

Abstract: *Over the last ten years an increasing number of sites with well preserved waterlogged deposits have been excavated. These have produced large numbers of finds made of organic materials, which have put new demands on existing conservation resources. Freeze-drying is one of the methods that has been developed to preserve waterlogged organic materials for study and display. It is quicker than the traditional PEG impregnation methods and on the whole the results are more reliable. To get consistently good results, however, a range of factors including the wood species and its condition have to be taken into consideration. There are some objects which are best treated by other methods and these are discussed, as well as the storage and display conditions required for freeze-dried wood.*

Introduction

Freeze-drying was originally developed to extend the storage time for biological materials such as viruses and foodstuffs. The water in these materials was frozen and then removed by sublimation, and the dried products could then be stored until required. This technique should not damage the cell structure, so that on the addition of water the organic material can be reconstituted and ready for use. With archaeological materials one is only concerned with the drying phase of the technique so that the objects can be stored and displayed in normal environmental conditions.

The technique is very effective at dehydrating waterlogged wood, but the method has three phases which can potentially cause additional damage to the wood cell structures - namely freezing, freeze-drying, and exposure of the dried material to normal temperatures and humidities. In order to overcome such problems, freeze-drying techniques have been modified by the introduction of a pretreatment stage, where some of the water inside the wood is replaced with a solute such as polyethylene glycol (PEG), or all of the water substituted by a high melting point alcohol, such as tertiary butyl alcohol (Jespersen 1979, 69-76). The freeze-drying can be accomplished either in a vacuum chamber or under suitable atmospheric conditions. This paper deals only with the freeze-drying of wood from aqueous PEG solutions under vacuum conditions, as few institutions in the UK can handle hazardous chemicals such as tertiary butyl alcohol on any scale, and our winter climate is not cold enough or of sufficient duration to attempt exterior atmospheric freeze-drying (Grattan and McCawley 1978, 157-67).

The conservation of waterlogged wood really needs to begin as soon as the material is exposed on site. Drying of the surface will produce cracks that cannot be closed by any conservation treatment, and obviously this can result in the loss of important surface detail. Where possible it is advisable to lift the wood soon after discovery, and store it in sealed polythene in cool, dark conditions to prevent the growth of fungi and algae. It is also a good idea to leave some of the soil on the surface to act as a buffer against drying out. Providing that the objects are dealt with rapidly there should be no need to use fungicides, which are not really effective in keeping

micro organisms at bay, yet can be toxic and in some cases affect radiocarbon dates.

When dealing with large groups of material it is worth having all the specialists on hand before cleaning the timbers, in order to minimise the delays before the wood can go into active treatment. After washing, all wood with visible tool marks should be recorded by photography (Lawler 1980, 35), and examined by specialists if available. At this point samples for dating and identification should be taken, and the decision made as to which conservation treatment to use.

Wood species and condition

The nature of waterlogged wood found on British excavations varies enormously, from massive structural timbers of heartwood oak, so hard they have to be sectioned for dendrochronology dating with a chain saw, to very degraded roundwood from prehistoric sites where the residual woody material comprises less than 10% of the wet weight. In between these two extremes are the many small personal items, tools, containers and utensils which are commonly well preserved but very fragile.

For conservation purposes wood can be divided by species into four groups (Watson 1981, 237-8): i) oak, ii) medium density woods such as ash, maple, beech and fruitwoods; iii) low density woods, mainly the coppiced woods such as alder, hazel, willow and poplar; and iv) conifers. This grouping gives an indication of the porosity and to some extent the residual woody tissue in a piece of timber. Obviously porosity affects the diffusion of consolidants and the removal of water vapour, and the extent of residual woody tissue will determine if the object can stand up to the drying stresses any treatment may put on it. The condition of waterlogged wood is normally expressed by its water content based on the oven dry weight; the oven dry weight is all that is left of the wood tissue plus minerals and is equal to 100%. The difference between this figure and the wet weight represents the amount of water in the sample and can be anything from 80% to in excess of 1000% (Hoffman 1981, 83).

The main features within wood which affect conservation are the vessels and rays. Vessels provide longitudinal transport of water and dissolved minerals in the living tree, and during conservation provide passageways for consolidating solutions and the removal of water vapour. Different wood species have vessels of differing sizes, and in some cases these are blocked by natural deposits. Ray cells provide the radial distribution of food materials, food stores, and are depositories of waste materials in the tree (Cutler 1975, 1.6). In archaeological wood these cells are often blocked with various deposits and can be impossible to penetrate with consolidating solutions. This results in surface cracking as, on drying, the wood will tend to crack along the rays, probably because the rays are naturally consolidated and do not shrink, unlike the adjacent wood fibres.

i) Oak is probably the most difficult wood to conserve, mainly because of the scale of the objects involved which are often large structural timbers. It is difficult to consolidate with polymers which have large

monocyles, as both the vessels and the rays are often blocked. Consequently oak is particularly prone to both cross-checking on radial surfaces and to wide cracks in tangential surfaces. The sapwood, if it survives, is usually very degraded while the heartwood remains dense and difficult to penetrate. The water content of the wood changes across the annual rings, with the heartwood containing between 150-250% of water, while the sapwood can contain 300-900%. The average water content of a piece of waterlogged oak is between 250-400%. On air-drying the sapwood tends to shrink and fragment, while the heartwood will crack radially.

The oak from many excavations has a high iron content. This is usually in the form of a sulphide which has become incorporated in the wood as a result of bacterial action (Hodgson and Thompson 1985, 46). The presence of these salts can interfere with the penetration of polymers, but more important, they will probably continue to oxidise in the treated wood releasing acids which will further degrade the wood. Iron salts tend to be insoluble in most chelating agents, and can only be dissolved in concentrated mineral acids which would cause considerable damage to the wood before having any effect on them (Watson 1984). Current research suggests that the oxidation of these iron salts may be suppressed by adding antioxidants to the pretreatment solutions (Cook *et al.* 1984), but this work is at an early stage of development.

ii) Medium density woods are usually recovered from excavations in the form of small domestic items. Such objects tend to be thin and fashioned three dimensionally so that any treatment which causes differential shrinkage produces warped objects. The water content of these items frequently falls in the range 400-900%.

iii) Low density woods are frequently found in a very degraded condition, with water contents between 300-900%. This group includes the coppiced woods which make up the structural elements on prehistoric sites such as trackways and wattle, so that individual objects can be quite large. Willow and poplar have the lowest density of these woods, which is approximately half that of oak. On air-drying the cells tend to collapse, and the object will twist and warp out of shape.

iv) Few conifers are recovered from British excavations. Only pine, juniper and yew are indigenous and these do not appear to have been used extensively. Roman sites have produced objects like writing tablets and barrels made of non-native conifers, such as larch, silver fir and cedar. When recovered, yew is commonly in good condition with little degradation. There are many instances where air-drying has been successful, for instance the long bows from the Mary Rose. The conifers treated by freeze-drying have responded well to this method, probably because their simple structure allows for the easy impregnation of PEG and the removal of frozen water vapour.

Fungal decay is a problem in all woods, as on drying affected items will tend to split and fragment. This decay is not always recognisable on the surface of the object, but can be seen in the thin sections taken to identify the wood species.

Pretreatment

Waterlogged wood should not be freeze-dried without some pretreatment, and solutions of polyethylene glycol (PEG) have been found particularly effective:

i) 20% PEG 400 is often used for little degraded wood: oak, box and other woods up to 400% moisture

content. Soaking time is between 1 to 6 months depending on the size of the object.

This concentration is used rather than the 10% recommended by Ambrose (1970) in order to prevent bacterial slimes forming in the soaking bath. At concentrations above 20% micro-organisms are dehydrated by osmosis and cannot survive.

ii) 10% PEG 400+15% PEG 4000. This is used on the more degraded pieces. Initially the wood is soaked in 10% PEG 400 for approximately one month, and then PEG 4000 is added to this bath in 5% increments at fortnightly intervals. Wood is then left in the final concentration for a further three months (Watson 1981, 241).

This will produce better results on wood that has been attacked by fungi before burial, or has accidentally dried out during excavation or storage, than the single PEG solution.

The concentration of PEG 4000 can be increased to 20-25% for very degraded wood; it is possible to remove the excess PEG with soft decorator's paintbrushes after freeze-drying. However, the PEG concentrations should not be increased above 55% as this is a water/PEG eutectic and could produce problems on freezing and during freeze-drying (Gratton 1981a, 179).

The reasons for using PEG 400 in a freeze-drying system are:

i) It sequesters minerals in solution so that they do not crystallise inside the wood before or during freezing. This is very important when iron pyrites is present, because when this mineral oxidises, gypsum is formed and this is taken up by the PEG. Otherwise gypsum will readily precipitate from solution, forming rosettes of prismatic crystals which, if large, rupture the wood cells and can cause collapse.

ii) It compensates for the expansion in volume when water freezes, and as PEG 400 has a molecular range it has fractionated freezing points: that is the different molecular weights freeze at slightly different temperatures. On freezing, ice crystallises out of solution first, and PEG can move to accommodate it (Ambrose 1976).

iii) PEG 400 can replace chemically bound water in the wood structure, making the treated wood more stable to fluctuating humidities at normal room temperatures. However, it seems that this reaction can only take place when all the bound water has been removed. It is essential that the temperature of the freeze drying chamber does not rise above -15° C, as if the wood is allowed to thaw during freeze drying, PEG solution migrates to the outer surfaces and remains there as a stain. The interior and underside are then starved of PEG and this results in cracking and cross-checking. On degraded low density woods this can cause severe cracking and warping.

PEG 4000 in a freeze-drying system acts purely as a bulking agent for the more degraded areas. At present there is no evidence to prove that it chemically bonds with cellulose.

If the wood requires consolidation, it is advisable to use PEG 4000 incorporated in the pretreatment rather than using a polymer in solvent after freeze drying (Watson 1981).

Freezing and freeze-drying

The wood is removed from the pretreatment solution and excess PEG is blotted off the surface. The objects are then wrapped in cling film or put into polythene bags,

excluding as much air as possible. It is essential that the surface is sealed before freezing, to prevent PEG migrating towards the surface as evaporation takes place (see above).

The sealed wood is then frozen. This can be done in the freeze drying chamber but most commonly a domestic deep freeze is used which can achieve temperatures of -18° to 23° C.

When frozen, the cling film is removed and the object placed in the freeze-drying chamber, at a temperature of -32° to -40° C. The wood is further chilled to -25° before applying a vacuum.

When freeze-drying begins the temperature of the outer frozen layers drops dramatically due to the loss of the latent heat of sublimation. As the ice front passes, the temperature of the dried wood increases. The sublimed water vapour migrates to the colder areas of the freeze-drier (external condenser, or internal condenser coils) where it condenses as solid ice. The loss of vapour from the ice surface is encouraged by applying a vacuum or by passing cooled air over the surface (Amoignon and Larrat 1984).

The rate of freeze drying is normally monitored by weighing, and when the weight is stable the drying phase is considered to be complete. This is more reliable than using temperature variation, as it is difficult to guarantee that thermocouples are placed exactly in the centre of the object.

The drying rate of a piece of wood will depend on three things:

i) Chamber conditions - if the temperatures are too low the rate of sublimation will be reduced, but above -15° C there is a risk of thawing. It is advisable to have the condenser 10° C colder than the chamber to encourage a reasonable rate of sublimation.

ii) Ratio of surface area to mass - thin objects will dry more rapidly than those with a large cross-section.

iii) Pretreatment solution used - the presence of PEG 4000 increases the freeze-drying time, probably because it blocks the exitways for the water vapour. If concentrations of PEG 4000 in excess of 40% are used, then heat may have to be applied in the later stages of drying to remove the last traces of water.

Results

Thin objects, such as bowls, freeze-dry very well and can be repaired and restored afterwards. A suitable adhesive for repairing freeze-dried wood is polyvinyl butyral (*Butvar B79*) (Keene 1981) made up in amyl acetate and acetone. Extensive gapfilling is difficult on treated items, but balsa thinly surfaced with BJK dough (Plenderleith and Werner 1971, 341) can produce satisfactory results. BJK dough on its own is heavy and hard, which can put a strain on the treated wood.

Providing the concentration of PEG 4000 is kept below 25%, the excess can easily be removed from the surface after drying. This means that important tool marks and decoration should not be damaged or smoothed out by the treatment, as can happen with other methods. However, after drying, fine detail may not appear as crisp as it was in the wet state, therefore it is a good idea to record essential detail before active conservation. Charred wood will not take up PEG 4000 and the excess will have to be removed after freeze drying with swabs of ethanol.

Objects made of wood and metal can be freeze-dried providing a recommended antioxidant is used (Cook *et al.* 1984).

Bark does not shrink as much as the wood, and seems to restrict the penetration of PEG into the interior. During freeze-drying it usually cracks severely and falls off, sometimes leaving the wood inside with cellular collapse. Better results can possibly be achieved using a standard PEG 4000 impregnation rather than freeze-drying.

Good results with freeze drying depend on the cellular structure of the waterlogged wood being intact and able to support its own weight. Objects that have dried out during excavation or prolonged storage will not respond well to freeze-drying. If the surface has begun to crack this will be enhanced by the treatment, not masked. Also wood that has been frozen without pretreatment cannot be treated by this method, because the wood structure is severely damaged during freezing. Wood that has been subjected to the physical stresses of drying or freezing responds better to PEG replacement methods.

Storage and display

Wood freeze-dried from PEG 400 should be less hygroscopic than dry wood, PEG 400 or PEG 4000 impregnated wood (Grattan 1981). It should therefore be able to withstand a range of humidities without adverse effect, the recommended range being between 45-60% RH for storage and display.

At normal to high humidities PEG is corrosive to most metals except for high quality stainless steel, and it is not advisable to use mild steel or brass pins for support in display. Obviously any contact between treated wood and archaeological metalwork should be avoided.

Low light levels should be recommended for display as both lignin and cellulose can be degraded by photo oxidation (Stamm 1970, 2).

During storage, treated wood should be kept in buffered packaging to try and maintain the local RH. Objects should be packed in cardboard boxes with soft tissue, these materials will absorb moisture and release a little if the environment becomes too dry. Often timbers are too large for standard cardboard boxes, and larger boxes can be made from corrugated plastic sheeting.

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