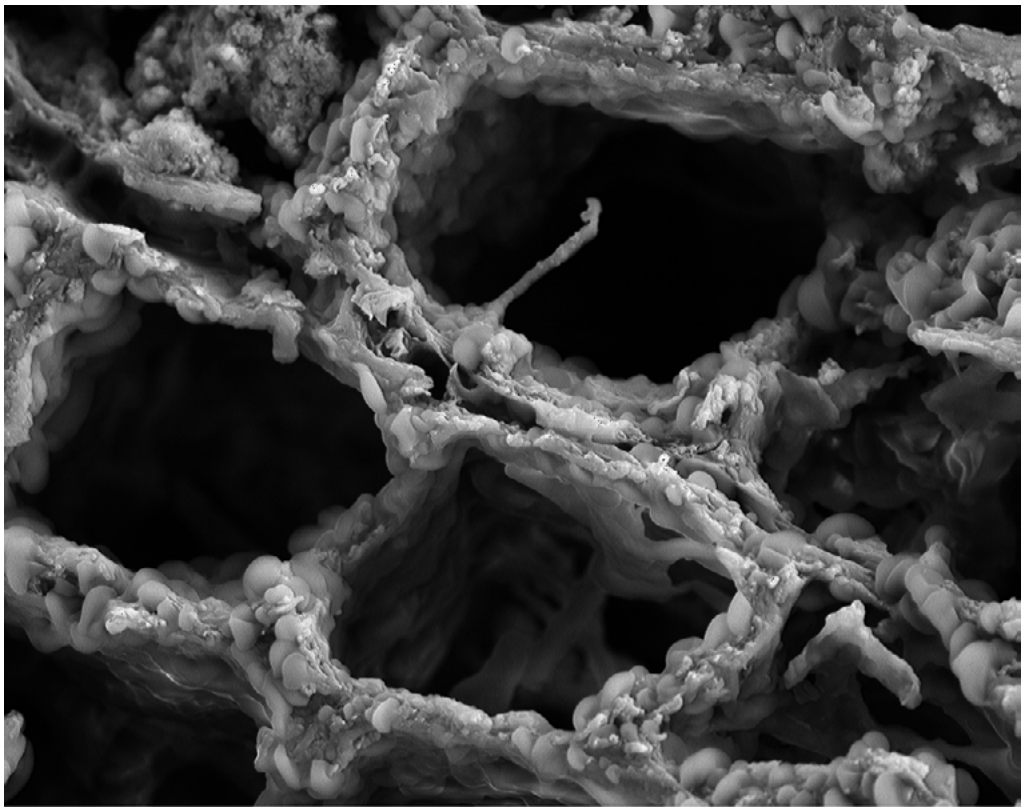

Figure 1. Excess PEG has been flushed from wood cells by immersion in MTMS. Remaining PEG has been chemically bonded to the cell walls.

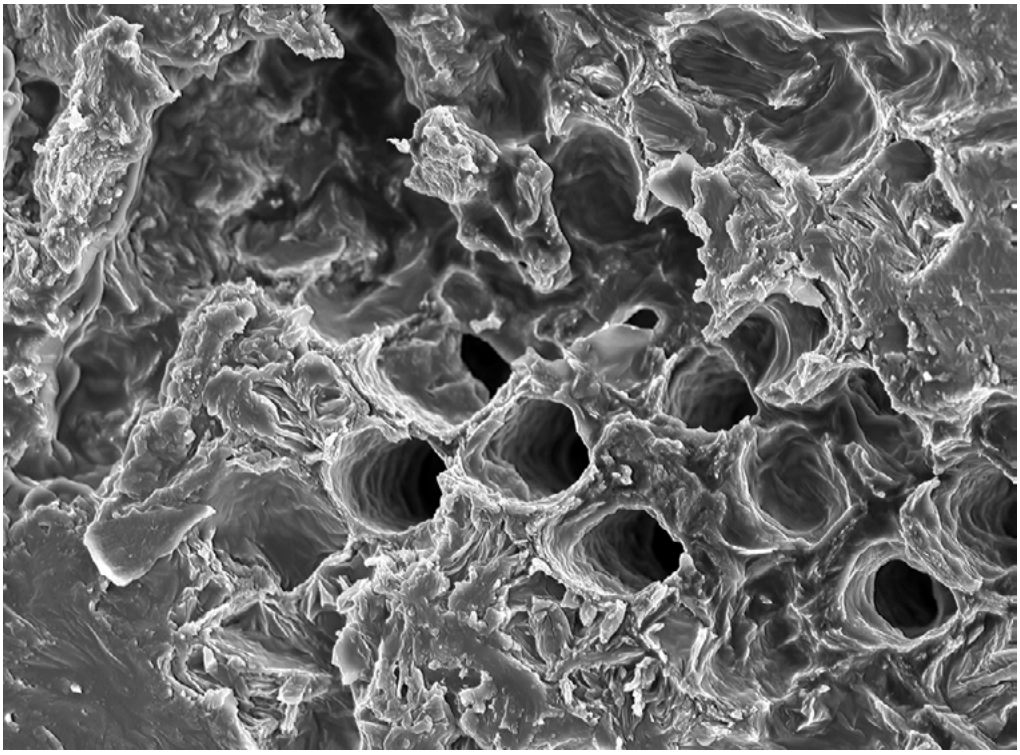

Figure 2. Cross-section view of PEG-treated, waterlogged wood. Cells are filled with water miscible, waxy PEG.

Rethinking Conservation Paradigms for the Preservation of Waterlogged Wood

C. Wayne Smith, Associate Professor, Nautical Archaeology Program
Department of Anthropology, Texas A&M University

ABSTRACT

One important outcome of the 1978 ICOM Committee for Conservation Conference in Zagreb, Croatia, was the creation of a list of eight areas of research topics deemed to be problematic in the field of artifact conservation. The author will discuss shortfalls of this list with respect to past history, current issues and complications in using traditional treatment strategies for the preservation of waterlogged wood. Additionally, a case study on the preservation and evaluation of waterlogged wood treated using organic polymers will be presented. A critical assessment of traditional and newly developed treatment methods will be presented with suggestions for new research opportunities.

One important outcome of the 1978 ICOM Committee for Conservation Conference in Zagreb, Croatia was the creation of a list of eight research topics deemed to be problematic for the preservation of waterlogged wood. In his address to the Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa, 1981, Colin Pearson, a Materials Conservation Specialist with the Canberra College of Advanced Education, Australia, noted the research topics outlined at the Zagreb 1978 conference [1]:

1. Use of detergents in the conservation of waterlogged wood
2. Use of tetraethyl ortho silicate
3. Problems with the salvage of waterlogged wood
4. Freeze-drying
5. Methods of analysis of PEG in waterlogged wood
6. Use of sucrose
7. Use of organic polymers
8. Irradiation techniques

The following additional topics of research were added by newsletter from the ICOM Waterlogged Wood Working Group after the conference:

9. Analysis and research
10. Treatment of large ship's timbers
11. Acetone/rosin processes
12. Controlled drying
13. PEG impregnation
14. General interest

In spite of the numerous research areas outlined, however, most research since that conference has focused on preservation of waterlogged wood using sucrose and PEG/freeze-drying strategies. Cliff McCawley,

David Grattan and Clifford Cook advanced research into the effects of PEG/freeze-drying waterlogged wood [2][3]. Per Hoffmann conducted some invaluable studies indicating 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 waterlogged wood conservation continue, some of the long-term problems of waterlogged wood treatments using PEG and other bulking agents are coming to light. In his address at the Ottawa ICOM Conference, Dr. Allen Brownstein, 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 with 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 and the miscibility/chemical reactivity of PEG with oxides and compounds found naturally in waterlogged timbers. Sadly, it appears that Brownstein may have been correct in stating that "PEG treatments may not be the perfect solution to difficult problems."

Using some of Allen Brownstein's suggestions, we started researching organic polymers (topic number seven in the Zagreb list) with a series of experiments entitled "Treatment of Waterlogged Wood Using Hydrolyzable, Multi-Functional Alkoxysilane Polymers." This was conducted to study the use of tri-functional polyols both to stabilize and to maintain the physical attributes of waterlogged wood samples. Instead of just creating a "very hard and durable finish," as Brownstein suggested, experimentation was also directed at impregnating a variety of waterlogged wood samples with a self-condensing polymer to form a stable resin throughout the pore structure of the wood. As we perceived it, there were some benefits to this type of resin-forming chemical reaction. Contrary to rapid water/PEG displacement, which often causes cellular collapse or cell wall distortion, water/methyltrimethoxysilane (MTMS) displacement does not appear to distress waterlogged wood, resulting in thorough impregnation with a reduced chance of cellular distortion. Using trace amounts of water, the alkoxysilane MTMS condenses, forming a triol of resins that preserve physical and structural attributes of an organic artifact without causing distortion of cell walls or appreciable shrinkage. Post-treatment microscopic and NMR (Nuclear Magnetic Resonance) 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. (fig. 1) Visually, the wood is aesthetically pleasing without the somewhat waxy, dark coloration associated with PEG-treated wood. (fig. 2) Most importantly, resins formed appear to prevent chemical reactivity due to the presence of oxides in the wood. The end result of this research was a unique method of preserving waterlogged wood that used intracellular water in wood samples to create a durable resin, which preserved both the microstructure and the general physical attributes of an artifact.

Once these initial experiments were completed, it was immediately evident that peer review within the conservation community was going to be difficult. First, conservators did not like the idea of forming resins inside of an artifact. Correctly, they observed that these processes were not reversible. Second, the language and direction of our experiments were better suited for the discipline of organic chemistry. Ultimately, we determined that the best way to obtain an accurate assessment of

the chemical mechanisms and the viability of prescribed treatment methodologies outlined from experimentation was to apply for patents within United States and Europe. Our research was then assessed by people knowledgeable in the use of such chemistries, thus alleviating any doubt about the viability of the materials and chemical mechanisms we were using for conservation research. The following five patents outline our research:

Klosowski, J., C. Wayne Smith and Donny Leon Hamilton
Conservation of Organic and Inorganic Materials. United States patent 6,881,435

Smith, C. Wayne and D.L. Hamilton
Method of Preserving a Sample with Methyltrimethoxysilane. U.S. patent 6,835,411

Klosowski, J. M., C. W. Smith and D. L. Hamilton
Methods of Conserving Waterlogged Materials. United States patent 6,020,027

Klosowski, J. M., C. W. Smith and D. L. Hamilton
Conservation of Organic and Inorganic Materials. United States patent 6,022,589

Klosowski, J. M., C. W. Smith and D. L. Hamilton
A Method of Conserving Waterlogged Materials. United States patent 5,789,087

What remained, then, was to demonstrate the combination of these tested chemical mechanisms with organic materials collected from submerged archaeological site excavations. This research, including accelerated weathering tests, was conducted at Dow Corning Corp., Midland, Michigan, over a period of months in 1997.

Evaluating the aesthetic nature of artifacts preserved using MTMS and other organic polymer chemistries is, in fact, a very difficult task. Initially, we observed that, while dimensionally stable, some artifacts preserved using functional polymers with cross-linking additives managed to retain their physical structure but were not aesthetically pleasing. We later found that after we impregnated waterlogged wood with functional polymers, washing the surfaces of the wood with rinses of MTMS to remove excess polymers produced natural appearing wood surfaces that were pleasing to the touch. So while there are no standards that apply to the aesthetic nature of artifacts, the conservator must consider the provenance and long-term curatorial considerations of artifacts when determining the aesthetic appeal of an artifact.

At present, the alkoxysilane polymer MTMS is expensive; therefore, its use as a principal treatment agent is only practical in the preservation of small artifacts. To alleviate this problem, the addition of hydroxyl-ended, functional polymers such as Dow Corning's SFD-1 extends both the working volume and the cost-effectiveness of using MTMS. Stoichiometrically, a traditional addition of 3-5% MTMS by weight of the hydroxyl-ended polymer should be an ideal bulking agent for most organic, waterlogged materials. To date, more than 3000 waterlogged artifacts have been conserved with this combination of functional polymer and cross-linker and are on display in the Bob Bullock Texas State History Museum in Austin, Texas. Numerous other artifacts are also on display in a variety of locations: the Canadian Museum of Civilization, Gatineau, Québec; the Oklahoma History Center, Oklahoma City, Oklahoma; the Del Norte County Historical Society Museum, Crescent City, California; the Corpus Christi Museum of Science and History, Corpus Christi, Texas; and the Texas Maritime Museum, Rockport, Texas.

Our initial research was designed 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 has been

shown to produce a more stable and less chemically reactive bulking agent. Mankind has learned to manipulate bonding/polymerization processes, but in truth, polymerization is a natural process. Most of the components of a tree, themselves polymers, work together to impart rigidity, strength, flexibility and intracellular transport of vital fluids necessary to promote growth. Use of functional polymers for the preservation of wood appears to be a natural fit. Our concerns about using polymerizing agents to preserve the physical integrity and microstructure attributes of artifacts may be misplaced since material science research indicates that organic polymers may interact more predictably than PEG with natural polymers within the structure of organic artifacts. This, in turn, should promote long-term, predictable artifact preservation. Before implementing any conservation strategy, it is natural to be concerned about the chemical reactivity of materials we are introducing into the matrix of waterlogged artifacts. Hindsight has shown that the adoption of PEG for the treatment of some waterlogged artifacts may have been hasty and possibly lacking sufficient research regarding chemical decomposition over time, as well as chemical reactivity within the artifact itself.

Ironically, the non-reversible nature of the functional polymer process may hold the key to reducing the chemical reactivity that remains problematic with PEG. When any bulking agent is introduced into the cell structure of wood, some degree of chemical bonding and potential polymerization takes place. Accordingly, the stable nature of materials being introduced into waterlogged wood and other organic materials should be of concern. 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.

References

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