

# Waterlogged Artifacts: The Challenge to Conservation

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Wood has been a plentiful and versatile material utilized by man since earliest times. From it were fashioned many things, including shelters, boats, tools, weapons, bowls and a host of other utilitarian and decorative articles. After such objects were lost, broken or otherwise abandoned, they ordinarily perished quickly from the agents of decay. Most burial conditions, whether on land or under water, are generally unfavourable for the preservation of wood and other organic substances; they are subject to deterioration by chemical processes and by attack of many kinds of bacteria and fungi. Many factors determine the nature and extent of wood degradation. These include the type of wood (soft or hard), the period of burial and a number of properties of the burial medium, such as moisture content, degree of aeration, pH, temperature and microbiological make-up.

However, wood does survive over long periods of time, under certain favourable conditions. When the environment surrounding the wood is anaerobic (oxygen free), for example, the destructive power of bacteria and fungi is drastically reduced, and wooden artifacts may be preserved for thousands of years. In marine burial, such conditions can be found at depths where temperatures are low and the water holds little dissolved oxygen. On land, the same favourable conditions are characteristic of bogs and other localities where archaeological wet sites are found. Here the pores of the soil, because they are saturated with water, do not permit entrance of oxygen. Once the original oxygen content of the soil layers is gone, the processes of degradation are slowed considerably. It would be wrong, however, to think that degradation ceases altogether. In anaerobic conditions, wood continues to decay due to anaerobic microorganisms and the hydrolytic action of acids in the soil or, in the case of marine burial, the salinity of the water.

Nevertheless, much wood survives sufficiently intact to allow it to be recovered. Since the upsurge of interest in archaeological excavation which took place in 19th-century Britain and Europe, waterlogged wood has appeared with regularity and in quantity. And, much of it is still lying in the basements of museums awaiting treatment. More recently, a wealth of waterlogged wood and other organic materials has been collected from excavations during the past few years at wet sites on the Pacific coast of North America. This amount of waterlogged material will undoubtedly increase, as archaeologists say that more and more wet sites will be found across the entire continent. Moreover, the growing interest in scuba diving during the past few decades or so, and its utilization and acceptance as an exploration tool, has resulted in the discovery of many underwater sites, especially along sea coasts. Locations are today known of literally hundreds of sunken wooden ships, which await the finances and expertise required to raise and conserve them. For all this

historically and scientifically irreplaceable material, the conservation profession must find suitable methods of stabilization and preservation.

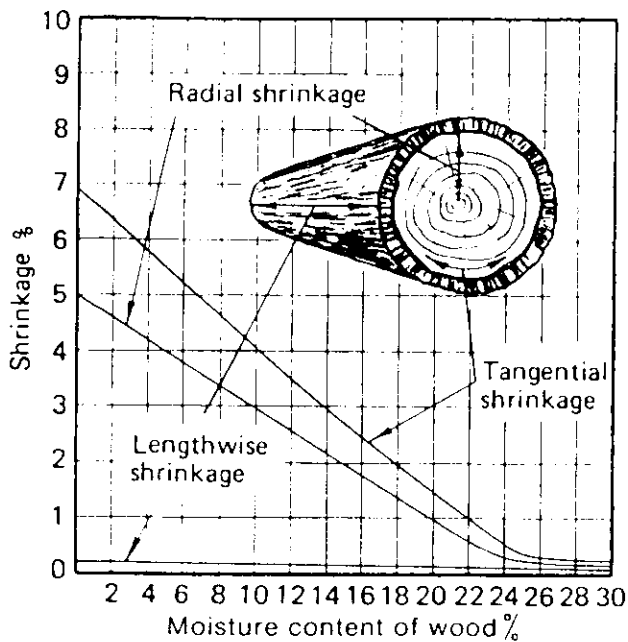
## The Nature of the Problem

Waterlogged wood when excavated may appear fresh and sound or, if badly degraded, may be soft, spongy, and almost black in colour. As wood becomes more and more degraded, its specific gravity and mechanical strength become lower and its permeability and porosity greater. Moreover, each piece of wood is quite unlike any other, and therefore one should expect it to behave quite differently when recovered and treated.

The mechanical strength of a piece of wood is provided mainly by the walls of the wood cells. In waterlogged wood that is badly degraded, these have normally undergone extensive decomposition resulting in a great loss of mechanical strength. Cell walls, made up largely of cellulose, lignin and hemicelluloses, contain multitudes of submicroscopic capillaries. The cellulose chains of the cell walls contain alternating crystalline and amorphous regions. Water enters the amorphous regions and forms hydrogen bonds with the polar terminal groups, such as hydroxyl (OH), on the cellulose chain. Because water cannot enter the more closed crystalline regions, only adsorption takes place. The wood swells as this take-up of water continues, making available more sites, such as interstitial spaces, for adsorption bonding of water to occur. The amount of water adsorbed will reach an upper limiting value, known as the fibre saturation point (normally between 25-30% in fresh wood), which is dependent upon humidity and, to a lesser extent, temperature. This water, known as hygroscopic water, will remain in the wood after equilibrium has been reached with the ambient humidity. Beyond this point, for example when the wood is soaked in water, free water fills the voids until total saturation takes place.

In badly degraded waterlogged wood, after most of the cellulose and hemicellulose have disappeared, the average diameter of the submicroscopic capillaries has increased, resulting in a corresponding decrease in surface area and producing many more voids to be filled with free water. In waterlogged wood, free water acts first as a bulking agent helping the wood to retain its shape; second, by bonding to the hydroxyl groups of the remaining cellulose, it prevents them from bonding with each other and forcing a shrinkage of the cell wall inwards. This latter function is particularly important since, in waterlogged conditions, hydrolysis of the crystalline regions of the cell wall and the resulting depolymerized cellulose chains make available more polar terminal groups for bonding. Thus, the water is the conserving agent, and the wood will remain reasonably stable as long as it is kept

Shrinkage of wood.



Shrinkage and cracking of waterlogged wood resulting from uncontrolled drying.



wet. However, if allowed to dry, a number of rapid and damaging reactions occur.

Everyone is familiar with the tendency of wood to change its shape by swelling or shrinking with differing humidities. The wood will take up an amount of water, depending on the humidity level of the surrounding atmosphere, until an equilibrium is reached (equilibrium moisture content). In doing so, swelling occurs. When the wet wood is transferred to a drier environment, this water is lost, with accompanying shrinkage, until equilibrium conditions are again reached. However, the exact former dimensions and moisture content of the wood are never reached (hysteresis effect). The magnitude of the dimensional changes are proportional to the magnitude of the humidity changes. With sound wood, and wood that is not too badly degraded, shrinkage occurs in an anisotropic fashion, that is, varying in three major directions. In sound wood, the shrinkage in the longitudinal or fibre direction is generally small, averaging less than 0.5%. This increases to between 3%

and 6% for shrinkage in the radial direction, and between 5% and 10% for the tangential direction. Shrinkage and cracking in badly deteriorated waterlogged wood will be less well differentiated than in sound wood. Depending upon the nature of the decomposition, waterlogged wood can decompose completely on drying. Hence, when dried in air, waterlogged wood displays this abnormal behaviour and shrinks, cracks, and warps. Unfortunately, these changes are irreversible. Once degraded wood has dried out, it will not return to its original dimensions. One possible explanation is that the polar groups on adjacent cellulose molecules bond together and are therefore unavailable for future water adsorption. Another equally important cause is the aspiration of pits, which are openings in the cell wall for water transport.

can be React.

Why do these severe dimensional changes occur? When wood is allowed to dry, the free water is the first to evaporate. In sound wood, this will occur without shrinkage until the fibre saturation point is reached and hygroscopic water begins to disappear. With badly degraded wood, in which the water content can be more than 100% based on the dry weight, the shrinkage occurs well before this point, even at relative humidities as high as 98%. When the structure of the wood is greatly disordered and weakened, the surface tension of the receding water is greater than the strength of the remaining cell walls, and they collapse inwards. Furthermore, as already described, polar groups on the cellulose molecules tend to bond together when water is not present to neutralize the effect. The result is a collapsing inwards of the cell walls. These two factors cause the wood to shrink, crack, twist and warp. We now see that it is this resistance to drying, with the resultant dimensional changes, that makes the conservation of waterlogged wood such a problem.

### Approaches to Conservation

The conservation of waterlogged organic materials involves primarily the cleaning and stabilization of objects against further decay. Wooden objects saturated with water must normally be cleaned for two reasons. First, the greatly increased porosity of waterlogged wood and the lengthy burial in environments containing foreign organic materials and mineral products lead to the build-up of considerable extraneous material within the wood structure. This foreign material may act as a bulking agent and restrict shrinkage due to drying, but when conservation is attempted, it prevents the penetration of consolidants.

Second, when a wooden object or wood-related substance such as bark is unearthed, the archaeologist often sees a rapid darkening of its colour. Although the phenomenon obviously takes place when objects are exposed to the air, the specific causes of it are not fully understood. (Archaeologists digging at the Kwatna Site on the central British Columbia coast reported that plant fibre specimens were already unusually dark when excavated, indicating that they may not have been buried quickly but were exposed to the atmosphere for some time during waterlogging.) Cleaning, necessary in order to retrieve the original lighter appearance of such materials, is done in a variety of ways with varying degrees of success. Use has been made of mechanical methods (fine water jets or brushing) and chemicals (acids or sequestering agents).

For many obvious practical and aesthetic reasons, the water in a recovered waterlogged artifact must be removed. The aim of stabilization is to remove it in such



*Waterlogged perishable artifacts must be kept in water, often including a fungicide, until treatment. At the CCI laboratory, wooden objects from the Lachane Site are continuously washed with running water for several months before treatment. This removes some of the extraneous material which adheres to the object after centuries of burial.*

a way that little or no dimensional changes occur to the wood, and so that the object can be kept at normal museum conditions (typically 65% relative humidity and 20°C temperature). Because wood swells when saturated with water, one must decide whether the object when conserved should have the same size and shape as when newly made or as when found. Experience, I think, shows that we can only attempt to approximate the size and shape when found. Badly deteriorated wood often requires improvement of its mechanical properties, so that it can sustain its own weight and be easily handled. Also, the treatment must leave the wood with an acceptable appearance as regards surface texture and colour. And, the treatment should, if possible, be reversible. Any materials added to the wood should be easily removable in the event that time shows the added materials are in some way damaging the object.

— The stabilization method one chooses to use will depend partly on whether one wishes the treated wood to behave as natural wood and be responsive to temperature and humidity changes, or whether the wood is to be altered to such an extent that it no longer behaves like the natural product. In the latter case, it essentially becomes a synthetic material resembling the original wooden object only in appearance and size.

— Five basic approaches to the dimensional stabilization of wood are: (1) the total or partial bulking of the spaces within the cell walls, normally occupied by water, with a solid material which prevents collapse and increases the mechanical strength of the wood; (2) the removal of free water in such a way as to avoid normal drying stresses; (3) the reduction of the permeability of wood to water vapour by use of internal or external coatings; (4) the chemical modification of the structural units of wood to reduce its hygroscopicity; (5) the chemical cross-linking of the wood's structural units to restrict swelling or shrinkage and to increase mechanical strength. Of these alternatives, the first two have been most extensively used and studied. It can be seen also that two or more approaches might be included in a single treatment.

### Older Conservation Methods

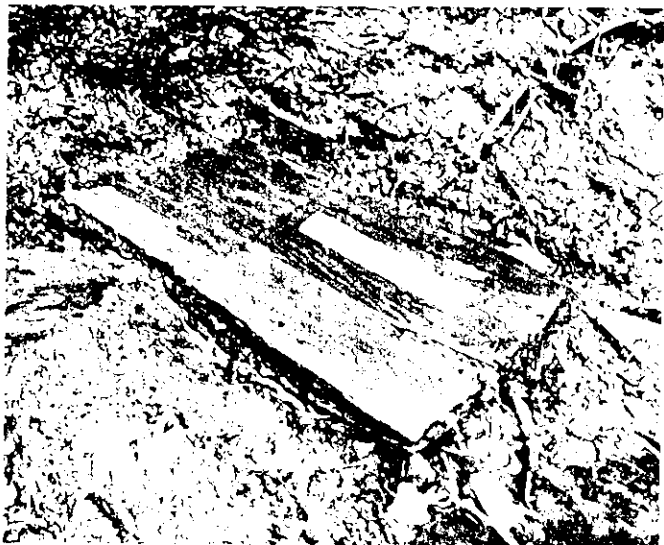
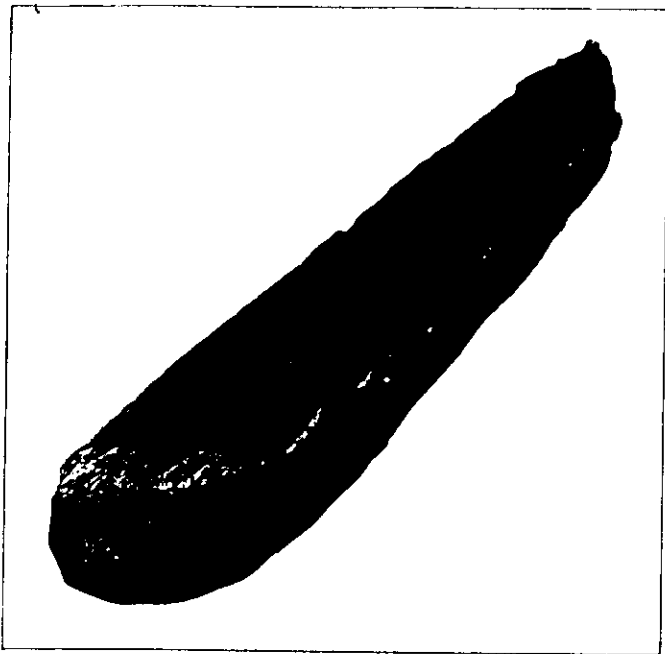
Little documentation exists which records early attempts to conserve waterlogged wooden objects.

Rather, conservators of the past viewed the tendency of wood to shrink and distort as inevitable, and the problem was largely ignored.

In the mid-19th century, the archaeological assistant to King Frederik VII of Denmark, a man named Jørgensen, made reference to the so-called alum method for treating waterlogged wood. This technique, with modifications, was used as the standard waterlogged wood treatment method by the National Museum of Denmark for almost 100 years. Initially, the method involved soaking the wood in a hot (95°-100°C) super-saturated solution of alum (potassium aluminum sulphate,  $K Al (SO_4)_2 \cdot 12H_2O$ ). The object was boiled in the solution for at least two hours and was then allowed to dry slowly. The aim of this method was to replace the free water in the wood with the solid alum.

Subsequent modifications involved the absorption of linseed oil into the alum-impregnated wood, and then varnishing the dried object to prevent any further intake of moisture. At a later date, the linseed oil/varnish impregnation step was replaced by continuously coating objects with a gelatin "glue" solution. Attempts to use glycerol and glycerol jelly in place of the alum were discouraging, but led to the adoption of an alum-glycerol-water bath for treatment. Later modifications dealt more with finding a suitable surface coating than with replacing the alum. Coatings used included shellac, beeswax, nitrocellulose varnishes, various oils and others.

While many treatments have been successful with the alum method, it is nowadays generally considered unsuitable. Its use was abandoned by the National Museums of Denmark in 1962. The reasons for this are not very difficult to find. Examinations of unsuccessful alum treatments have shown that in many cases the impregnation was incomplete, the alum penetrating only the surface to a depth of a few millimetres. Moreover, alum itself is hygroscopic and dissolves in a small amount of water, so it is easily affected by humidity changes. The addition of glycerol makes this problem worse. Glycerol is significantly hygroscopic, easily taking up moisture in damp surroundings and losing it in dry conditions. Thus the treatment itself encourages dimensional changes and cracking of the wood. The increased absorption of water caused by the glycerol, followed by drying, results in successive stages of solution and crystallization of the



Top to bottom: a waterlogged dugout canoe recovered from a lake at Maniwaki, Quebec, and presently at the CCI for treatment; cedarbark rope from the prehistoric village site at Ozette on the coast of Washington [see page 5]; a collapsed red cedar box in a wet deposit at the Lachane Site, northern British Columbia, where over 400 perishable artifacts were found.

alum. This results in increased cracking and often the migration of alum to the surface where it is deposited as an unsightly white powder. Furthermore, glycerol can impart an undesirable sheen to the surface of an object, and often produces a strong odour. It is also said to increase mould growth.

In treating objects by the alum method, one must also carefully control the humidity of the surrounding atmosphere. Artifacts poorly treated with alum have been recovered by dissolving out the alum with water, dehydrating with acetone, replacing the acetone with white spirit, and then, after heating to 60°C, adding paraffin wax until the bath has reached a high concentration. Reported results of this technique have been quite encouraging.

One common fault of early experimenters with waterlogged conservation techniques was their failure to keep adequate records of treatments. Generally, only hints are left as to what was actually used. Treatments which have been recorded include: the use of a solution of gum dammar in benzol for impregnation, followed by surface treatment with a wax-bitumen mixture; the impregnation with a solution of gum dammar in ethyl ether; and the slow drying of fairly sound timbers, accompanied by surface applications of a mixture of linseed oil and kerosene.

Probably the first application of the use of synthetic polymers took place in 1936, when the American scientist A.J. Stamm, after trying several, found phenol formaldehyde resins to be the best. This was followed by several attempts using cellulose nitrate solutions. Perhaps the most important advancement, in light of present treatments, was in 1956 when Stamm introduced the use of carbowaxes or polyethylene glycols. This date might conveniently be taken as the starting point of modern approaches to conserving waterlogged materials.

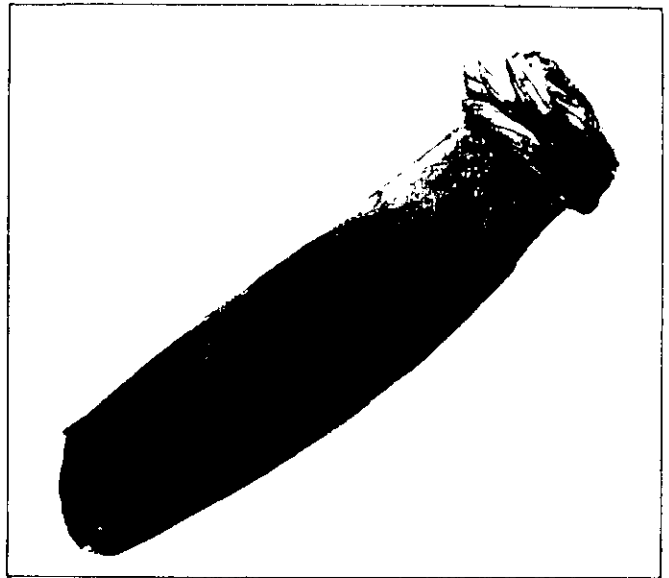
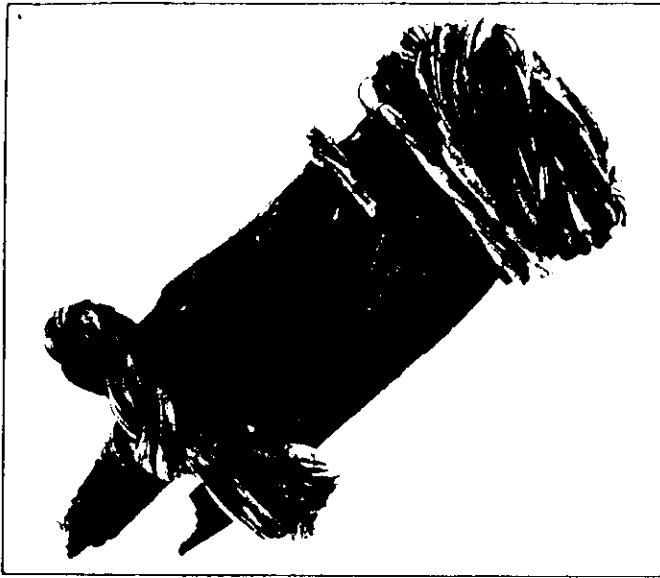
### Modern Conservation Approaches

Conservation of an artifact should begin, ideally, the moment it is found in an archaeological site. The object should be kept wet at all times, whether in transport or in storage — at no time should it be allowed to dry out. To prevent continued or renewed deterioration, it should be treated with a biocide. If one knows which treatment method will be used, this can be started while the object is in storage. The example, an object to be treated with polyethylene glycol can be stored in a solution of it.

The practical methods that have been followed over the past decade or so are best discussed within the framework of the five basic approaches listed previously. There are perhaps three major factors which determine the choice and likelihood of success of a conservation method. These are the kind of wood, the degree of decay, and the size of the object. The effects of these parameters will be discussed in the following descriptions of treatments.

#### [1] Total or partial bulking

In this operation, the water which fills the spaces between the cell walls is replaced by a non-volatile solid which prevents collapse and increases the mechanical strength of the wood. This can be achieved in various ways. Solid material can be introduced as a solution in water or an organic solvent at room temperature or at elevated temperatures. Or, if the melting point of the solid is reasonably low, the molten material can be used directly. In the first case, the water or solvent is allowed to evaporate, leaving the solid behind in the wood.



Two wooden wedges from prehistoric wet sites. The wedge on the left was treated with polyvinyl acetate in the field and then allowed to dry out. The other was treated at the CCI with the alcohol-ether dehydration method, using rosin for impregnation.

The ease of penetration depends largely on the size and shape of the molecules and the viscosity and concentration of the liquid. Alternatively, solids can be deposited in the wood by first impregnating it with a liquid monomer or resinoid, which is then polymerized or condensed with high-energy gamma radiation, heat or a catalyst.

A number of methods, which fall into a miscellaneous category, have been tried with varying results. For example, a mixture of stearyl and cetyl alcohols obtained from spermaceti oil, known as Cetalol S.A., has been used. After initial dehydration in ethanol, the wood was kept in a molten bath (60°C) of Cetalol for several days. On removal, the wood twisted and developed cracks. In another experiment, a similar substance derived from spermaceti oil also met with little success. The wood was immersed in molten Jasperol (sulphonated fatty alcohols) for several days, but had an unacceptable soft, waxy appearance after treatment.

Impregnation of wood using electrokinetic techniques has been done in Poland. The piece of wood to be treated was suspended between metal electrodes across which a current was passed. The potential drop between the electrodes encouraged liquids to migrate towards the negative electrode and, in so doing, impregnate the wood with different inorganic materials. These included single solutions and mixtures of water glass ( $\text{Na}_2\text{O} \cdot \text{SiO}_2$ ), calcium chloride ( $\text{CaCl}_2$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and others. It was also found that the method worked equally well when the solution was replaced with sand saturated with the solution. This enabled in situ treatments at an archaeological site to be carried out. Unfortunately, the promising results reported have not yet been reproduced elsewhere.

Hardening and structural stabilization of wood has been reported following treatment in aqueous solutions of sodium bichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) and chromium trioxide ( $\text{CrO}_3$ ), which after chemical modification within the wood are deposited as chromium chromate ( $\text{Cr}_2(\text{CrO}_4)_3$ ) and calcium chromate ( $\text{Ca}_2\text{CrO}_4$ ). As a final step, the wood is given a protective coating by immersion in linseed oil. A recent paper describes the successful use of tetraethyl orthosilicate for preserving waterlogged archaeological materials. Two quite com-

mon substances, sucrose and sodium chloride, have been shown from preliminary studies to have greater shrinkage-restraining effects than polyethylene glycol.

Finally, concluding this list of miscellaneous methods, is the use of water soluble organic materials such as methyl cellulose, polyvinyl acetate and polybutyl methacrylate. In general, these have not been successful. The degree of penetration is not good and gives little protection against shrinkage and warping. However, there is some prevention of surface checking.

A method that has proved over the years to be excellent for the treatment of small timbers is the *alcohol-ether-dammar resin method*. Derived from the work of B. Brorson Christensen in Copenhagen, this method involves the slow dehydration of the wood using successive changes of ethanol. This is accomplished over a period of several weeks. When dehydration is completed, the alcohol is exchanged for ethyl ether. After being in ethyl ether for approximately two weeks, the wood is placed in a bath of ethyl ether saturated with dammar resin for a further two or three weeks before being allowed to dry. The treated wood usually has a light brown colour and a generally natural appearance. It usually shows only a slight tendency to crack or warp. Occasionally a mixture of dammar resin and rosin (colophony) is used, and results with this are good as well.

Unfortunately, because ethyl ether is extremely flammable and has strong narcotic effects, it is not suitable for use on a large scale without complicated and extensive facilities.

The *polyethylene glycol method* is, at the present time, considered to be the most suitable way of stabilizing waterlogged wood. Polyethylene glycols (carbawaxes) are polymers of ethylene oxide with the general formula  $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$ , where  $n$  represents the average number of oxyethylene gaps. All polyethylene glycols, except polyethylene glycol 1500 (recently redesignated 540), are designated by a number that approximates the average molecular weight. From the point of view of waterlogged wood, the most useful property of these polymers is that they are all soluble in water and also in many organic solvents. With increasing molecular weight, water solubility, vapour pressure and hygroscopicity decrease, whereas freezing or melting



range and viscosity increase. In appearance, they range from clear viscous liquids (lower molecular weights 200-600) to white, waxy solids (higher molecular weights 1000-6000).

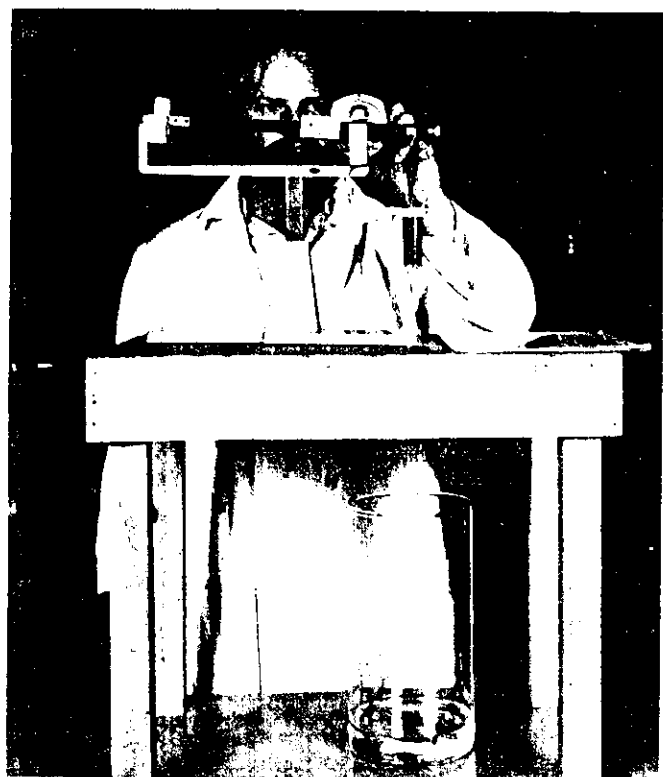
Ease of penetration into the wood depends on the size and shape of the penetrating molecules, which increase with increasing molecular weight. In polyethylene glycol 4000, the size of the molecule is approximately 250 angstroms when it is in stretched form. If the molecule is in coiled form, it could be too large to pass through the pit pores of the wood, and hence penetration would be greatly reduced. More badly degraded wood allows use of higher molecular weight polymers. As a general rule, the less badly degraded is the wood, the lower the molecular weight polyethylene glycol must be used. This is particularly true when treating objects fashioned from the heartwood of oak. In the living tree, movement of water ceases in the heartwood and tannins are deposited which prevent decay, therefore, ironically, making treatment more difficult. Eventually, vessels become blocked by growths called tyloses (this occurrence is particularly prevalent in white oak, which was widely used for ship-building). Iron, which is often present in some quantity in waterlogged wood, also has a preservative effect. When iron compounds are present, they block movement of polyethylene glycols and probably catalyse the depolymerization of the polymers.

There have been two main approaches to the treatment of wood with polyethylene glycols. One involves spraying the wood constantly with a polyethylene glycol solution. To treat parts of the hull of the Swedish warship *Wasa*, which was raised from Stockholm harbour in 1961, a 35% solution of the 4000 grade was sprayed onto the oak timbers which were being slowly dried at a relative humidity of around 70%. A mean concentration of about 40% polymer was achieved, the surface naturally being considerably higher. If one disregards, for the moment, the question of how much impregnation actually takes place, the main drawback to this process is the length of time the treatment takes.

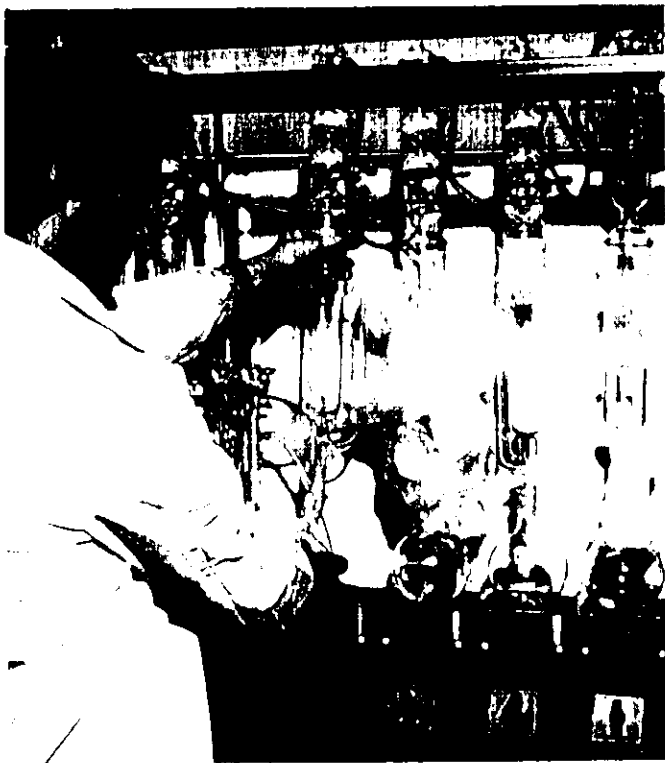
The treatment can be speeded up considerably by placing the wood in a heated bath of polyethylene glycol solution. A typical treatment would be to place the wood in a low concentration of the polymer (typically 10%) which is maintained at 60°C. The concentration of the polymer is then gradually increased on a daily basis by additions of the pure material. This can be continued until a sufficiently high concentration of polymer has been obtained. Some experimental work suggests that the treatment is probably completed when a concentration of 70-80% has been reached. During this process, the original volume of water is maintained. Finally, the wood is cleaned of excess polymer and allowed to dry slowly.

Tanks for this process have been fabricated from stainless steel, heavy-duty polyethylene and fibreglass. Copper, zinc, iron and aluminum are not suitable since they can cause depolymerization of the polyethylene glycol.

Impregnation of waterlogged wood with materials such as polyethylene glycol is largely a process of diffusion. That is, water passes out of the wood while the polymer diffuses into it. The rate of diffusion is expressed by the diffusion constant, which is inversely proportional to the molecular weight of the compound. Thus we can say that the time taken for a particular substance to diffuse will be proportional to its molecular weight. Polyethylene glycol 1000 will diffuse approximately 18 times slower than ethanol, which has a molecular weight of 55. Dilute



*During consolidation of a waterlogged wooden object, a conservator can periodically measure its specific gravity to check the progress of the treatment. As the water exchanges with other liquids or solids, the specific gravity also changes. This Inuit figurine [top], carved in Dorset style but found in the remains of a Thule house, is from the Grinnell Peninsula of northwestern Devon Island, and dates to roughly 1200 A.D. Although it was excavated from permafrost, the carving can be considered waterlogged with respect to treatment.*



Chemical analysis for lignin and cellulose provides an indication of how badly degraded a piece of wood is. Here, a CCI scientist tests for the amount of lignin, which can remain in wood after years of burial, simply by removing the cellulose, easily hydrolyzed by acids, and weighing what is left.

solutions will have a proportionately higher diffusion constant than concentrated solutions, and it is for this reason that treatment is commenced at low concentrations where the diffusion constant of the solution is comparable to that of water. If too high a concentration is used at the beginning, partial dehydration of the wood — and irreparable damage — can occur while the wood is in the treatment bath. This happens when water diffuses out of the wood at a much faster rate than the concentrated polymer solution can replace it. This often leads to consolidation of the surface zones only, and not the interior of the object. High temperatures seem to make this problem worse, especially with sound oak. Similarly, overtreatment, that is, continuation of the treatment until the solution has a high concentration, is also damaging and uneconomic. This tendency results in the wood having a very low water content (less than 10%), which is far less than the ultimate equilibrium water content after treatment (20-30%) when the object is maintained at ambient conditions.

In summary, from the accumulated data of treatments with polyethylene glycols, we can say that the condition of the wood dictates which grade of polyethylene glycol can be used. Badly degraded material can be treated with high molecular weight grades, whereas reasonably sound timbers can only be treated with lower molecular weight grades. A molecular weight of around 3000 has been mentioned as the maximum size which will penetrate reasonably sound wood. The lower molecular weight grades are unfortunately quite hygroscopic, and objects treated with these grades are unsuitable for handling and require carefully controlled environments for display.

Although polyethylene glycols are extensively used, their suitability for other than small objects is being questioned. It appears that the size of an object could be the determining factor in whether a polyethylene glycol treatment is successful or not. In large timbers, penetration appears to be confined in many cases to the external zones. Unfortunately, in the majority of examples, a high degree of consolidation appears necessary for lasting stabilization.

The *acetone-rosin method* was developed specifically for the treatment of large, sound, waterlogged oak timbers, which have proved extremely difficult to conserve using polyethylene glycol. The wood is given an initial treatment in hydrochloric acid (3%) in an attempt to remove extraneous deposits and to restore the usually darkened oak to its original lighter colour. After the excess acid has been removed by washing in water, the wood is dehydrated in several changes of acetone. Then rosin (colophony) is added to the bath and the temperature raised to 51°C, the concentration of rosin at this temperature reaching 67%. After treatment, the excess rosin is removed with acetone swabs or fumes.

Dimensional stability of the oak after the acetone-rosin treatment is greatly improved, and there is little or no cracking or splitting. The object is lighter in colour (although not as natural a colour as obtained with the alcohol-ether-resin method), and has a weight approximately the same as before being waterlogged. Polyethylene glycols, on the other hand, leave the wood dark in colour and quite heavy. Preliminary studies using the scanning electron microscope show that, in small objects, the rosin penetrates all of the cells to give good stabilization and strength.

Whether or not the acetone-rosin method can be successfully used for very large timbers is not yet certain. Of obvious concern is the highly flammable nature of acetone. Again, facilities meeting proper safety requirements would be expensive to construct and in many places would require specially designed fire-proof and explosion-proof buildings.

A method involving the *in situ* polymerization of monomers has been a subject of research in recent years. (*In situ* is not used here in any archaeological sense, but refers to what is done to the monomer while it is in the wood.) The waterlogged wood is stabilized by impregnating it with monomers and then polymerizing *in situ*, either by high energy gamma radiation, by the use of chemical catalysts or by heat. Polymeric systems which have been studied, either for conservation or industrial applications, include styrene/divinyl benzene, vinyl

chloride, vinyl acetate/styrene, methyl methacrylate, butyl-methacrylate, and 2-hydroxyethyl methacrylate. In a similar way, oligomers of methyl methacrylate and dimethyl siloxane have been used.

Some of the advantages gained by using such a treatment derive from the fact that monomers have low molecular weights; hence the diffusion coefficients of the pure liquid or its solutions are similar to that of water and other solvents. This means that some of the problems encountered in the polyethylene glycol method are removed. Similarly, the small size of a monomer makes penetration into the wood easier.

Results of in situ polymerization of monomers to date are quite promising, and usually show greatly improved dimensional stability of the wood with little shrinkage. In some cases, however, the wood has been left with an unacceptable, high gloss. With gamma ray polymerization, the immediate drawback is the very expensive requirement for irradiation facilities. And, the fact that some monomers are not water soluble means that the wood first has to be dehydrated. This could be a problem with large timbers when large volumes of solvents would have to be used.

*Impregnation with synthetic resins* involves the use of low molecular weight resin systems, such as urea-formaldehyde, melamine-formaldehyde (Arigal-C) and phenol-formaldehyde. The condensation products formed have been shown to reduce the shrinkage and increase the strength of the wood. The Arigal-C method, however, which is perhaps the best known, often causes the treated wood to have a whitish, bright appearance and does not always prevent splitting and cracking.

A recent and rather novel treatment involves soaking the wood in a sugar solution, then chemically modifying the sugar to produce an aqueous resin solution. The addition of a catalyst, followed by heat curing, results in the formation of a water insoluble, inextractable material within the wood. The results are reportedly good.

Resin systems have been used somewhat successfully in treating waterlogged wood. However, the short time required for condensation to occur is not suitable for large timbers where impregnation would be slower. This problem could disappear with the continuing industrial advances being made in the area of resin systems.

## [2] *Removal of free water*

Removing free water from wood must be accomplished in such a way that drying stresses are avoided. The damage caused to wood by the receding water surface on drying is due to the high surface tension of water. Attempts have been made to prevent this damage by replacing the water with a solvent with a lower surface tension and then allowing the solvent to evaporate. Ethyl ether was first tried and, with very small objects, was somewhat successful. However, shrinkage did occur and the method was altered to include a consolidating agent — the alcohol-ether-resin method. A much more recent attempt using commercially available dewatering fluids was reported to be successful, but an evaluation by other workers suggested that dewatering fluids did not prevent shrinkage and deformation, and that any success had been due to the inherent soundness of the wood.

An alternative method is to replace the water with a liquid which, when frozen, can be removed by sublimation under vacuum. The essential feature is that sublimation takes place without a liquid phase being present. Trimethyl carbinol was the liquid of choice by several laboratories, but the results were not promising.

Cracking and checking appeared on many artifacts so treated.

Freeze-drying, a technique much used in the food industry, is now being used more and more in the conservation of waterlogged wood. In the freeze-drying method, no initial replacement of water is necessary. The water is simply sublimed away under vacuum. This requires that the vapour pressure of the water above the ice surface is less than that at the ice surface, a condition that can be achieved by the use of vacuum and a condenser. To collect the sublimed water vapour, the condenser must be considerably colder than the wood itself. To obtain a practical rate of sublimation, it is also necessary to heat the wood during the treatment. This is necessary to replace the latent heat of sublimation used in the conversion of solid ice to water vapour.

Initial freeze-drying experiments were reasonably successful, although the wood still suffered some shrinkage and cracking. This is due to the strain caused by rapid freezing of the wood (water undergoes a 12% volume increase on freezing) and the damage caused by the absorption of atmospheric moisture after the treatment. These problems were removed to a great extent by soaking the wood before freeze-drying in a 10% solution of polyethylene glycol 400. A 10% solution undergoes a volume increase on freezing less than half that of water. This, combined with the solution's low vapour pressure and low surface tension, greatly reduces damage. Results have generally been good, and work assessing the efficacy of this method for large timbers is in progress.

## [3] *Internal or external coatings*

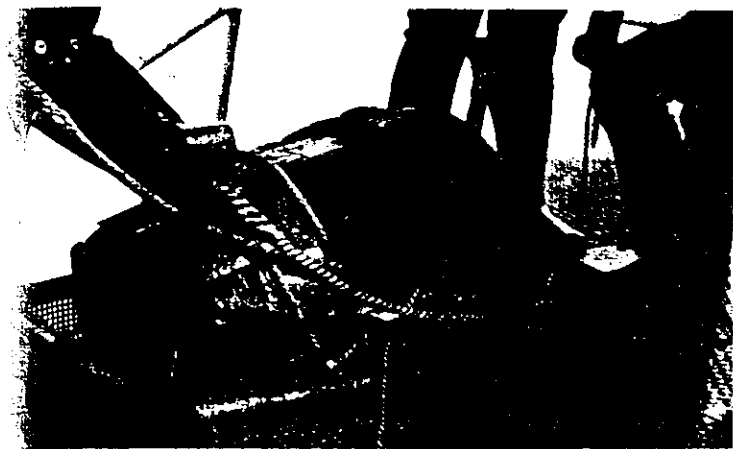
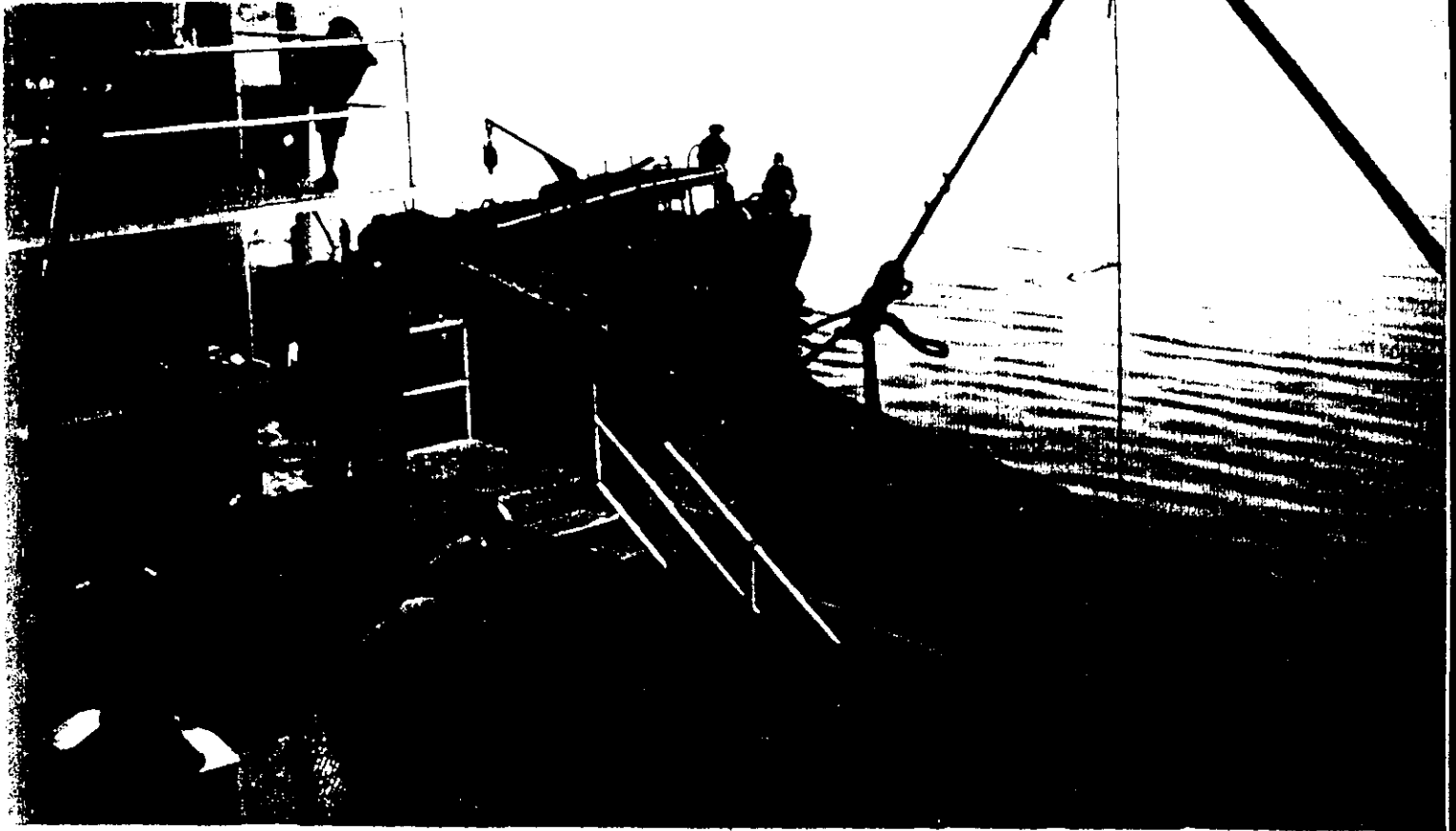
The use of surface coatings is aimed at reducing the permeability of wood to water vapour. Alternatively, partially coating the inner surfaces with so-called water repellents, such as waxes, has been tried in attempts to achieve the same effect. A wide variety of materials, from linseed oil to epoxy resins, have been used, but the results are generally unsatisfactory. The rates of swelling and shrinkage are reduced, but in the end the amount is not much altered. No dimensional stabilization is achieved.

## [4] *Reduction of the natural hygroscopicity of wood*

Attempts have been made to reduce hygroscopicity by chemically modifying the cellulose and lignin molecules. Acetylation has shown some success in industrial applications, although some of the success is thought to be due to bulking effects caused by interaction with the cell walls. Similar experiments done in the CCI's Conservation Processes Research laboratory on badly degraded wood were completely unsuccessful, probably because of damage caused to the wood structure by the acetylating agent. It appears likely that this method will not be successful until new and less powerful treating agents are found. One alternative might be to reduce the hygroscopic nature of the impregnating agents (for example, polyethylene glycol 400) before treatment. This has apparently been tried with isocyanates.

## [5] *Chemical cross-linking*

In this method, it is assumed that chemically linking the cellulose chains will prevent swelling due to moisture increases and will, therefore, confer dimensional stability to the wood. Formaldehyde, ethylene oxide and other materials have been tried, but with only limited success,



*Cables creaking, the three-ton rudder of the French frigate Machault is slowly raised from shallow water in the estuary of the Restigouche River near Campbellton, New Brunswick [above]. Built in 1758, the Machault carried supplies for French troops and was deliberately scuttled in 1760 when her passage was blocked by a British warship. Tidal mud apparently covered the vessel soon after, for it is remarkably well preserved. Massive portions of the hull, such as this midship section [below], were raised in one piece. The recovered cargo includes barrels of salt pork [left], glassware and fine porcelain, as well as military supplies such as cannonballs and other munitions. These items, and portions of the vessel itself, will be housed in an Interpretation Centre to be built near the wreck site by the National Historic Parks & Sites Branch.*

even in sound wood. This, as in the hygroscopicity reduction experiments, is due to the extreme conditions required for the reactions to occur.

### The Challenge of Waterlogged Materials

For the past few years, the status of conservation research has been hovering somewhere between that of a "kitchen art", complete with a book of established recipes, and that of a legitimate science. It is now becoming more and more apparent that to hope for any lasting success with conservation problems such as waterlogged wood, we must seek a far deeper understanding of the materials themselves as well as of the physical and chemical processes involved in their deterioration and preservation.

While much of the fog surrounding many conservation difficulties has been cleared away by research so far, imposing problems have yet to be overcome. For example, while there is no great difficulty involved in successfully treating small artifacts, quite formidable problems arise when one is required to treat very large

