 18 hours. The samples were removed from the MTMS solution and placed on paper towels in a fume hood and air-dried for 2 hours. All of the samples were then placed in a large Ziploc bag along with an aluminum weighing dish containing 15 g of tap water. The bag was sealed, creating a closed, humid environment. After 24 hours of exposure to water vapor, the Group 1 wood was removed from the bag and allowed to air-dry in a fume hood. Measurements of the treated wood were then taken in order to assess the conservation process.

## **Group 2 Wood**

Two sections of the plank, W2 and W3, were chosen for treatment with alkoxy silanes. W2 was placed in a beaker containing one liter of industrial-grade acetone and dehydrated at ambient pressure and room temperature for 24 hours. The wood was then placed in fresh acetone for an additional 24 hours of dehydration. After 48 hours of dehydration, W2 was transferred to a beaker containing one liter of MTMS and placed into a desiccator vacuum chamber. A reduced pressure of 5333.33 Pa (40 torr) was applied for 10 hours. The wood was left in the solution at ambient pressure and room temperature for an additional 12 hours. Following acetone/MTMS displacement, W2 was removed from the solution and placed into a Ziploc bag. An aluminum weighing dish containing 20 g of tap water was placed inside the Ziploc bag, in close proximity to the MTMS-treated wood. The bag was sealed and the wood was allowed to sit for 18 hours. The wood was then removed from the bag and placed in a ventilated fume hood for an additional 24 hours. After air-drying, the wood was weighed and measured.

Like W2, W3 was placed in a beaker containing one liter of industrial-grade acetone and dehydrated at ambient pressure and room temperature for 48 hours. The wood was then transferred to a beaker containing one liter of Q9-1315 and placed into a desiccator vacuum chamber. A reduced pressure of 5333.33 Pa (40 torr) was applied for 10 hours. The wood was left in the solution at ambient pressure and room temperature for an additional 12 hours. After acetone/Q9-1315 displacement, W3 was removed from the Q9-1315 solution and placed in a Ziploc bag with a rag, dampened with 20 g of tap water. The bag was sealed and the wood was allowed to sit for 18 hours. The wood was then removed from the bag and placed in a ventilated fume hood for an additional 24 hours. After air-drying, the wood was weighed and measured.

Because there were no indicators as to the quantity required to initiate condensation, it was determined that MTMS-treated wood might require elevated humidity to initiate the condensation process. Accordingly, Group 2 samples were exposed to 20 g of water

while air-drying. Realizing that industrial-grade acetone containing approximately 6% water had been used to dehydrate the waterlogged wood samples, the decision was made not to air-drying Group 3 wood samples at elevated humidity.

### **Group 3 Wood**

The sixteen treenails were first dehydrated in a series of three ethanol baths, each lasting one week. Dehydration was then continued in a series of three acetone baths, changed at two week intervals. For the last 10 hours of dehydration, the samples were placed in a large vacuum chamber and treated at a reduced pressure of 5333.33 Pa (40 torr). During this phase of dehydration, the samples were monitored closely to ensure that they remained immersed in the acetone.

Eight of the treenails were randomly selected, and carefully transferred to a large beaker containing one liter of MTMS. The remaining treenails were transferred into a beaker containing one liter of Q9-1315. Both beakers were then placed in a vacuum chamber and treated at a reduced pressure of 5333.33 Pa (40 torr) for 24 hours. The treenails were then stored at ambient pressure in their respective polymers for an additional seven days.

All of the treenails were then removed from the solutions, surface dried with paper towels, and placed in a fume hood where they were allowed to air dry for 24 hours.

### **Observations**

#### **Group 1 Wood**

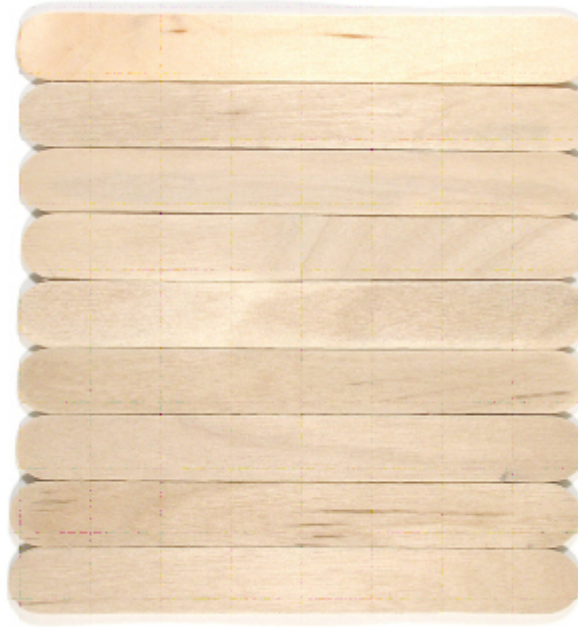
The average wet weight of the Group 1 wood was 5.63 g. After air-drying, the average weight was reduced to 2.59 g, representing a weight reduction of 54.00% (Table 1). The average width of the waterlogged tongue depressors was reduced from 17.89 mm to 13.67 mm, representing a 23.59% reduction (Table 2). The average length of the same samples was reduced from 152.37 mm to 151.74 mm, representing a reduction of 0.41% (Table 3). The average thickness of these samples was reduced from 0.17 cm to 0.15 cm, or 11.76%. A control tongue depressor and several air-dried Group 1 samples are illustrated in Figure 7. Shrinkage, distortion and color change are evident in these samples.

The dimensions and aesthetic attributes of all of the Group 1 MTMS-treated wood samples were well-maintained after treatment. Changes in length were minimal following treatment, with a reduction of only 0.41% after MTMS treatment (Table 4). Change in width of the samples was noticeably high, with an average post-treatment reduction of 9.62% (Table 5). One control tongue depressor and eight MTMS-treated wood samples are illustrated in Figure 8.

After air-drying, the color of the waterlogged tongue depressors had changed from a natural light yellow brown color (10 YR/8/2 Munsell), ranging from a light gray-brown (2.5Y/7/2 Munsell) to a darker brownish-gray (10 YR/6/2 Munsell).



**Figure 7:** Control tongue depressor (top) and air-dried waterlogged tongue depressors.



**Figure 8:** Control tongue depressor (top); eight MTMS-treated, waterlogged tongue depressors (below).

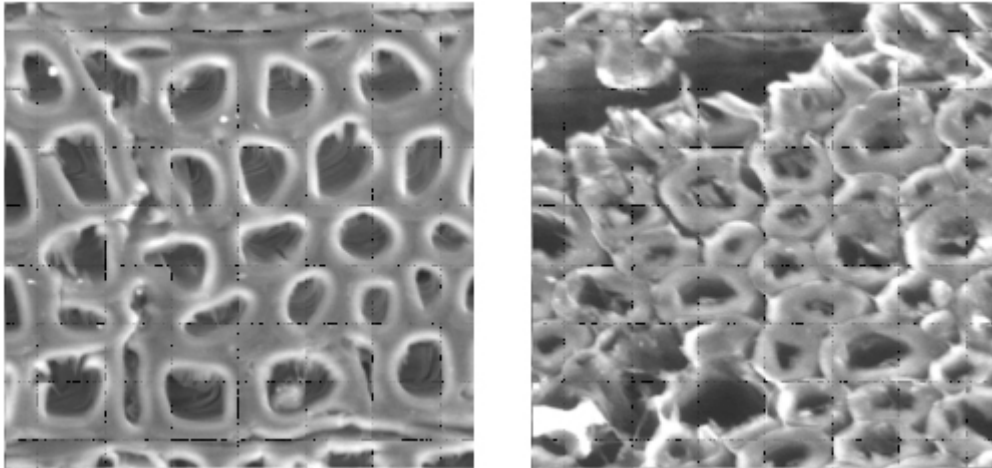
### **Micro-Structure of the Group 1 Wood Samples**

Cross section samples of control, untreated waterlogged wood, air-dried wood and MTMS-treated tongue depressor samples were analyzed using an environmental scanning electron microscope (ESEM). For analytical consistency, photographs of each sample were recorded at 1000-X amplification. Cell shape retention, cell wall integrity and general appearance were used to assess the effectiveness of the treatments.

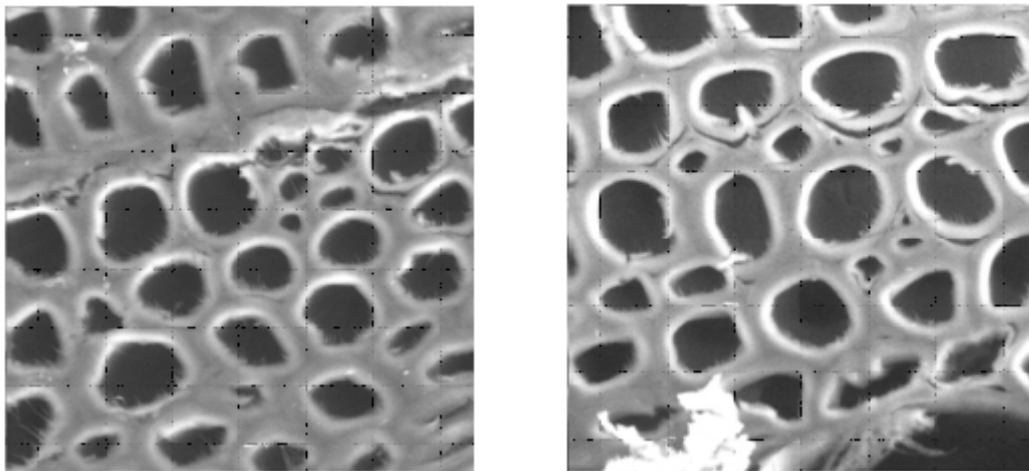
In Figure 9, the left image is a 1000-X amplification of the cross-sectional surface of an untreated birch (*Betula papyrifera*) control tongue depressor showing uniformly shaped, thick-walled tracheids. In contrast, the tracheids in the waterlogged wood sample (right) are irregular in shape with deterioration of the middle lamella. Figure 10 shows two views the micro-structure of a Group 1, MTMS-treated sample of wood. Cell walls

collapse is negligible and there is very little distortion and structural loss of middle lamella.

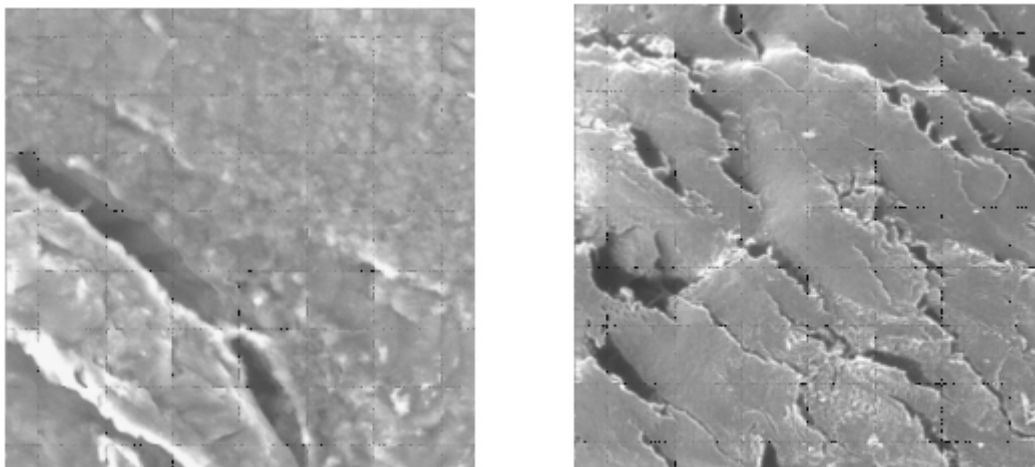
In Figure 11, two cross-section views indicate that, after air-drying, the cell structure of the Group 1 waterlogged wood samples collapsed, causing extreme shrinkage and distortion of the wood.



**Figure 9:** Control Group 1 tongue depressor on the left and image of a waterlogged Group1 tongue depressor on the right, viewed at 1000-X amplification.



**Figure 10:** Two cross section microscopic views (1000-X amplification) of a Group 1 tongue depressor treated using MTMS.



**Figure 11:** Two cross-section views of Group 1, air-dried wood samples. In both images, cellular distortion and collapse is apparent, resulting in extreme warpage and distortion.

## **Observations Group 2 Wood**

Prior to air-drying, W1 weighed 104.3 g and measured 2.00 cm wide, 1.87 cm thick and 12.20 cm long. After 24 hours of air-drying, the wood weighed 10.5 g, representing a reduction of 89.93%. The water content of this sample was calculated to be 893%. When removed from the warming oven, the wood had completely collapsed and fragmented into five sections.

The final length of W1 was impossible to determine due to fragmentation during air-drying. Prior to treatment, the thickness of W1 was 1.87 cm. Average thickness of W1 wood fragments after treatment was 0.42 cm, representing a reduction in thickness of 77.54%.

W2 was sectioned from the plank adjacent to W1. This section of wood had a wet weight of 115.7 g and measured 4.13 cm wide, 1.86 cm thick and 14.68 cm long. W2 was designated for treatment in MTMS, after dehydration in acetone.

After treatment in MTMS, W2 appeared uniformly dry and light in color. Only slight dimensional changes were noted. The wet weight of sample W2 was reduced from 115.7 g to 28.7 g, representing a reduction of 75.19%. The width of W2 measured 4.13 cm prior to treatment. After treatment it measured 3.96 cm, representing a reduction of 4.12%. Thickness of W2 prior to treatment was 1.86 cm. After treatment, W2 measured 1.85 cm thick, indicating that no significant change had occurred in thickness. After treatment, W2 measured 14.63 cm, compared to its pre-treatment length of 14.68 cm, representing a loss of 0.34%.

Prior to treatment, the entire plank of wood was dark brown in color (10 YR/3/3 Munsell). After treatment, W2 was a light, gray-brown color (10 YR/6/2 Munsell). The surfaces of the wood show no signs of checking and the wood looks very natural. After treatment, however, W2 is very light in weight, but the preserved wood has withstood extensive handling with no signs of deterioration or wear.

Sample W3 had a wet weight of 91.3 g. Its wet measurements were 3.14 cm wide, 1.84 cm thick and 14.73 cm long. W3 was treated with Q9-1315 after an initial dehydration in acetone. The wet weight of W3 was 91.3g. After treatment, W3 weighed 26 g, representing a weight loss of 71.52%. The width of the sample was reduced from 3.02 cm to 2.98 cm, representing a reduction in width of 5.10%. The thickness of W3 was reduced from 1.84 to 1.62 cm, representing a reduction of 11.96%. The wet length of W3 was 14.73 cm. After treatment, the wood measured 14.54 cm, representing a reduction in length of 1.29%.

While shrinkage was more of a problem with sample W3, the end result was aesthetically pleasing. Prior to treatment, W3 was dark brown in color (10 YR/3/3 Munsell). After treatment, the wood was slightly darker (10 YR/4/2 Munsell) than W2. Both W2 and W3 wood samples were natural in appearance and dry to the touch. The post-treatment coloration of W2 and W3 is illustrated in Figure 12.

The remaining section of wood, W4, was treated by air-drying. Prior to treatment, its wet weight was 104.3 g. Its wet dimensions were 3.05 cm width, 1.87 cm thick and 12.27 cm long. W4 was the largest of two air-dried samples from the original plank of waterlogged wood. In comparison to W1, W4 was more similar in size to the sections of wood treated with alkoxy silane polymers. Prior to treatment, its wet weight was 104.3 g. After treatment, it weighed 10.3 g, representing a weight loss of 90.12%. Its width was reduced from 3.05 cm to 2.55 cm, representing a reduction in width of 16.39%. The thickness of the sample was reduced from 1.87 cm to 0.72 cm, a reduction of 61.50%. Post-treatment length of W4 was difficult to determine as the sample splintered into six large sections, each exhibiting gross distortion of its edges. Prior to air-drying, the sample measured 12.27 cm at its longest point. After treatment, W4 measured approximately 10.41 cm in length, representing a loss of 15.16% (Table 6). Figure 12 illustrates the post-treatment condition of samples W1, W2, W3, and W4.

Group 2 samples were limited in number, simply because extraneous pieces of archaeological wood are in short supply for experimental purposes. The plank selected for experimentation was uniform in thickness and appeared to be uniformly soft to the touch. After 24 hours of treatment, sample W4 had deteriorated into a pile of splinters, making a comparison of pre-and post-treatment dimensions impossible. The wood was calculated to have a water content of 788.64%.



**Figure 12:** Group 2 wood after treatment. W1, oven dried wood; W2, MTMS treated wood; W3, Q9-1315 treated wood; W4, air-dried wood in vented fume hood. Note the comparatively lighter color of section W2.

## Observations

### Group 3 Wood

Prior to treatment, the average percentage water content of the Group 3 waterlogged treenails was 285%, appreciably lower than the water content of 788.64% calculated for the Group 2 wood samples. During initial cleaning and desalination, the treenails were found to be less spongy than the sections of plank and the wood was noticeably harder. Many of the ends of the treenails had either broken or been slightly splayed under the force of being removed from the ships timbers.

Group 3 wood samples treated using MTMS alkoxysilane polymers experienced only slight changes in post-treatment weight and dimensions in comparison to the Group 3 Q9-1315 treated wood. After treatment, the average weight of MTMS treated treenails was 40.48 gm, representing a percentage weight change of -45.45%. Treenails preserved using Q9-1315 polymer had an average weight of 39.32 grams after treatment, representing a percentage weight change of -43.89% ( Table 7).

Group 3 treenails preserved using MTMS had an average change in length of -0.36%. The change in length was higher for Q9-1315 treated treenails, with an average post-treatment length of 121.76 mm., representing a percentage shrinkage of -0.49% (Table 8).

Similarly, the average change in diameters for the Group 3 MTMS-treated treenails was substantially less than the average change in diameter for Q9-1315-treated treenails. The post-treatment average diameter for MTMS treated wood was 25.56 mm, representing a change in diameter of -3.41%. Q9-1315 treenails had an average change in post-treatment diameter of -9.40% (Table 9).

The most noticeable difference between the MTMS and Q9-1315 treated treenails was color. In all cases, the color of the MTMS-treated wood is much lighter. The Q9-1315-treated wood tends to be darker in color with fewer wood grain and surface features visible.

## Discussion

NMR spectral analysis, ESEM analysis and empirical data indicate that the structural integrity of the Group 1 tongue depressors was sufficiently degraded that the wood samples can be used to evaluate preservation treatments for waterlogged timbers from shipwrecks. Group 1 wood samples provide a reasonably homogeneous source of wood that allows quantitative and qualitative analysis of the effectiveness of consolidants being tested for use in conserving waterlogged wood. Regularity of size and species and the availability of non-waterlogged control samples make the Group 1 wood samples invaluable for wood experimentation. Because of inherent inconsistencies in waterlogged archaeological wood, similar comparative data can not be derived for archaeological samples.

Air-dried Group 1 wood samples experienced average weight loss of -54.00%, average reduction in width of -23.59% and average reduction in length of -0.41%. All of the samples were warped and twisted after air drying.

MTMS-treated Group 1 wood samples were generally well preserved. Average reduction in length was -0.41% after treatment. Average reduction in width of the same samples was -9.62%. These figures seem high but a comparison of the MTMS-treated samples shows that they are nearly identical to the untreated control tongue depressors, indicating that the treated wood was restored to dimensions nearly identical to those of the control wood samples. Swelling that occurred during the waterlogging process had been greatly reduced after the wood was treated in MTMS. ESEM evaluation of these samples confirms that cell dimensions and shapes were similar to those of the control wood samples. Slight shrinkage of the middle lamella was noted after treatment.

Acetone/MTMS displacement of the Group 1 samples was conducted in a reduced pressure environment. In this environment, the boiling point of acetone is lowered, resulting in faster and more thorough vaporization of the solvent. Testing conducted in developing procedures for this experiment indicated that ambient pressure evaporation of acetone is sufficient to allow the uptake of MTMS without causing shrinkage or

distortion of the wood being treated. Use of a reduced pressure environment, however, accelerated the displacement process.

After treatment, all of the Group 1 tongue depressors are slightly gray-brown in color (10YR 7/2 Munsell) as compared to the color of the control tongue depressors (10YR 8/4 Munsell). This shift in color is the result of changes in the wood caused by long-term immersion in water.

Group 2 wood samples were highly degraded. The computed water content of the samples was between 788.64% and 822.61%, suggesting that water content was reasonably uniform throughout the plank. Oven-dried sample W1 and air-dried W4 were much darker in color than sections W2 and W3. This is the result of extreme cellular collapse and warpage that occurred as the result of air drying. Both samples of wood disintegrated to the point that accurate physical measurements could not be obtained.

The conservation of wood samples W2 and W3 was considered successful as their physical dimensions, surface textures, and individual characteristics were accurately maintained. Lower rates of shrinkage were observed in the MTMS-treated wood sample W2. This section of wood is lighter in color than sample W3, which is darker due to the slightly higher degree of shrinkage that occurred as the result of treatment in Q9-1315.

MTMS is 97% pure with a 3% addition of alcohols. Q9-1315 is a less refined solution containing approximately 44% MTMS mixed with organic solvents and trace amounts of dimethyldimethoxysilane. Accordingly, the resin-forming capabilities of the Q9-1315 solution are insufficient to preserve the dimensional characteristics of the wood. This is evident from the slightly higher rates of shrinkage for sample W3.

The diagnostic attributes of W2 and W3 were preserved because sufficient resins were formed as the result of condensation to prevent cellular collapse of the wood. Waterlogged tongue depressors and the archaeological wood samples preserved with the MTMS solution, which has a higher percentage of hydrolyzable, multi-functional alkoxysilane polymers, were the best preserved specimens. In contrast, the Q9-1315 solution, containing a lower percentage solution of the same multi-functional alkoxysilane polymers, was insufficient to preserve the diagnostic attributes of the wood. The waterlogged tongue depressors, calculated to have a moisture content of 215.96%, were very well preserved using MTMS.

Wood treated using a higher percentage MTMS solution looks natural in color and texture following treatment. No surface checking was noted in either the Group 1 wood samples or the archaeological wood. During the waterlogging process, the natural color of the wood was altered, resulting in a slight grayish cast. The wood, however, is dimensionally stable after treatment in the silane. Experimentation indicates that resins created as the result of condensation can preserve even badly waterlogged wood very well. As C. V. Horie [9] and others have suggested, conservation strategies using silicone oils are not reversible. However, over time, the solubility of many adhesives and

consolidants currently in common use in conservation are also affected, rendering these techniques also non-reversible.

Additional experimentation is needed to determine if the addition of small percentages of silicone oils might increase the bulking ability of MTMS and Q9-1315, effectively reducing shrinkage. A small percentage addition of a low viscosity silicone oil to Q9-1315 may increase its bulking ability despite its high alcohol content, making it an effective treatment.

## Index - Tables

**Table 1** Weight Changes for Group 1 MTMS-Treated Wood

<b>TD</b>	<b>Wet Weight /g</b>	<b>Post Treatment Weight /g</b>	<b>% Change</b>
1	5	2.7	-46
2	5.8	2.6	-55.17
3	5.3	2.4	-54.72
4	5.5	2	-63.64
5	5.7	2.3	-59.65
6	5.9	3	-49.15
7	5.4	2.5	-53.7
8	5.8	2.6	-55.17
9	5.7	3	-47.37
10	5.7	2.8	-50.88
11	5.5	2.5	-54.55
12	5.5	2.5	-54.55
13	5.8	2.7	-53.45
14	5.7	2.6	-54.39
15	5.8	2.6	-55.17
16	5.7	2.6	-54.39
17	5.6	2.5	-55.36
18	5.8	2.8	-51.73
	<b>Average Wet Weight / g</b>	<b>Averaged Post-Treatment Weight / g</b>	<b>Average % Change in Weight</b>
	5.63	2.59	-54

**Table 2** Width Change of Air-Dried Waterlogged Tongue Depressors

<b>TD</b>	<b>Wet Width / mm</b>	<b>Air-Dry Width / mm</b>	<b>% Width Change</b>
1	17.9	13.47	-24.75
2	17.87	14.32	-19.87
3	17.87	13.24	-25.91
4	17.91	13.43	-25.01
5	17.9	14.6	-18.44
6	17.88	12.9	-27.85
7	17.87	14.36	-19.64
8	17.89	13.53	-24.37
9	17.9	14.25	-20.39
10	17.91	12.61	-29.59
	<b>Average Wet Width / mm</b>	<b>Average Air-Dry Width / mm</b>	<b>Average % Change</b>
	17.89	13.67	-23.59

**Table 3** Change in Length of Air-Dried Tongue Depressors.

<b>TD</b>	<b>Wet Length / mm</b>	<b>Air-Dry Length / mm</b>	<b>% Length Change</b>
1	152.5	151.08	-0.93
2	152.22	150.88	-0.88
3	152.47	150.86	-1.06
4	152.26	151.03	-0.81
5	152.48	150.97	-0.99
6	152.51	151.09	-0.93
7	152.59	151.77	-0.54
8	152.48	151.11	-0.9
9	152.35	151.76	-0.39
10	152.34	151.62	-0.47
	<b>Average Wet Length / mm</b>	<b>Average Air-Dry Length/mm</b>	<b>Average % Length Change</b>
	152.37	151.74	-0.41

**Table 4** Changes in Length for Group 1 MTMS-Treated Wood Samples

<b>TD</b>	<b>Wet Length / mm</b>	<b>Preserved Length / mm</b>	<b>% Change</b>
1	152.49	151.75	-0.49
2	152.46	151.6	-0.56
3	152.34	152.04	-0.2
4	151.97	151.17	-0.53
5	152.48	152.03	-0.3
6	152.58	152.1	-0.31
7	151.82	151.33	-0.32
8	152.48	151.94	-0.35
9	152.68	151.96	-0.47
10	152.5	151.97	-0.35
11	152.59	151.55	-0.68
12	152.5	151.65	-0.56
13	152.46	151.97	-0.32
14	152.21	151.58	-0.41
15	152.58	151.99	-0.39
16	152.56	151.85	-0.47
17	152.51	152.14	-0.24
18	151.48	150.78	-0.46
	<b>Average Wet Length / mm</b>	<b>Average Post-treatment Length / mm</b>	<b>Average % Change in Length</b>
	152.37	151.74	-0.41

**Table 5** Changes in Width for Group 1 MTMS-Treated Wood Samples

<b>TD</b>	<b>Wet Width / mm</b>	<b>Post Treatment Width / mm</b>	<b>% Width Change</b>
1	19.71	17.59	-10.76
2	19.78	17.95	-9.25
3	19.66	17.35	-11.75
4	19.7	17.95	-8.88
5	19.8	17.7	-10.61

6	19	17.79	-6.37
7	19.72	17.93	-9.08
8	19.8	17.33	-12.47
9	19.77	17.95	-9.21
10	19.75	17.94	-9.16
11	19.79	17.62	-10.97
12	19.64	17.24	-12.22
13	19.7	17.05	-13.45
14	19.87	17.09	-13.99
15	19.59	17.79	-9.19
16	19.71	17.61	-10.65
17	19.7	17.18	-12.79
18	19.9	17.48	-12.16
	<b>Average Wet Width / mm</b>	<b>Average Post-treatment Width / mm</b>	<b>Average % Change in Width</b>
	19.76	17.86	-9.62

**Table 6** Pre and Post-Treatment Measurements for Group 2 Wood Samples

		<b>W1*</b>	<b>W2</b>	<b>W3</b>	<b>W4**</b>
<b>Weight (grams)</b>	<b>Pre:</b>	39.1	115.7	91.3	104.3
	<b>Post:</b>	4.4	28.7	26	10.3
	<b>% change:</b>	-88.75%	-75.19%	-71.52%	-90.12%
<b>Length (cm)</b>	<b>Pre:</b>	12.2	14.68	14.73	12.27
	<b>Post:</b>		14.63	14.54	10.41
	<b>% change:</b>		-0.34%	-1.29%	-15.16%
<b>Width (cm)</b>	<b>Pre:</b>	2	4.13	3.14	3.05
	<b>Post:</b>		3.96	2.98	2.55
	<b>% change:</b>		-4.12%	-5.10%	-16.39%
<b>Thickness (cm)</b>	<b>Pre:</b>	1.87	1.86	1.84	1.87
	<b>Post:</b>	0.42	1.85	1.62	0.72
	<b>% change:</b>	-77.54%	-0.54%	-11.96%	-61.50%

\* Fragmentation precluded post-treatment length and width measurements.

\*\* Fragmentation precluded exact post-treatment length measurements; the value is an approximation.

**Table 7** Changes in Weight for Group 3 Treenail Artifacts

Treenail/Treatment	Wet Weight/ g	Post-Treatment Weight/g	% Change
1 - AIR DRY	68.2	17.8	-73.9
2 - AIR DRY	82.1	17.85	-78.26
	<b>Average Percent Weight Loss, Air Dried Wood:</b>		<b>-76.08%</b>
3 - MTMS	83.8	44.13	-47.33
4 - MTMS	59.8	32.42	-45.79
7 - MTMS	66.2	37.99	-42.61
9 - MTMS	65.7	35.36	-46.18
10 - MTMS	91.1	50.75	-44.29
12 - MTMS	67.4	38.32	-43.15
15 - MTMS	75.5	38.67	-48.78
18 - MTMS	84.2	44	-47.74
	<b>74.21 g average wet weight</b>	<b>40.48 g average post-treatment weight</b>	<b>-45.45%</b>
5 - Q-9-1315	69.7	37.83	-45.72
6 - Q-9-1315	62.2	32.86	-47.17
8 - Q-9-1315	77.8	40.85	-47.49
11 - Q-9-1315	64.4	36.59	-43.18
13 - Q-9-1315	82.1	46.94	-42.83
14 - Q-9-1315	55.5	33.43	-39.77
16 - Q-9-1315	91.5	53.9	-41.09
17 - Q-9-1315	63.5	36.32	-42.8
	<b>70.84 g average wet weight</b>	<b>39.75 g average post-treatment weight</b>	<b>-43.89%</b>

**Table 8** Changes in Length for Group 3 Treenail Artifacts

Treenail / Treatment	Pre Treatment Length / mm	Post Treatment Length / mm	% Change
1 - AIR DRY	106.5	92.53	-13.12
2 - AIR DRY	145.39	122.69	-15.61

	<b>Average Percent Reduction in Length of Air Dry Wood:</b>		<b>- 14.37%</b>
3 - MTMS	140.84	140.3	-0.38
4 - MTMS	115.43	115.06	-32.00%
7 - MTMS	148.55	148.18	-0.25
9 - MTMS	111.36	110.74	-0.56
10 - MTMS	122.47	12205.00%	-34.00%
12 - MTMS	108.61	108.11	-0.46
15 - MTMS	144.59	144.29	-0.21
18 - MTMS	137.75	137.27	-0.35
	<b>128.70 mm average wet length</b>	<b>128.24 mm average post-treatment length</b>	<b>-0.36%</b>
5 - Q-9-1315	128.73	127.89	-0.65
6 - Q-9-1315	113.28	112.76	-0.46
8 - Q-9-1315	121.91	121.32	-0.48
11 - Q-9-1315	115.53	114.86	-0.58
13 - Q-9-1315	13018.00%	129.62	-0.43
14 - Q-9-1315	124.13	123.62	-0.41
16 - Q-9-1315	142.42	141.68	-0.52
17 - Q-9-1315	102.68	102.29	-0.38
	<b>122.36 mm average wet length</b>	<b>121.76 mm average post-treatment length</b>	<b>-0.49%</b>

**Table 9** Changes in Diameter for Group 3 Treenail Artifacts

<b>Treenail /Treatment</b>	<b>Pre Treatment Diameter / mm</b>	<b>Post Treatment Diameter / mm</b>	<b>% Change</b>
1 - AIR DRY	26.85	22.32	-16.87
2 - AIR DRY	24.87	20.93	-15.84
	<b>Average Percent Change in Diameter of Air Dried Wood :</b>		<b>- 16.36%</b>
3 - MTMS	27.45	26.29	-4.23
4 - MTMS	25.05	24.14	-3.63
7 - MTMS	26.11	25.44	-2.57

9 - MTMS	27.92	27.14	-2.79
10 - MTMS	27.38	26.39	-3.62
12 - MTMS	26.75	25.65	-4.11
15 - MTMS	25.2	24.36	-3.33
18 - MTMS	27.39	26.56	-3.03
	<b>26.66 mm average wet diameter</b>	<b>25.75 mm average post-treatment diameter</b>	<b>-3.41%</b>
5 - Q-9-1315	27.01	23.81	-11.85
6 - Q-9-1315	26.83	24.27	-9.54
8 - Q-9-1315	29.3	26.6	-9.22
11 - Q-9-1315	26.77	24.82	-7.28
13 - Q-9-1315	27.02	24.15	-10.62
14 - Q-9-1315	22.31	20.68	-7.31
16 - Q-9-1315	27.55	25.26	-8.31
17 - Q-9-1315	27.58	24.62	-10.73
	<b>26.80 mm average wet diameter</b>	<b>24.28 mm average post-treatment diameter</b>	<b>-9.40%</b>

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