

New materials used for the consolidation of archaeological wood – past attempts, present struggles, and future requirements

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Abstract

Given the perilous state of the Oseberg find from Norway, the University of Oslo is looking into new methods for treating waterlogged wood. While numerous polymers have been previously tested, most do not stabilise the wood sufficiently, penetrate far enough, or remain stable without degassing toxic fumes. A few of the more common examples are: Alum salt, $KAl(SO_4)_2 \cdot 12H_2O$, which was used for treatment earlier but does not penetrate well and leaves the wood very acidic. After WW2, conservators began using poly(ethylene glycol) (PEG) but this material degrades over time and thus cannot support the finds for very long. Melamine-formaldehyde (Kauramin) has also been used and while it is fairly stable, it also fills the wood enough to turn it into a 'block' of plastic. It is proposed that the single most vital requirement for a stabilising agent is to leave an airy structure in order to allow re-treatment in the future. This might be accomplished by foaming a polymer, or by combining nanoparticles with a polymer 'spider web' network to keep them in place. It may also be possible to construct a frame using biomimetic materials (an 'artificial lignin' either alone or as a polymer component) or through biomineralisation (an inorganic 'skeleton'). In any case, the recent advances in materials science must be considered and implemented if we are to develop new, airy, re-treatable, durable consolidants for archaeological wood.

1. INTRODUCTION

Knowledge of previous treatments of archaeological wood and their consequences becomes more and more important in conservation. When problems and damaging processes caused by past conservation are recognised, possible re-treatment procedures and preservation strategies have to be considered. However, materials chosen and the criteria for evaluating suitable re-conservation methods must be implemented. The historic treatments teach us that no method – no matter how well suited to the task it seems to be at the time – will preserve objects forever. For this reason, conservation ethics claim that every material used must be removable or, more generally, leave the object re-treatable. The American Institute for Conservation of Historic and Artistic Works (AIC) code states that, “The conservation professional must strive to select methods and materials that, to the best of current knowledge, do not adversely affect cultural property or its future examination, scientific investigation, treatment, or function.” [1]. Unfortunately, practice is usually more complicated than theory.

This ethical dilemma is exemplified by the alum-conserved wooden objects from the Oseberg find, excavated in 1904 from a burial mound in Vestfold, Norway [2]. This uniquely richly carved Viking Age find contained the skeletons of two women, fifteen horses and an ox, food, numerous tools and travelling equipment for land and sea – even sleds. The wooden objects have been alum-treated (a short description of the treatment is given in the section below). The collection also contains the famous Oseberg ship but as this was never alum-treated, it is in far better condition than most of the rest of the collection. In the century which has passed since the treatment of the artefacts, they have become increasingly unstable [3]. Most are now unable to support their own weight and cannot be safely removed from their current display frames. Very low pH inside the objects, and metal ions from both treatments and the numerous metal screws and nails used to fasten the many wooden bits to the metal frames, complicates the matter even further. If nothing is done, the most famous Viking Age find in Norway will be irrevocably lost!

The complex problems concerning the development of a re-conservation and preservation strategy for the Oseberg find may be a model case for the future handling of problems caused by historical conservation treatments. Even if the artefacts are stabilised, a future re-treatment (possibly in a hundred years) must be taken into account. After all, the consequences of the alum-treatment teach us how vital it is to have this option.

Materials for wood conservation available today are removable only by washing out using water, organic solvents, or supercritical carbon dioxide. Indeed several polymers used in the conservation of waterlogged wood (such as polyethylene glycol or melamine formaldehyde) may not be completely removable. A future re-treatment of objects of high complexity – like the ones from the Oseberg find – will be almost impossible given current conservation procedures. Additionally, previously used bulking materials typically have undesirable drawbacks such as darkening the wood, filling it so that no further work is possible, or degassing toxic reactants [4]. Thus, to secure wooden cultural heritage in the future, we must first look to the past and propose new strategies without the shortcomings former materials .

1. PREVIOUSLY USED MATERIALS

Several materials have been used for the conservation of waterlogged wood. The most important of these as well as their consequences will be briefly discussed since it is essential understand said consequences if new materials are to avoid known 'pitfalls'.

Restoration of historical finds have (until relatively few years ago) relied upon polymers which were not tailor-made to the object in question and eventually caused damage to the artefacts. This, for example, is the case with many resins which were thought to be reversible when applied to artefacts during the 1960's. Removal of polymer material is generally very difficult, resulting in damage to the finds [5]. Also, many of the treatments originally thought to be reversible are not so – as was for example studied with various polymers for the treatment of ceramics [6].

Polymers used for the conservation of wood must also be polymerised *in situ* or be very small as anything with a diameter larger than about 0.55 nm cannot penetrate into the cell wall to replace adsorbed water [4]. Depth (or time) of penetration becomes a vital factor when treating archaeological wood.

A few of the more commonly used consolidants will be mentioned below. In addition to these, many different consolidants have been tested. An overview of how to choose between the most common ones was recently presented at the 10th international ICOM-WOAM Conference [7]. A more complete list of treatments can be found in Ref.[4].

Alum is the salt $KAl(SO_4)_2 \cdot 12H_2O$ (potassium aluminium sulphate dodecahydrate). During impregnation, objects are boiled for about two hours in a supersaturated alum solution at close to 100°C. Alum crystals form on the surface of the objects [4]. Additionally, recent experiments, made by Hartmut Kutzke and Susan Braovac at the Museum for Cultural History at the University of Oslo, indicate that sulphuric acid is released in the wood during the hot alum treatment¹. This means that the pH value of alum-treated artefacts becomes so low that even the lignin remaining in the objects is actively degraded.

Poly(ethylene glycol) (PEG), also known as poly(ethylene oxide) or – more correctly – poly(oxyethylene), is a polymer with the repeating unit $(OCH_2CH_2)_n$. Long chains of PEG do not easily penetrate far into the wood, while short chains do not stabilise the surface in a satisfactory way [8]. Therefore, a two-step process for PEG impregnation has been recommended, using a low-weight chain (such as PEG 200) to penetrate far into the wood and hopefully stabilise the core. A long-chain PEG (such as PEG 3000 or 4000) bath is then used to stabilise the fractured outer layers of the wood [4]. Problems with optimal freeze drying temperature when using mixtures of PEG200 and PEG2000 have led to the conclusion that it is probably sufficient to use only relatively long-chained PEG in conservation [9]. Unfortunately, a degradation of PEG occurs inside the treated objects which seems to indicate a random cleavage of for example the PEG in the Swedish warship *Vasa* [10].

Melamine formaldehyde consolidation has been developed in Germany where the treatment is also referred to as the 'Kauramin method'. Solubility in water and the small molecular size of the components allows for good penetration into wood. Treatment time is fairly short (from weeks to a year plus subsequent drying for weeks, months, or years in polyethylene wrapping) but the cured polymer is difficult to remove from the surfaces of treated objects. Finally, the chalk-containing surface is treated to improve colour tone [11].

1 S. Braovac and H. Kutzke, *The Presence of Sulphuric Acid in Alum-conserved Wood – Origin and Consequences*, contribution at “Wood Science for Conservation of Cultural Heritage”, WoodCultHer COST Action IE061, Hamburg, 7th-9th October, 2009.

Despite the good chemical stability of melamine formaldehyde, the method tends to fill any voids in the structure, leaving no room for later retreatment. This means that treated objects more or less become blocks of plastic with a limited lifetime.

Silicon-containing polymers have been tested with relatively promising results. They are applicable to both wood and leather [12]. Consolidants such as dicarboxylic acids have been proposed since they can penetrate far into wood and have melting points in the range 50-100°C [13]. Unfortunately, more thorough data on stability and degradation is still needed before the effectiveness of these polymers can be properly evaluated.

2. OTHER FIELDS AND MATERIALS

The enormous development of material sciences may provide us with completely new materials, strategies, and approaches when designing materials meeting special requirements. We may see terms like ‘re-conservation’ or ‘re-treatment’ from a new angle. Ideas on how such a new generation of wood consolidants might be designed were recently expressed (independently) by A. Truyen at a COST workshop².

The Museum of Cultural History and the Department of Chemistry, both part of the University of Oslo, have dedicated a PhD research project to help develop and test new materials for wood conservation.

Above all, it is vital that the object has an open structure after treatment, leaving room for further re-conservation of the artefact in case the current consolidant proves to be unstable. Rather than worry about the reversibility of methods used, conservators should look to such methods which guarantee re-treatability due to ‘air’ in the structure – possibly introduced through emulsion of the bulking agent and/or later freeze-drying of the treated object.

Since the majority of the leftover wooden material consists of lignin [14], it is particularly interesting to look to lignin-like materials – either a kind of artificial lignin or actual lignin re-used as part of the treatment. Having lignin-like properties means that it will be easy to get the bulking agent into the wood – and that even if it gets stuck in there it will not drastically alter the properties of the artefact (at least not from a chemical viewpoint).

It has been proposed that excess lignin from the industry might be reused as a consolidant to prevent washout of sandy ground. Cheap and environmentally friendly products for this purpose already exist [15]. Wood-like lignin has been synthesised with the amount of available monomers and the pH affecting the structure of the final product [16]. Dehydrogenate polymer (DHP), a model compound made from enzymatic polymerisation of coniferyl alcohol, seems to form onion-like layers when polymerised at neutral pH at room temperature [17]. In another test where lignin was extracted directly from wood to form lignophenols – possibly a future source of fuel – it was found that the polymerised matrices held powdery substances effectively [18]. Since some dry, degraded archaeological wood is powdery, this idea might be transferable to the field of cultural heritage.

Lignophenol has been applied to archaeological wood where it overall gave better strengthening than PEG4000. Unfortunately, pure water may not be a suitable solvent for impregnation [19].

We propose that existing lignin – such as the surplus from the paper industry – could be treated to adhere better to the archaeological wood. This may require acetylation or similar modification of the wood and/or lignin. Alternatively, lignin may be used as a filler material when impregnating the wood with a polymer. In this way, degraded wood can be strengthened by what is, chemically speaking, more wood. In this way it would be insured that dimensional change during fluctuations in relative humidity would be identical for the wood and the consolidant.

Phenol-formaldehyde is currently being investigated at the University of Oslo. While the curing process is irreversible, the polymer has a structure very similar to lignin but is much harder to degrade. The first commercial plastic, BakeliteTM, was a phenol-formaldehyde, and items made from it are the only plastic objects which have endured a hundred years worth of real-time ageing [20].

² ARNOLD TRUYEN, *Conservation of wood - selected experiments*, lecture at “Consolidation, reinforcement and stabilisation of decorated wooden artifacts”, WoodCultHer COST ACTION IE0601, Prague 30th-31st March 2009.

Unfortunately, most phenolic compounds used are glues (for instance for making plywood) and it is important that these do *not* penetrate too far into the wooden material [21]. This makes it hard to use the experience from the industry in the field of cultural heritage (where thorough penetration is necessary).

Even though phenol-formaldehyde has been used for a century, the exact relationship between different reaction sites and ratio of reactants is still being discovered. It has been found that hexamethylene tetramine (HMTA), a common cross-linker, preferably reacts with a PF with a high ratio of ortho linkages. A slight surplus of phenol (1.2 to 1.3 phenol per formaldehyde) promotes this orientation [22]. Thus it may be possible to affect the structure in similar ways to promote greater compatibility with the wooden matrix.

Phenol-formaldehyde has been used in conservation of metals [23] fossils, and wood [24] but often at high temperature and with less satisfactory results than urea-formaldehyde [25]. It can be difficult to find references for wooden treatments and problems with too fast curing times (despite excellent penetration), possible de-gassing of formaldehyde, and above all the irreversibility of the curing process caused the method to be discontinued for treatment of wooden artefacts during the 1940's [4], [24]. Thus it must probably be modified in order to insure a better treatment. The lack of published information further makes it difficult to evaluate how effective the method is and if and how recent discoveries in phenol-formaldehyde research can be applied to the field of cultural heritage.

Other molecules than unmodified phenol can be incorporated into the structure of PFs, for example bisphenol A [26] or sucrose and similar carbohydrates (with xylitol giving the best result) [27]. Phenol can even be entirely substituted with furan [28]. It has also been proven that lignin can be incorporated into the PF structure [29] or even react directly with formaldehyde without the use of phenol [30].

The current goal is to introduce such a polymer through an emulsion or force it to form a 'spider web structure' which strengthens the lignin without filling the object completely. Various 'fillers' are also considered – including lignin as well as inorganic materials like calcium carbonate. Polymerisation in buffer solutions can be used to both control the rate of curing of the polymer and even neutralise the very acidic alum-treated wood from Oseberg and similarly affected artefacts.

One possibility is to introduce aliphatic chains between pre-polymer conglomerates to ensure a certain flexibility so the polymer can swell and shrink with the wood. Such a polymer would be similar to wood in structure and resistant to most solvents (due to the phenolic groups) while maintaining enough flexibility to swell with the wood and avoid being as brittle as traditional phenol-formaldehyde.

Another possibility is to learn from nature. Biomineralisation, the process by which biological organisms produce minerals (such as the shells on molluscs and algae, or skeletal parts of vertebrates), has been used to grow artificial bone material for the medical industry [31] – and even used to create highly durable non-organic 'copies' of wood [32]. In the study in question, silicon carbide strings penetrated into wood cells to form a heat-resistant 'copy' upon calcining. Such techniques, along with biomimetic and composite materials, should be further investigated to see if it can be adapted to create a strengthening of archaeological wood, possibly by 'growing' a bionic 'skeleton' framework inside the degraded wood. The advantages of biomineralisation may be that the material can be dissolved in chemicals which do not affect lignin (such as weak acids), making it both durable and reversible. Self-organising materials, on the other hand, may elegantly permit us to implement recent lignin into a weakened archaeological framework.

Some ideas from materials science have already been implemented in treatment of non-wooden cultural heritage – such as using nanoparticles for the stabilization of wall paintings. The small size and large surface areas of these particles allow for good penetration. In addition, inorganic materials can be reinforced with the exact same material as the artefact is made from [5]. The successful integration of Si-containing polymers [12] means that Si-based particles will likely also adhere fairly well to a wooden matrix. Hydroxides might be used to neutralise acid generated inside the conserved objects – this has already been tested on wood from the *Vasa* [33]. It will be imperative to test these materials further to determine if they can be incorporated into degraded wood and thus help save wooden cultural heritage. Nanoparticles might be usable either as fillers in a polymer structure or even coated to provide a surface which will adhere to both remaining wood and newly introduced bulking agents.

3. OVERVIEW OF SOME METHODS

Advantages and disadvantages of various proposed methods are presented in the table below.

Consolidant	Advantages	Disadvantages
Phenol- or melamine-formaldehyde	Phenol structure similar to lignin Penetrates easily in water Real-time ageing tests (PF) Very hard and durable Resistant to solvents/pH	Fills the wood as a 'block' of plastic Irreversible/Unremoveable Formaldehyde is toxic Literature only on high temp./pressure Rather brittle
Lignin	Wooden structure Cheap Can be part of polymer	Large molecules cannot penetrate Probably irreversible Dark colour
Nanoparticles	Commercially available May neutralise acid Can be coated to adhere better Can be very durable	Difficult to disperse and penetrate May become too alkaline for wood Stabilising effect is unknown
Nanotubes	Compatible with wood structure Resistant to solvents/pH	Very hard to penetrate Black colouration
Alifatic polymer	Flexible <i>In situ</i> polymerisation possible	Insufficient stabilisation Difficult penetration if not <i>in situ</i> Not completely reversible
Biom mineralisation	Fits/fills structure "Built" <i>in situ</i> Re-treatable	Sensitive to pH Possibly incompatible with wood Not tested thoroughly

4. CONCLUDING REMARKS

No matter which approach is attempted, however, there are many requirements for a stabilising agent for archaeological wood, the consolidant must be workable in a museum environment (at normal temperature, pressure, and without emitting toxic fumes). The material cannot expand, contract or otherwise warp the wood. Likewise, it must have a slightly acidic pH value suitable for wood. It must be able to penetrate the wood thoroughly and last for a *very* long time. As mentioned, the most important aspect is the 'open' structure which must be possessed by the bulking material in order to ensure that retreatment is possible.

When combined, these diverse fields may provide new ways of looking at the consolidation of archaeological wood. Such a combination might entail forming composite materials where nanoparticles fill the bulk of the wood while being held in place by polymer material which adheres to both the particles and the existing wooden structure. This may be done as a kind of 'spider web' which envelopes the wood without reacting with it, or a 'co-polymer' system which bonds chemically to the leftover lignin.

It is hoped that these ideas and requirements can help cross-disciplinary collaboration and encourage people working with wood – be they chemists, wood technologists, or conservators – to think along new lines in order to secure our cultural heritage.

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References

- [1] *Code of Ethics and Guidelines for Practice* (14/8-2009)
<http://www.conservation-us.org/index.cfm?fuseaction=page.viewPage&pageID=858&nodeID=1>
- [2] Rosenqvist, A. M. (1959), *The Stabilizing of Wood found in the Viking Ship of Oseberg – Part I*, *Studies in Conservation* **4**(1): 13-22
- [3] *The Oseberg find 100-year anniversary – the great adventure in Norwegian archaeology*
<http://www.khm.uio.no/utstillinger/oseberg/indexE.html> (18/08-2009)
- [4] Unger, A., Schniewind, A.P., and Unger, W. (2001), *Conservation of Wood Artifacts*, Springer-Verlag Berlin Heidelberg.
- [5] Baglioni, P., and Giorgi, R. (2006), *Soft and hard nanomaterials for restoration and conservation of cultural heritage*, *Soft Matter* **2**: 293-303.
- [6] Favaro, M., Mendichi, R., Ossola, F., Russo, U., Simon, S., Tomasin, P., and Vigato, P.A. (2006), *Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering*, *Polymer Degradation and Stability* **91**: 3083-3096.
- [7] Hoffmann, P. (2009), *On the efficiency of stabilisation methods for large waterlogged wooden objects, and on how to choose a method*, In: Huisman & Strætkvern (eds). *Proceedings of the 10th ICOM Group on Wet Organic Archaeological Materials Conference*: 323-350, Amsterdam, Drukkeri Stampij, Amersfoot.
- [8] Rowell, R. M., and Barbour, R. J. (Eds.) (1990), *Archaeological wood: properties, chemistry, and preservation*, American Chemical Society, Washington DC, USA.
- [9] Jensen, P., and Schnell, U. (2004), *The implication of using low molecular weight PEG in impregnation of waterlogged archaeological wood prior to freeze-drying*. In Hoffmann, P., Strætkvern, K., Spriggs, J. A., and Gregory, D. (eds). *Proceedings of the 9th ICOM Group on Wet Organic Archaeological Materials Conference*: 279-307, Copenhagen.
- [10] Almkvist, G., and Persson, I. (2009), *Iron catalysed degradation processes in the Vasa*, In: Huisman & Strætkvern (eds). *Proceedings of the 10th ICOM Group on Wet Organic Archaeological Materials Conference*: 499-505, Amsterdam, Drukkeri Stampij, Amersfoot.
- [11] Wittköpper, M. (1998), *Der aktuelle Stand der Konservierung archäologischer Naßhölzer mit Melamin/Aminoharzen am Römisch-Germanischen Zentralmuseum*, *Arbeitsblätter für Restauratoren Gruppe 8: Holz Heft 2*: 277-282.
- [12] Wayne Smith, C. (2003), *Archaeological Conservation Using Polymers: Practical Applications for Organic Artifact Stabilization*, Texas A&M University Press, College Station, USA.
- [13] Chaumat, G., Albino, C., and Blanc, L. (2007), *Development of new consolidation treatments from fatty acid resin solution*, In: *Program and abstracts of papers and posters ICOM – WOAM Conference*, Amsterdam.
- [14] Colombini, M. P., Orlandi, M., Modugno, F., Tolppa, E.-L., Sardelli, M., Zoila, L., and Crestini, C. (2007), *Archaeological wood characterisation by PY/GC/MS, GC/MS, NMR and GPC techniques*, *Microchemical Journal* **85**: 164-173.
- [15] Shulga, G., Betkers, T., Shakels, V., Neiberte, B., Verovkins, A., Brovkina, J., Belous, O., Ambrazaitene, D., and Žukaiskaite, A. (2007), *Effect of the modification of lignocellulosic materials with a lignin-polymer complex on their mulching properties*, *BioResources* **2**(4): 572-582.
- [16] Terashima, N., Atalla, R.H., Ralph, S. A., Landucci, L.L., Litpierre, C., and Monties, B. (1996), *New Preparations of Lignin Polymer Models under Conditions that Approximate Cell Wall Lignification*, *Holtzforshung* **50**: 9-14.
- [17] Micic, M., Jeremic, M., Radotic, K., Mavers, M., and Leblanc, R.M. (2000), *Visualization of Artificial Lignin Supramolecular Structures*, *Scanning* **22**: 288-294.
- [18] Nagamatsu, Y., and Funaoka, M. (2003), *Design of recyclable matrixes from lignin-based polymer*, *Green Chemistry* **5**: 595-601.
- [19] Kataoka, T., and Kurimoto, Y. (2009), *Conservation of archaeological waterlogged wood by lignophenol*, In: Huisman & Strætkvern (eds). *Proceedings of the 10th ICOM Group on Wet Organic Archaeological Materials Conference*: 315-322, Amsterdam, Drukkeri Stampij, Amersfoot.
- [20] Crespy, D., Bozonnet, M., and Meier, M. (2008), *100 Years of Bakelite, the Material of a 1000 Uses*, *Angewandte Chemie International Edition* **47**: 3322-3328.
- [21] Monni, J., Alvila, L., and Pakkanen, T.T. (2007), *Structural and Physical Changes in Phenol-*

Formaldehyde Resol Resin, as a Function of the Degree of Condensation of the Resol Solution, Industrial & Engineering Chemical Research **46**: 6916-6924.

- [22] Huang, J., Xu, M., Ge, Q., Lin, M., Lin, Q., Chen, Y., Chu, J., Dai, L., and Zou, Y. (2005), *Controlled Synthesis of High-Ortho-Substitution Phenol-Formaldehyde Resins*, Journal of Applied Polymer Science **97**: 652-658.
- [23] Sleicher, H.M., and Everhart, J.L., *Mounting of small metallographic specimens and metal powders in Bakelite*, Metals & Alloys **5**, p. 59-60, 1934.
- [24] Ventikou, M. (1999), *Old treatment, New Problem: Bakelite as a Consolidant*, V & A conservation journal **32**: 5-7.
The paper is accessible at the time of writing at:
http://www.vam.ac.uk/res_cons/conservation/journal/journal32/oldtreatment32/index.html
- [25] Biek, L., Anstee, J.W., and Cripps, E.S. (1958), *A wooden bucket restored*, The museums journal **57**: 257-261.
- [26] Liu, Y., Zhang, C., Du, Z., and Li, H. (2006), *Preparation and Curing Kinetics of Bisphenol A Type Novolac Epoxy Resins*, Journal of Applied Polymer Science **99**: 858-868.
- [27] Conner, A.H., River, B.H., and Lorenz, L.F. (1986), *Carbohydrate modified phenol-formaldehyde resins*, Journal of Wood Chemistry and Technology **6**(4): 519-613.
- [28] Kumpinsky, E. (1995), *pH Effects on Phenol-Formaldehyde Runaway Reactions*, Industrial & Engineering Chemistry Research **34**(9): 3096-3101.
- [29] Turunen, M., Alvila, L., and Pakkanen, T.T. (2003), *J. Rainio, Modification of Phenol-Formaldehyde Resol Resins by Lignin, Starch, and Urea*, Journal of Applied Polymer Science **88**: 582-588.
- [30] Kharade, A.Y., and Kale, D.D. (1998), *Effect of lignin on phenolic novolak resins and moulding powder*, European Polymer Journal **34**(2): 201-205.
- [31] Thackray, A.C., Sammons, R.L., Macaskie, L.E., Yong, P., Lugg, H., and Marquis, P.M. (2004), *Bacterial biosynthesis of a calcium phosphate bone-substitute material*, Journal of Materials Science: Materials in Medicine **15**: 403-406.
- [32] Shin, Y., and Exarhos, G.J. (2007), *Conversion of cellulose materials into nanostructured ceramics by biomineralization*, Cellulose **14**: 269-279.
- [33] Giorgi, R., Chelazzi, D., and Bagleoni, P. (2009), *Nanoscience contribution to the preservation of acidic shipwrecks*, In: Huisman & Strætkvern (eds). Proceedings of the 10th ICOM Group on Wet Organic Archaeological Materials Conference: 525-534, Amsterdam, Drukkerij Stampij, Amersfoort.