Bruno MÜHLETHALER

CONSERVATION OF WATERLOGGED WOOD AND WET LEATHER

EYROLLES

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Centre international d'études pour la conservation et la restauration
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TRAVAUX ET PUBLICATIONS

XI

CONSERVATION OF WATERLOGGED WOOD AND WET LEATHER

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EDITIONS EYROLLES
61, boulevard Saint-Germain — PARIS-V^e
1973

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Table of contents

1

INTRODUCTION

The problem of the conservation of waterlogged wood from finds in the ground or from fresh or sea-water can be at present considered as solved for smaller objects. If the subsequent climatic condition of storage do not present any extreme fluctuations, one can pick and choose to-day among various methods and even take into account other aspects depending on the techniques of conservation, such as energy consumption, costs or aesthetic demands. Extreme climatic conditions cut down the possibility of choice with increasing size of the wooden objects. In the case of large objects, ships, bridges, etc., the least dimensional changes (shrinkage due to the variation of the water-content percentage) are summed up, so that, for instance, the separate parts of a large object can no longer be fitted together. L. Barkmann (unpublished report) concludes from a series of tests with polyethylene glycols 1 500 and 4 000 on oak wood from the Wasa warship that penetration and distribution are not sufficient to avoid shrinkage satisfactorily. The same result has been obtained from all experiments and this is also clearly expressed by B. Brorson-Christensen [107], that consolidation of waterlogged wood *without contraction of any kind* is almost impossible.

Nevertheless, for large scale treatment of huge objects at present polyethylene glycols only can come into strong consideration, provided that low molecular grades of up to 1 000 of polyethylene glycols are used and the treatment be over a lengthy period. There exist indications that improvements can be achieved with the use of monomeric plastic substances.

2

a) Typical properties of waterlogged wood

When wood has remained for a long time in a medium saturated with water structural changes appear. The chemical and physical processes have changed the wood substance. Along with them fungi and microorganisms are active. The kind and the extent of the process of degradation are determined [1] by the initial composition and structure of the wood,i. e. of the wood species and the history of its growth (the chemical composition comprises also the extractives, metabolites and the substances which had entered from outside into the cell cavities and the intercellular space) and [2] by the ambient conditions, the medium, humidity, temperature, airing, pH value, etc. These conditions of the ambient medium determine the species of microorganisms which actually bring about the degradation of wood. Under the surface of the soil or in water, with only little oxygen, they are anaërobic microorganisms. It is known that they play a greater role in degradation than purely chemical effects ; the exotic woods whose resinous extractives have a rot-inhibiting effect, are preserved under rigorous marshy or primaeval-forest conditions incomparably better than the middle-European coniferous woods rich in resin under much milder conditions. Another factor for the type and extent of the degradation is the duration of the action of aërobic fungus communities on the wood, prior to its having sunk under the soil or into water ; the destruction which had taken place in the air, when the wood was a part of a used or a derelict construction facilitates the subsequent anaërobic degradation. The third important factor the degradation of the wood is the duration of the various effects.

Detailed studies into the microbial degradation processes were conducted, in the first place, in Japan, India, Russia and France. After the soluble wood extractives had disappeared by hydrolysis into the surrounding medium there takes place, firstly, a hydrolysis of the not very stable hemicelluloses (pectins, pentosans). The more stable hemicelluloses (galactones, polyuronides) are attacked only by a few specific microorganisms. The decomposition of the cellulose occurs in parallel or simultaneously. There remain finally the stable lignin substances. It is true that an anaerobic degradation of lignin has been established already [1-17].

The chemical changes due to microorganisms are characteristic of the species. The species of the microorganisms can be recognized on the basis of metabolites. However this becones difficult or impossible when, after a protracted storage in water, the specific degradation products have diffused away.

The few research papers [17] dealing with the microscopic investigations of waterlogged archaeological wood point to two forms of decomposition of the cell walls, that is of the structural elements of the wood, which are responsible for mechanical strength. The first from begins in the interior of the cell with the degradation of the tertiary wall, and proceeds outwards (figs. 1, 2a, 2b) ; the other form (fig. 4) starts from the peripheral parts of the secondary wall, shifts (with the dissolution of the middle lamella) to the adjacent cells, and thus dissolves the cell bonding. In the former case there remains a very brittle wood which, upon drying, shrinks strongly and alters its form. Such wood withstands very little the penetration of liquids. Besides sapwood, also heartwood undergoes a decomposition of this kind. Oak wood is considered a special case. In places with a high concentration of tannins one observes slight degradation phenomena ; in particular the medullar rays remain often well preserved (fig. 3).

In the second form of decomposition wood loses its anatomical structure and disintegrates completely after drying. As a rule, such forms of decomposition do not spread over the entire piece, but are locally limited.

The knowledge of the behaviour of waterlogged wood at normal air humidity [18-21] is of importance for the evaluation of the possibility of conservation. If wood of a relatively recent felling, which became completely saturated as a result of protracted soaking in water, is exposed to air, it dries up to an extent at which an equilibrium has been attained

FIG. 1. — Cross-section of a fir stem from the pheriphery to the pith. Fully deteriorated zones are marked with black patches. The more extended area where cell walls have altered their structure is marked with dots and indicates important alteration of the inner structure of wood.

(*Drawings by O.N. Chistyakova*) [17].

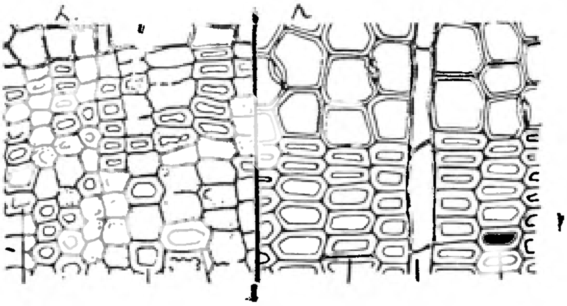


FIG. 2. — a) Shows a magnified cross section of the same fir stem of fig. 1 near the boundary of the 9th annual ring with cells showing different stages of deterioration.

b) Comparative specimen of sound pine-wood.

(*Drawings by O.N. Chistyakova*) [17].

The type of deterioration shown in fig. 1 and 2 leads to very fragile objects which on drying undergo considerable shrinkage and deformation. On the other hand the wood does not seriously obstruct penetration of liquids into the structure of the cell and the filling up of the cavities. It was also observed that this first type of deterioration occurs in the hardwood as well as in the softwood of various species. Oak-wood is considered to be a particular case, i.e. tanning matter in parenchyma cells and medullary rays are not subject to deterioration.

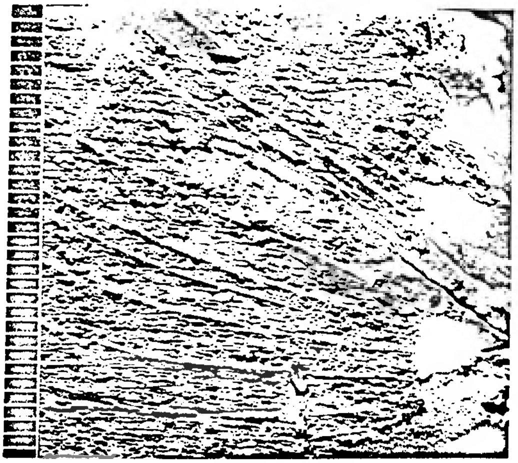


Fig. 3. — It has also been observed that the cells of large medullary rays remain unaltered in a cross section through heavily deteriorated oak-wood.

between the moisture content of the wood and the relative humidity of the ambient air. The equilibrium value depends on temperature. Along with the drying the volume of wood is reduced ; the wood shrinks. This is caused by the submicroscopic structure and by the related sorption properties. We possess accurate information [22, 23] with respect to the morphological structure and the arrangement of the functional groups (hydroxyl groups of cellulose) responsible for the hygroscopicity of the wood. Wood is a porous body which consists of the cell-wall substance and of cavities filled with air. The cell wall has a highly organized heterogeneous structure of a capillary system with submicroscopic dimensions. The latter fluctuate between 1/1,000,000 mm (intermicellar fissures) and a few hundred-thousandths of one millimetre (distance between the microfibrils). The former are the spots of the swelling phenomena, the latter contain the embedded lignin substance. The capillary system with an internal surface area of roughly 200 m^2 per 1 gram contains the *hygroscopic water*. This water remains after the equilibrium with the ambient humidity has been established in the wood and, in the case of relatively young wood, amounts to not less than about 30 % of the weight of the wood.

Unlike relatively young wood one observes in waterlogged archaeological wood, as a result of the loss of the cellulose material, an enormous increase of the average diameter of submicroscopic capillaries ; consequently the size of the internal surface area is reduced correspondingly. Therefore the places of hygroscopic phenomena have also become less numerous ; the swelling power of the wood has decreased. In other words, the wood is changed from the originally colloid-capillary-porous body towards a capillary-porous body. This means that the cavity system there remains virtually only *freely-moving water.* Porosity and permeability increase with the progressing degradation.

As degradation progresses the specific gravity and strength decrease. The determination of the moisture content from the specific gravities of the saturated and dried waterlogged wood provides useful indications for the choice of the method of conservation and about the maximum amount of the conserving agent, that can penetrate into the wood.

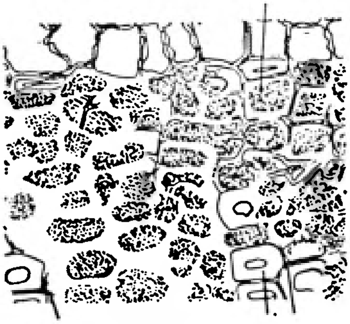


FIG. 4. — The final state of the second type. The wood looses its anatomical structure. This is very rarely met with except in sections of otherwise well preserved objects [17].

(Drawings by O.N. Chistyakova) [17].

The deterioration of the second type is less abundant. In general it was found in logs, pavement blocks and in separate planks. The deterioration starts in the thin cell walls of medullary rays and the adjoining cells. Thus middle lamellae and peripheral zones of cell walls are altered first. In a cross section the disintegrated cells appear as shapeless lumps.

The increase of the cavity system and the prolonged time of stay in a wet soil has resulted in an accumulation of extraneous organic substances (putrescent mud, marsh dyes, etc.) and of mineral substances (clays, colloidal metal hydroxides). These extraneous substances assume in individual cases during the drying process a certain supporting function which may become so important as to permit one to speak about the self-conservation of the wood. On the other hand they render the penetration of the conserving agent more difficult and impart to the wood, as far as colour is concerned, an unnatural appearance. If thermosetting synthetic resins are used during conservation, the process of condensation or of polymerization can be disturbed by metallic salts and by organic acids.

The most striking property of waterlogged wood is its abnormal behaviour when dried in air [1, 19]. When comparing with a wood of recent date, one finds that the first to evaporate is the freely-moving water, after which the cell walls begin to yield hygroscopic water and this lasts until the equilibrium state when the ambient medium has been reached. The decrease in the volume of wood corresponds roughly to the volume of the liberated hygroscopic water. The shrinkage phenomena occur when the moisture content of the wood reaches 30 %. With respect to the main anatomical directions of wood these phenomena differ in their extent : about 10 % in the tangential direction, about 5 % in the radial direction, and below 1 % in the longitudinal (or fibre) direction. In the case of the waterlogged archaeological wood the shrinkage phenomena begin much above the fibre-saturation range. Owing to the surface tension of the water in the capillary spaces the tensile forces of the capillary water are greater than the strength of the softened cell walls. The wood shrinks, cracks and warps in the manner generally known. Thus one can witness the remarkable phenomenon, viz. that, in spite of the ambient humidity of up to 98 % and of very careful drying, the waterlogged archaeological wood reveals an abnormal shrinkage.

b) The properties of waterlogged wood in two particular cases

A detailed investigation into the condition of the waterlogged wood from the cog of Bremen has been accomplished by D. Noack [19]. Tables 1 and 2 demonstrate the changes of the physical, chemical and structural properties of this wood that had lain for 570 years in the river Weser, under sand and clay layers 3 - 4 inches thick.

The still fairly solid and durable oak heart wood displays, on average, relatively small changes in its chemical composition. On the contrary, in the less resistant oak sapwood and beechwood a far-reaching degradation of cellulose has taken place. Consequently the percentage of the lignin substance rose to 65 %. Much as the wooden elements of the cog appear to be fairly unchanged, yet the investigation shows that, the cell walls consist only of the thin middle lamella rich in lignin and of the adjacent thin primary wall. The loss of cellulose resulted in a considerable reduction of the mechanical strength of the wood ; for instance, in the case of oak sapwood one could measure a compression strength parallel to the fibres, amounting to 10 kg/cm^2 (140 psi). For the recent watersaturated wood the corresponding figure is 300 kg/cm^2 (4 000 psi). Heartwood has, on the contrary, lost lost only about one-third of its original strength.

Noteworthy is also the high ash content amounting to a few per cent of the dry substance of the wood and caused by the embedding of extraneous mineral matter in the larger cavities of the wood.

The moisture-absorption power increases with the progressing decomposition of the wood. Oak heartwood and beechwood, of recent date, have in the water-saturated condition, a maximum moisture content of about 120 %. The less intensively degraded oak heartwood from the cog showed, depending on the degree of decomposition, moisture contents of between 120 and 145 %, whereas the moisture content of the strongly decomposed oak sapwood and beechwood was extremely high, attaining about 600 % (table 1). This value characterizes the high increase of the pore volume, due to the degradation of cell walls. In the case of beechwood the increase of the pore cavities is also expressed by the fact that the free-moving water in the pores can be easily squeezed out by hand, just as from a sponge.

The mechanical strength of the considerably degraded beechwood and oak sapwood of the cog of Bremen was reduced to a fraction of the strength of normal wood (table 2). On the other hand, the durable oak heartwood, of which the ship's hull is made, shows substantially lesser strength losses, especially when the test-pieces had been taken from the little decomposed zones within the thicker timber elements. In water-saturated condition the compression strength amounts to 250 kg/cm^2, i.e. about 65 % of the compression strength of the oakwood of recent date. When the wood specimens had been conditioned very carefully, in the course of 3 years, down to a moisture content of about 13 %, one could measure even a compression strength of 555 kg/cm^2. Hence this strength equals the compression strength of the conditioned, fresh oak wood, which should be explained by the fact that the specific density of the dried old oak heartwood is by about 30 % higher (table 2). On the other hand, the modulus of elasticity in compression, in the case of conditioned specimens of old wood, decreased due to degradation processes by about 20 % as compared with the wood of recent age.

TABLE 1. — *Some physical and chemical properties of oak-wood.*

property	heartwood of oak		sapwood of oak	
	old, water-logged wood (Bremen cog)	fresh wood	old, water-logged wood (Bremen cog)	fresh wood
maximum moisture contet in %	120 to 145	120	600	145
density in g/cm^3				
of water-saturated samples	1,20	1,22	1,04	1,18
of oven-dry samples	0,87	0,67	0,54	0,55
content of holocellulose in %	46	67	17	67
content of lignin in %	36	25	62	25
ash content in %	5,3	0,3	7,7	0,3
linear shrinkage from water-saturated to oven-dry condition				
radial in %	9 to 10	4,8	18 to 19	4,0
tangential in %	20	10,6	54 to 63	9,4
longitudinal in %	-	0,4	10 to 13	0,4

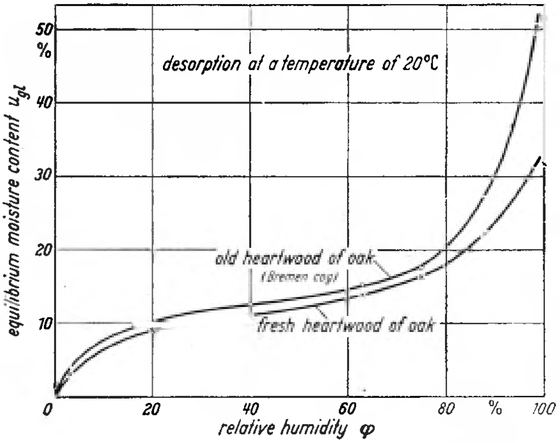
TABLE 2. — *Some mechanical properties of oak-wood.*

property	heartwood of oak		
	old, water-logged wood (Bremen cog)	fresh wood	
maximum compression strength in kp/cm^2	250	380	(of water-saturated samples)
-"- in kp/cm^2	570	555	(of air-dry conditioned samples)
modulus of elasticity in compression in kp/cm^2	102000	130000	(of air-dry conditioned samples)
maximum bending strength in kp/cm^2	250 to 415	680	(of water-saturated samples)
modulus of elasticity in bending in kp/cm^2	30000 to 60000	100000	(of water-saturated samples)

The bending strength and the modulus of elasticity in bending of the old oak heartwood (table 2) lie still between about 35 and 60 % of the corresponding properties of the oak wood of recent age. On the contrary, in the more degraded surface zones of the wood of the cog of Bremen one finds, depending on the degree of decomposition, substantially greater strength losses. However, on the whole the wood of the cog of Bremen is still fairly strong and thus provides favourable propects for the reconstruction of the ship.

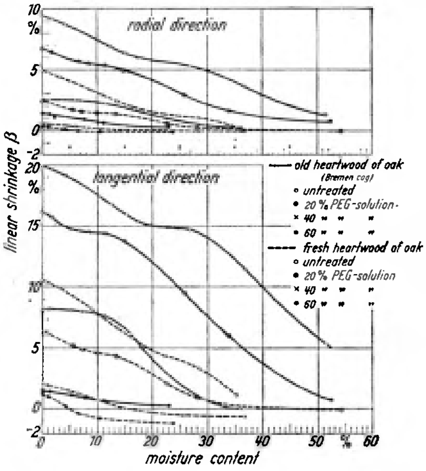
The shrinkage behaviour of the wet wood, described in chapter 2, is likewise observed in the oakwood of the cog. For the oak heartwood of recent age the equilibrium moisture content is shown in table 3 as a function of the relative air humidity at a temperature of 20 °C. table 4

TABLE 3. — *Sorption-isotherms of oak-wood.*



shows the course of the decrease of the wood volume of oakwood of recent age (shrinkage in tangential and radial direction as a function of the moisture content of wood). If in the exhibition rooms of museums the average relative air humidity lies at about 60 % then under these conditions wood does not dry completely, and in the course of time there appears an equilibrium moisture content of about 13 % (table 3). The resulting volume shrinkage which roughly corresponds to the sum of the tangential shrinkage (7 %) and the radial shrinkage (3,5 %) lies then, for the oak heartwood of recent age, in the order of magnitude of 10,5 % (table 4).

TABLE 4. — *Shrinkage-moisture content.*



When the old waterlogged wood of the cog of Bremen is exposed to a relative air humidity of 60 %, an equilibrium moisture content of about 15 % is established in it (table 3). According to table 4 this brings about a volume shrinkage of about 22.5 % (16 % in the tangential and 6.5 % in the radial direction of the wood). Thus the shrinkage is roughly twice as great as that in the case of the wood of recent age ; it produces great form changes and cross-section deformations (fig. 5, 6). Since this ship is an object comprising large elements, these elements ought to undergo a conservation treatment which completely compensates for his shrinkage tendency ; otherwise the reconstruction of the ship is called in question.

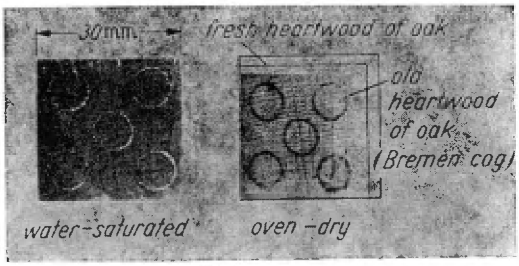


FIG. 5. — Cross sections of shrinkage samples.

An accurate study of the conditions of the wood was also made in the case of the warship Wasa : the Wasa hull and many of the ship's sculptures are made of oak. The physical properties of the oak were analysed to judge the possibilities of preserving the wood successfully. The compressive strength in the direction of the grain σ_t, the flexural strength σ_b, hardness perpendicular to the direction of the grain $H\psi$, and impact strength A_B have been determined from inner and outer samples, with the latter taken from 10 to 15 mm. from the surface. The samples are from heartwood as there is practically no sapwood in the hull. There was no significant difference between the inner and outer samples. The results of the analyses in Table 5 below reflect the average of 10 samples.

From the impact it appears that the cohesion between the fibres has been weakened.

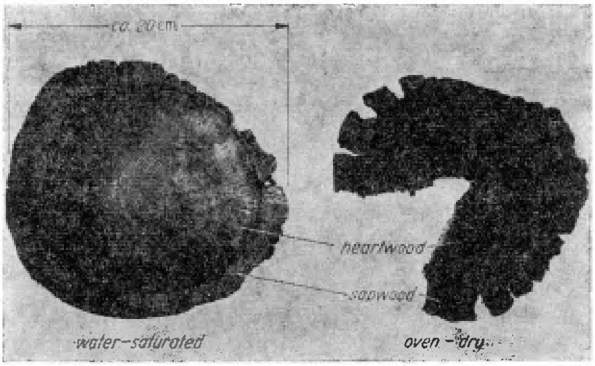


FIG. 6. — Disk from oak-wood of the Bremen cog.

TABLE 5. — *Strength values for Wet Oak.*

	Volumetric weight g/cm³	Compressive strength σt kg/cm²	Flexural strength σb kg/cm²	Hardness $H\psi$ kg/cm²	Impact strength A_B kgm/cm²
Wasa Oak	0,46	171	350	284	0,35
Normal Oak	0,65	300	600	450	1,30

Microscopical examinations have been made of wood samples of Wasaoak for microbial attack, that means for hyphae of fungi, for bacteria and for their action on the cell walls. In sea-water the main destructors of wood are, beside the wood boring animals Teredo and Limnoria, marine fungi belonging predominantly to the Ascomycetes and Fungi Imperfecti.

The outermost 1 or 2 cm of the wood has been affected by rot along the walls of the cells, especially the parenchymatous cells. Also, the bond between the cells has been partially decayed, as was expected from tests of the wood's physical properties. Traces of fungus have been found, but not enough to have caused the entire corrosion of the wood. A breakdown of the cell walls by soft-rot fungi has been observed only in the soft surface of the wood, together with strands of blue-stain hyphae. The attack of the inner portions of the wood can probably be ascribed to bacteria, chemical decay or other forms of corrosion.

Tests taken from the hull itself gave the following average values compared with fresh and fossile oak, the latter including some from southern Sweden estimated to be six million years old. All values have been calculated on ash-free wood.

TABLE 6.

	Lignin %	Pentosane %
Six million-year-old fossile samples	75,6	0
Wasa oak, surface sample	62,0	5,6
Wasa oak, inner samples	26,0	18,4
Fresh oak	27,5	23,4

The inner portion has a chemical composition approaching that of normal wood, whereas the outer layer has undergone a marked change in composition. The high lignin content is a reflection of the disproportionate removal of carbohydrate during the long submersion.

Another point of interest is that the attacks were less severe where there had been iron joints even though these had long since rusted away. The colour of the oak varies very much. By analysing the wood it was proved that the iron content of what is known as *black oak* is 0,2 per cent by weight or higher, while in the light-coloured parts the iron content is only 0,01 per cent by weight based on the dry weight of the oak.

Depending on the intensity of the attacks, the moisture content i.e. the quantity of water calculated in percentage on the dry weight of the wood, varies substantially. Variations of between 150 and 800 per cent have been found in the same piece of oak. For birch the percentage is often over 1.000.

Another fortunate circumstance, which has resulted in the oak — as a whole — being so well preserved is the fact that when the Wasa sank she was a brand new ship. The only treatment given by the shipbuilders of that time was a coat of pine tar, which has a very low protective effect.

It is obviously of great interest to know how much swelling the hull has undergone during 333 years beneath the water. The longitudinal movement of the wood is very small compared to the shrinkage tangential to the annual rings. The distance between two fixed points of a deck beam was measured and this distance was compared with that of the deck planks running across the beam. The swelling during the immersion could thus be estimated to one per cent.

3

THE PROBLEM OF CONSERVATION

The problem of conservation comprises two following points [24, 25, 26] :

1. Removal of the excess water until an equilibrium is established with the atmosphere surrounding the object, without causing any dimensional changes.

The results of modern wood research show that the attained constancy of the dimensions can be maintained only when the equilibrium referred to before can be kept constant, i.e. the temperature and humidity of the ambient air should be virtually constant and vary only within determined narrow limits.

2. The fragile object obtained as a result of drying is to be strengthened mechanically by means of consolidating agents. It should be able to carry its own weight and to be handled. Besides, its hygroscopicity should be changed in such a way that the object does not react to climatic variations undergoing a change of shape.

Methods are known of course in practice, which combine these two phases of drying and of consolidation. They take place simultaneously, or else drying is passed over, the mechanical strengthening being achieved when the wood is in the water-saturated state.

4

FIRST MEASURES IN THE FIELD

The anomalous behaviour of the waterlogged archaeological wood during drying makes it indispensable that, right at the excavation, one has to provide the best basic conditions for the subsequent conservation : first of all the pieces must not begin to dry. The objects can be placed in polyethylene bags with some water to which a fungicide had been previously added. The suitable fungicides are : 1 — 2 % TEGO 51 B, or 2 % FLURALSIL BS or a few grams thymol in granular form per bag volume of 10 — 20 litres. If it has been decided that further conservation will be carried out with polyethylene glycol, one adds to the water 0.6 — 1.0 % of a mixture of boric acid with borax (ratio 7 : 3). In this case the conservation treatment with low-molecular polyethylene-glycol grades (polyglycol 600 to polyglycol 1000) in a solution not stronger than 10 % can begin right at the excavation site, regardless of the adhering soil material. Also here a fungicide should be added to the solution. A modified procedure is reported by W. Ambrose using PEG 400 [48].

If the storage lasts too long before the final conservation has been achieved, or if it is not possible to keep the objects continuously wet, one can impregnate them with glycerol or ethylene glycol (antifreezing agent). Of course, if a method other than the polyethylene-glycol one is used for the final conservation, these substances must be washed out prior to conservation. Similarly, when fungicides are used, one should always bear in mind the nature of the ultimate conserving agent. Formalin, phenol and metallic salts reduce the ageing resistance of polyethylene glycols. They can also — and the same applies to acid additives —

disturb later the setting process of the two-component resins or the polymerization of monomeric plastics. There exists no danger when thymol or the nonionogenic wetting agents with fungicidal effect (TEGO 51 B) are used.

If fragile objects must be embedded for transportation in gypsum or in other hardening provisional supporting media the wood must be absolutely insulated preliminarily with aluminium foil or other suitable separating agents.

5

POSSIBILITIES OF CONSERVATION

a) Depending on the properties of the wood

Depending on the properties of the waterlogged archaeological wood there exist theoretically two possibilities [27].

With the first alternative the aim is to coat the outer surface of the wooden object with a protective layer and, as far as possible, to apply this protective coating also to the inner surface of the wood structure visible under the microscope (conducting vessels, cell cavities or damaged places, internal fissures, etc.). The coating ought to be, as far as possible, impermeable to water or water-repellent.

Experience gathered with the external protective coating showed in most cases that it was impossible to prevent for a longer period the exchange of moisture between the wood and the ambient air [28]. The point is that, when in the form of a thin film, virtually no material is completely impermeable to water. Such materials can merely reduce the rate at which the equilibrium is established between the moisture content of the wood and the ambient air. One achieves in this way a mild and slow drying which, in some cases, would suffice for the conservation of the wood, provided there are no unfavourable climatic variations. When only this measure is used the wood itself would remain in an incalculably unstable state. In the case of larger objects, such as the Kentmere boat [29] which had been well preserved in its interior, but revealed exfoliation and formation of craks on the surface, a satisfactory consolidation could be achieved by impregnation with a two-component resin (epoxide resin).

The other possibility consists in filling completely with a supporting material the cavities visible under the microscope and the submicroscopic capillary system. Nonvolatile solids are substituted here for water. If the introduced solid has distinct hygroscopic properties and if, as with polyglycol, it is introduced into a wood saturated with water, it also assumes partly the swelling function of the water, replacing the latter by way of diffusion and fixing the wood in a more or less swollen state. Conserving agents whose hygroscopicity exceeds that of the wood substance — salts, sugars, polyglycols — assume the loads of climatic fluctuations in a very wide range of humidity. In the case of the nonhygroscopic conserving agents the main thing is the permeability to water, viz. how far the hygroscopicity of the wood can still produce an effect.

Unlike the first possibility, the achieved mechanical strength of the entire object is here equal to that of the consolidating agent. In practice almost all of the successful methods of conservation belong to the second possibility.

Industrial methods which aim at reducing the hygroscopic properties of the wood itself [30-32], cannot be applied to the archaeological wood since the indispensable reactants — the highly hygroscopic hemicelluloses and celluloses — mostly do not occur to a sufficient extent.

b) Depending on the properties of the conserving agent

The choice of the method of conservation is partly determined by the state of aggregation of the conserving agents. *Solids* can be introduced into the cavity system of the wood either as a melt at a higher temperature or as a solution in water or in organic solvants at the normal or higher temperature. Here can also be classified most of the lacquers which dry either plysically, through the evaporation of the solvent, or by the absorption of the oxigen from air. Their power of penetration depends mainly on the size and form of molecules of the molten or dissolved solid [33-36]. Salts, sugars, low-molecular natural resins, drying oils, low-molecular polyethylene glycols, low-molecular initial products of the condensation resins (resinoids) — provide the best conditions for the penetration into the submicroscopic capillary system.

Liquids which set in the wood to form a solid can be introduced either as a liquid monomeric plastic material which is polymerized or polycondensed by means of catalysts, or as a liquid monomeric plastic material which is polymerized with high-energy gamma rays [37, 38, 39]. The former include styrene or the esters of the acrylic or methacrylic acids, which are polymerized with the aid of peroxides, next the liquid initial products of the phenol-, urea- [40, 41, 44, 45] and melamine-formaldehyde resins [46, 47], and the components of polyester [42] and epoxide [43] resins.

For the polymerization with gamma rays one uses, in addition to styrene, also the esters of the acrylic and the methacrylic acids. In view of the small molecular size of the initial products, the entire group provides the best conditions for a complete impregnation of the wood. As far as the future is concerned, we have in the plastic monomers which, as low-viscosity liquid, penetrate extremely easily into wood and can be set at any arbitrarily chosen moment the most suitable agents for achieving the complete consolidation of the waterlogged archaeological wood. With the exception of the water-soluble initial products of the phenol-, urea- and melamine-formaldehyde resin, all others require a far reaching dehydration of the wood.

c) Depending on the climatic conditions of storage

Other co-determining factors for the choice and success of the method of conservation are the climatic conditions under which the object will be stored after treatment.

If a controlled climate with a relative humidity between 50 and 65 % is foreseeable, it is sufficient for the purpose of conservation to fill the conducting vessels and the cell cavities, i.e. the larger wood cavities that are more easily accessible to the conserving agent. Since in this case it is not necessary to draw up very strict requirements with respect to water vapour permeability and to molecule size, a greater number of conservation agents can be taken in consideration.

If the contrary extreme climatic conditions are foreseen, it follows from all that has been said heretofore that one ought to aim at a penetration as complete as practicable of the conserving agent in the wood. The duration of the impregnation will become much longer and will increase with the size of the object under treatment.

6

DESCRIPTIONS OF METHODS

If, prior to the introduction of a consolidating agent, the waterlogged archaeological wood is to be dehydrated as completely as possible, one can choose one of the three following procedures :-

The water contained in the wood is frozen and then eliminated by vacuum sublimation. This method is knowns as that of freeze-drying [49-51].

A modification of the freeze-drying method consists of the water being substituted with liquids which freeze when cooled and can be then eliminated by vacuum sublimation. Tert-butyl alcohol (trimethyl carbinol) has been used with success for this purpose. A modified technique was recently described by B. Brorson-Christensen [107]. Water is replaced by tert-butyl alcohol, the latter being replaced then by a solution of PEG 4000 in tert-butyl alcohol which upon freezing is sublimed away, by thus leaving the PEG within the wood.

W. Ambrose [48] has reported a somewhat different technique for swamp-degraded wood. After soaking in a 10 % aqueous solution of PEG 4000, to which fungicides are added, for a period of 1-6 months the entire is frozen with CO_2 and finally the ice formed is sublimed away in a vacuum-chamber.

Liquids can be substituted for water, which, upon evaporation at a normal temperature and atmospheric pressure, or in a vacuum, leave the wood dry. In the case of the alcohol-ether-resin method water is first removed in a series of alcoholic baths, after which alcohol is exchanged against a solvent which contains the ultimate conserving agent in solution, - in this case ether.

Various methods of the past, including the *historic* alum-glycerol-linseed-oil method may be studied in literature [54-70].

For the materials used in the methods described below see the name of the manufacturer and supplier in an Appendix at the end.

a) The polyethylene-glycol methods (carbowax method)

The important feature of polyethylene glycols is their solubility in water ; when in dilute aqueous solutions, the low-molecular grades can penetrate into wood by diffusion. At the hygroscopic spots of the cell-wall substance there might also occur sorption processes. The hydroxyl and ether groups of the PEG molecule may carry out swelling functions, but when compared with water only to a limited extent [71-72].

When it is possible to achieve a satisfactory impregnation of the submicroscopic cavity system, one can attain a complete dimensional stabilisation of the wood [73, 74].

In the case of this method it is important to give the diffusion of PEG as much time as possible and to facilitate the diffusion by a preliminary washing, as thoroughly as possible, to remove the wood extractives (extraneous substances). In most cases known to us, failures are to be explained by too short a time of treatment, too rapid raising of the solution temperature, too high initial PEG concentration, too rapid raising of the concentration of PEG solution, or too high choice of the mean molecular weight of PEG [75]. The penetration power of the PEG increases as the mean molecular weight decreases. However, since at the same time the hygroscopicity of the PEG rises and the grades with a molecular weight below 800 either have a consistency of a soft ointment or are liquid, the choice of the types is limited to the range of molecular weight between 1 000 and 4 000. The treatment should start always with a low concentration of the solution (10 to 15 %) and whenever possible, the working temperature should be between 35° and 45 °C.

The conservations conducted with PEG in different laboratories differ in the choice of the PEG type, the initial concentration of the solution, the time of treatment and the working temperature.

1) Working techniques in museums

The method of Moren and Centerwall [76, 77].

The wood is only cleaned on the surface with water. The objects are completely covered in a suitable impregnation vessel with an impregnating solution of the following composition :

1 part by weight PEG 4 000
9 parts by weight tapwater
0.1 parts by weight sodium pentachlorophenate

The bath level is kept constant by replenishing of the solution. For this purpose a storage tank is suspended above the bath, for instance a plastic bottle turned upside down, with a perforated rubber plug with attached rubber tubing which ends at the bath-level height and supplies automatically as much supplementary solution as the amount of water which evaporates from the bath. The supplementary solution contains no sodium pentachlorophenate. The entire baths is equipped with a heating appliance. The reserve of the replenishing solution should be so adjusted as to ensure the objects being still covered with the PEG melt after all the water has evaporated. By measuring the temperature, the specific gravity and the pH value at regular intervals one checks the course of the exchange process and the condition of the bath. The stepwise-raised temperature should be continuously maintained day and night. The pH value of the bath should be always maintained between 7.5 and 10. In the course of the process it always drops towards the acid range, owing to which the water-soluble sodium pentachlorophenate is converted to the insoluble pentachlorophenol and can be precipitated. One of the causes of the pH shift is the presence of acid extractives in the waterlogged wood. The correction is achieved by the addition of small quantities of a 10 % aqueous solution of sodium carbonate. The impregnation treatment is completed when the concentration of PEG attains 100 % and this value remains unchanged for two to three days. Depending on the size, form and tree species the achievement of this state may require weeks, months, even years. It is possible to bring about a certain acceleration of the exchange process if one-half of the water is replaced with alcohol. In the replenishing solution alcohol can be present only until the PEG concentration in the bath has reached 50 %. In view of the rising bath temperature the evaporation rate of alcohol increases to such a degree as to make it indispensable to operate in a room with sufficient ventilation and without any possibility of ignition (motors, lighting switches etc.). The ignition temperature of ethanol vapour in air is about 40 °C !

The objects are removed from the bath, the excess of PEG is removed from the surface while still warm with filter paper or cellulose. After complete cooling any remaining PEG is washed off with 50 % aqueous alcohol or with toluene.

Research work of R. Lefève, Brussels [78].

In order to determine in what way PEG can be substituted in wood for the largest amount of water possible, Lefève ran experiments with a Roman pail made of yew wood, the sides of which were composed of 21 equal parts. Regular painting with a 62 % aqueous solution of PEG 4 000 during several days showed that water evaporated from the wood substantially faster than the rate at which PEG could penetrate into the wood. When the state of constant weight was reached only one-fifth of the water was replaced with PEG. Shrinkage in the tangential and in the radial direction was nearly the same as in an air-dried control test-piece. When the same experiment was carried out in a plastic bag, owing to which it was possible to maintain the air humidity around the object at a constant high level, water evaporated more slowly and, consequently, PEG has more time for penetration. In this way it was possible to replace roughly one-third of the water. The author achieved better results when the wood was laid into a 62 % solution of PEG 4 000. The bath was renewed twice ; after 160 days PEG was substituted for nearly two-thirds of the water. Finally it was found that one has to choose a low (maximum 40 %) initial concentration of the Carbowax solution in order to minimize the difference between the exchange rates. The PEG of such a high molecular weight is able to penetrate into wood only when sufficiently diluted.

The method of Organ, Bristish Museum [79].

Compared with the original method, this modification shows the following simplifications : initial concentration of PEG 4 000 - 12 % ; sodium pentachlorophenate is left out and, consequently, neither the addition of the sodium-carbonate solution nor the pH measurement involving costly apparatus are necessary. For the control of the process a few drops of the bath liquid are sampled from time on a glass plate, and, when dried, are compared with the initial material. If the wax has become dark-coloured, viscous and resinous, a fresh solution is substituted for the old one. The vessels are covered with aluminium foil. At the outset the object is placed in the vessel and one measures the amount of pure PEG, which is required to ensure that, at the end of the process, the object would still be completely covered by the melt. The vessel form should be so chosen as to permit the solution level at the outset to be 8 to 10 times as great as the height of the object. The whole is heated from beneath ; in the direct neighbourhood of the objects the conserving solution rises, because it had become specifically lighter owing to the removal of water from the wood. Thus a circulation is produced ; its effect is that, all things considered, the water from the wood diffuses into solution at a faster rate than the rate of evaporation of water from the bath surface. In the course of heating the concentration of the bath increases. The dehydration of the wood is completed before the concentration of the PEG-melt has reached 100 %. This method held good in the case of small, highly degraded objects. Coniferous woods required the process to be repeated twice.

The method of Albright, Smithsonian Institution, Washington [80].

The author attempted to shorten the time of impregnation by facilitating the diffusion. The washed weighed objects are placed in pure ethanol where they remain until the wood becomes dehydrated. The author uses preferably temperatures of up to 65 °C ; higher temperatures are inadmissible for reasons of safety (the ignition temperature of alcohol in air is 40 °C !). Treatment with alcohol is continued until the wood saturated with alcohol weighs about 20 % less than the water-saturated wood. Then PEG 4 000 and ethanol (ratio 1 : 1) are disolved in one another at 65 °C, and the pieces of wood are immersed completely. The vessels are covered so that alcohol can evaporate only slowly. Treatment is continued until the concentration of PEG attains 100 %. The criterion for this state is the setting of a small melt sample within 30 minutes. After being removed from the bath the objects are washed for a short time in hot water, dried up with absorbent paper and weighed. The final weight should exceed by about 25 % the minimum weight determined in the course of dehydration.

It was established that small and medium-sized objects from underwater ship finds keep very well. In the case of large-sized objects the possibilities of application are still being tested. The method in question is essentially a modification of the British Museum method.

The method of Brorson-Christensen, Copenhagen [81].

PEG is used only for objects of all sizes with a rough surface characteristic. One starts with a 10 % solution of PEG 4 000 in deionized water. Right from the outset a temperature of 60 °C is maintained, in order to kill fungi and micro-organisms. According to the size and nature of the wood the solution is allowed to evaporate in the course of 1 to 24 months, yielding finally and anhydrous PEG melt. After the excess of PEG has been removed from the surface of the objects the wood is coated with an epoxide resin or Bedacryl. The vessels consist of tin-plated copper and are electrically heated ; the constancy of temperature is ensured by a thermostat and the bath liquid is slowly circulated. The shrinkage measurements conducted with a great number of treated fragments of five Viking ships yielded very small values. Difficulties were encountered in the case of oak beams with well-preserved heartwood, which gave rise to further experiments that are described briefly as follows :

As is reported recently [108] by B. Brorson-Christensen several modified techniques for the treatment of oak timber include

— impregnation with PEG 4 000 after dehydration with (mono-) ethyleneglycol which occasioned no dimensional changes, owing to the simple fact that the (mono-) ethyleneglycol was retained in the core of the oak timber ;

— dehydration with methanol followed by impregnation with PEG 4 000 dissolved in methanol. This technique allowed concentration of the solution up to 90 % at a temperature of 40 °C with greater speed than in an aqueous solution. After the methanol had disappeared the rate of shrinkage of oak timber obtained was smaller than that observed with water.

The use of ethanol [80] has also yielded satisfactory results.

— another technique which is mentioned briefly in the beginning section 6, merits careful consideration as it has so many advantages :

Dehydration with tertiary butanol followed by impregnation with PEG 4 000 dissolved in tertiary butanol which finally is removed by sublimation. It may be expected that a possible process of deterioration of PEG rather takes place upon a prolonged contact with an aqueous milieu than with an organic solvent. Although the long-term properties of PEG are not yet published elsewhere, PEG can be expected to undergo deterioration under particular conditions. This in connection with its water solubility and little hygroscopicity was the motive for replacing PEG with other materials, e. g. waxes which may render the object totally inert to the environmental changes.

Research work of Wihr, Trier [82].

Small objects (up to 7 cm. in length and 3 cm. thick) were impregnated for three months at room temperature in 30 % Polydiol 4 000 and then for three weeks at 40 °C and for four weeks at 60 °C. The losses due to evaporation were always replenished with a 30 % solution of PEG. Next the wooden objects were wiped while hot and left alone to cool slowly. They remained afterwards unchanged in the course of two years.

Large objects, stem discs of 30-40 cm. in diameter and 6-8 cm. thick, and a piece of an oak beam (25 × 35 × 45 cm.) were at first impregnated for several weeks at room temperature in a 10 % Polydiol 4 000 and then the temperature was kept for 55 days at 40 °C. During the following 20 days the temperature was raised to 50 °C and kept at this level for 116 days, then it was raised in the course of 15 days to 55 °C and kept for 80 days and finally the temperature was raised within 20 days to 60 °C and maintained at this level for 70 days. After removal the pieces were washed hot and left to dry very slowly in air. After being stored for 9 months the form and mass remained unchanged, but during the following 5 months slight radial fissures did appear, which however did not change further.

Method of Seborg and Inverarity [83].

The authors describe the conservation of a 200-year old boat from Lake George, which is composed of coniferous and oak wood. The boat was left over winter at the place where it had been found, in a water-saturated state under moist sawdust. Sections of the boards (2-4 cm. thick) of the boat hull and of the planks showed, when dried in air, in the first place surface cracks and exfoliation and tangential shrinkage to an irregular extent. After many tests a wooden container was built for the boat, lined with polyethylene and filled with a 50 % solution of PEG 1 000. The boat was left for three weeks in the solution at room temperature, this being completely sufficient for the dimensional stabilization of the surface parts. After a 3-months' drying in open air there appeared only very thin hair fissures. Neither shrinkage nor form change could be found after that period. Even one year later this roughly 10 m. long boat remained unchanged.

2) Conservation of the "Wasa"

Preservation of single wooden objects. The large quantities of the wooden finds are preserved in two main vats. Considering that some objects have a length of more than 17 m. the vats are 20 m. in length. The width is of 1,65 and 2 m. respectively and the total volume is 80 m.^{3}. The continuous method is used. The vats are filled with pure water and the temperature raised to 60 °C. 2 % of a mixture of boric acid and borax at the ratio of 7 : 3 is added as a fungicide and polyethylene glycol 4 000 at an initial concentration of 15 %. During the first 12 months the concentration is increased very slowly : at 1/12 % per 24 hours. During the following 5 months the concentration is raised by 1/5 % and during the last month of all by 1/2 % per 24 hours. Before and after the preservation process the pieces are checked by weighing and sample testing.

After the immersion period of the preserving process is over, the objects are removed and dried out gradually while being surface-treated with a polyethylene glycol solution. This takes six months altogether and it is then possible to exhibit them. When the final surface treatment and the drying-out process is completed the moisture ratio stabilizes at between 10 % and 20 %. It is not until this state has been reached that there will be no further changes in the condition of the material, provided of course that from then on no extreme variations of the temperature in the museum take place. The drying-out period varies according to the size of the objects. The sculpture of the knight required on average two to three years.

Preservation of the hull. For both practical and economic reasons it was impossible to dismantle the hull and process it piece by piece, instead it had to be preserved in its entirety. It began with spraying done by hand in order that the hull should not dry out between the spraying periods a special humidifying system was needed to keep the air moist. In March 1965, however, a fully automatic spraying system with permanent sprinklers was introduced and this in its turn eliminated the need for humidification and made conditions more agreeable for visitors and for those working on the hull. In one year with the new system the wood absorbed more than double the amount of the preserving agent than during the preceding three years when hand-spraying was used. By the close of 1965 all the outer planking, the ribs and the interior fittings of a thickness of up to 18 inches had been permeated with the preserving fluid. In view of the fact that most of the wood was heart oak this was a highly satisfactory achievement. The preserving fluid was composed of 15 % of polyethylene glycol 1 500 and 4 % of a mixture of boric acid and borax at the ratio of 7 : 3.

Since it was raised in 1961 the hull has been drying out very, very slowly. It will be a couple of decades, however, before this gradual process will have been completed, though in fact this will not hinder the continued restoration work.

3) Conservation of the cog of Bremen (19)

According to the detailed investigations made by D. Noack of all the possibilities described in Chapter 5 for the stabilization of wet wood and dimensional stabilization, only the incorporation of chemicals into the cell walls of the wood was considered to be feasible for the conservation of the cog of Bremen.

Fig. 5 shows the result of the sorption and shrinkage measurements conducted with test-pieces of a cross section of 30 × 30 mm and a length of 5 mm, along the grain, and it provides information about the effect of polyethylene glycol in diverse concentrations on the shrinkage behaviour of wood.

In the waterlogged oak heartwood of the cog of Bremen the dimension-stabilizing effect of PEG is likewise clearly seen in table 4. A treatment with a 20 % solution of PEG results, it is true, in a slight reduction of the shrinkage only, but at the concentration of 40 % of PEG the shrinkage magnitudes are reduced to one-half ; in the case of a treatment with a 60 % solution of PEG the absolute shrinkage magnitudes in the tangential and radial direction amount to only 0.7 % each, which, compared with the high initial shrinkage magnitudes of 17.5 % and 7.5 % respectively corresponds to an almost complete stabilization.

These results show that the dimensional stabilization of the old oak heartwood of the cog of Bremen with polyethylene glycol 1 000 is possible provided sufficient quantities of this agent can be introduced into the wood by means of a suitable method.

The impregnation of the cog of Bremen by immersion was started by using very low PEG concentrations, viz. 5 - 10 %. In the course of many years the concentration was raised gradually up to about 60 %. In the case of the higher concentrations of the immersion bath a slight raising of temperature to 30 - 35 °C is foreseen, to accelerate the diffusion processes. In view of the partly very large cross-section dimensions of the structural elements a complete — or at least sufficient — impregnation will require a very long period of time, which might lie in the order of magnitude of about 20 to 30 years.

It is not acceptable, however, that the cog of Bremen which is at present stored as individual parts in huge water containers should remain for decades in a dismantled state. It was, therefore, decided to reconstruct the cog in the wet, water-saturated state, to be followed by an impregnation with PEG in a huge aquarium 24 m long, 7 m wide and 8 m high. The reconstruction of the cog of Bremen must be carried out by using the so-called wet construction in a 'mist atmosphere' of about 100 % relative air humidity, produced artificially by means of water sprayers. Successively the impregnation tank should be filled with water containing a small percentage of wood preservative. Salts of boric acid which do not interact with polyethylene glycol, were found to be effective for this purpose.

The walls of the impregnation tank will be fitted with large observation windows of glass, to enable the ship to be inspected by the public during the impregnation treatment lasting for many years. Water —

later the solution of PEG — will be relieved from the colouring wood extractives by continual purification in order to allow inspection through the windows.

When the conservation treatment will be completed the solution of PEG will be drained off and the residual water contained in the wood will be removed by normal air-drying.

As for the continual purification of the impregnation bath investigations of the posibility of continous filtration were carried out by the Section for technical application of the Borsig-Aktiengesellschaft, at Berlin-Tegel, using a specially developed model test plant. According to the proposed procedure the liquid would be filtered on filters of gravel and activated carbon which should arrest suspended particles and adsorb dissolved dyes while the colourless wood preservatives and the polyethylene glycol would not be affected (fig. 7) shows diagrammatically the layout of the testing installation. The total reservoir volume can be circulated once within about three days. This ensures also that the impregnating solution has the same concentration in all places of the bath.

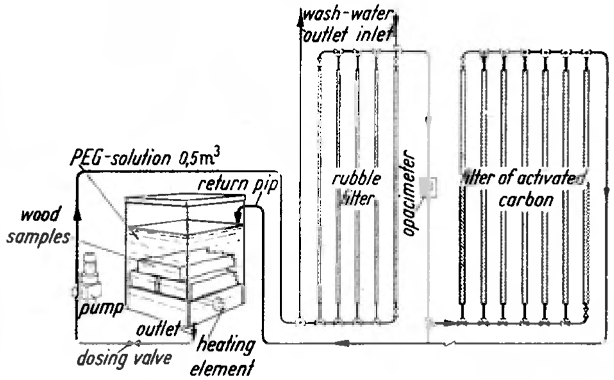


FIG. 7. — Schedule of the pilot clarification plant.

Experiments of impregnation and purification were carried out on a model scale. The testing plant consisted of a PVC container which could hold about 0.5 m³ of the impregnating solution and was fitted with an immersion heater for temperature control. The impregnating solution was first pumped by a double-membrane pump (the output of which could be controlled continuously from 0 to 50 1/h) through a battery of gravel filters, consisting of 5 units arranged parallel to each other, each unit being 3 m, in length and having an inside diameter of 35.9 mm. Next the impregnating solution was conducted through a battery of activated carbon filters consisting of 7 units, likewise 3 m. in length and with an inside diameter of 53 mm. The suitably arranged three-way stopcoks enabled the filter units to be connected in parallel or in series, and therefore the flow rate and the filter output could be varied within wide limits. The gravel filling had mostly a grain size of 1 to 2 mm., whereas only the activated carbon Hydraffin LW with a grain size from 0.5 to 3 mm., was found to stand a test as carbon filter material. A photoelectric turbidity meter inserted between the filter batteries indicated the moment when the filters were spent.

Tests in the model plant (fig. 7) were conducted with the original wood of the cog of Bremen, the ratio of the volume of the wood to that of the impregnating solution corresponding roughly to the conditions prevailing later. The criterion chosen for the grade of purification was the photometrically determined light transmittance of the impregnating solution. It is indicated in percentage in reference to the light transmittance of a 1 cm, layer of distilled water, which is adopted as 100 %. The light transmittance of a pure 10 % solution of PEG lies at about 99 %, and decreases only slightly with the increasing PEG content, as a 70 % solution of PEG shows still a light transmittance of 97 %.

Purification of the impregnation bath is feasible up to a filtration velocity of about 2 m/h. The light transmittance of the filtered impregnation solution lies then always in excess of 94 % ; to the naked eye it appears to be as clear as water, though its initial light transmittance did amount to only 20 to 29 %.

4) Wet-gluing of wood

A large proportion of the structural elements of the cog of Bremen are seriously damaged, and many elements must be reconstructed from numerous fragments. It is impossible to effect direct gluing of the water-saturated wood since adhesion between the adhesive and the moist wood surface is insufficient in the case of all glues. The usual drying before gluing is impossible in the case of the cog of Bremen. On the other hand, however, the theory requires only for the outermost surface layers of the wood elements to be dried to such an extent and to remain dry for such a period of time as will allow the complete hardening of the glue, because the adhesion between glue and wood surface will be sufficient. Gluing tests were carried out, in which at first the wood surface was strongly dried within a short time by using infra-red emitters (150 W) at a distance of 15 cm., from the wood surface, other parts of the timbers remaining in the water-saturated state. Under these conditions it was possible to glue the dried wood surface with a resorcinol-formaldehyde adhesive, keeping the joint under slight pressure for 12 hours. The glued timbers were immediately immersed in the water bath.

An investigation of the glue-line strength, carried out with the aid of block-shear tests, yielded a remarkably high shear strength of the 'wet-glued' oakwood, viz. from 40 to 60 kg/cm^2. along the grain, and about 25 kg/cm^2 across the grain.

Wet-gluing tests were also carried out with the wooden elements of the cog of Bremen, which had been preliminarily impregnated with polyethylene glycol. To achieve this one had to remove, prior to infra-red drying, the polyethylene glycol from the wood surface by repeated washing with clear water. The strength values evaluated by means of block-shear tests were (17 to 23 kg/cm^2) about one-half of the values for the untreated wood. The shear-rupture surface was almost confined to the glue line. Consequently the adhesion of the glue on the wood surface is substantially reduced also by ethylene glycol. However, the absolute gluing strength (about 20 kg/cm^2) is still high. Thus even at a later period one can produce sufficiently strong glue joints between wood elements which had been impregnated with polyethylene glycol. This is of particular importance in the case of wood elements which show already a distinct decomposition and whose surface layers, when untreated, cannot be subjected to an extreme drying. It is recommended that these degraded wood elements be treated, prior to gluing, with the solution of PEG until the wood zones which will be subsequently dried with infra-red radiation become sufficiently impregnated. This not only prevents the shrinkage phenomena, but also allows a certain strengthening of surface layers.

Gluing of wood preserved with PEG. Preserved fragments cannot be stuck together with any adhesive. It is, however, possible to make use of the fact that the end hydroxyl groups of the PEG molecule can form stable polyethers (urethanes) by way of esterification with isocyanates [84]. The excess of PEG is removed with toluene from the wood surface ; next the pieces are heated up to the melting point of the respective PEG type and laid, for about one hour, into a 25 % solution of Desmodur L in ethyl acetate, which has previously been brought to the same temperature. When the pieces have been removed from the solution the cross-linking comes gradually to an end as the solvent evaporates ; the fragments which, when removed from the solution, are immediately stuck together and left alone for several hours under a ligth pressure, join very well and are able to withstand carreful handling, provided the objects are not too heavy.

Following the hardening process the excess of the polyurethane resin on the surface of the wood produces, circumstances permitting, lustrous layers. To prevent his, one should rinse off the excess with ethyl acetate prior to complete hardening.

It is, however, also feasible to let the fragments harden individually after their removal from the solution of Desmodur, whereupon they are stuck together with the use of solvent adhesives available on the market.

The water-resisting property of the polyurethane formed has the additional effect of a moisture barrier which, in a humid ambient climate, slows down the sweating ouf of the hygroscopic PEG.

b) The Arigal-C method of the Museum of History, Berne (46,47,85) ; the Russian method by Grabar (44), the method of Lehmann, National Museum, Poznan (45)

Arigal-C is a melamine-formaldehyde resin which, when in aqueous solution, is present in the resinoid form. The condensation is initiated by adding to the aqueous solution a catalyst which shifts the pH from over 9 to below 7. The progress of condensation is shown by the increasing turbidity of the solution. In the course of 24 to 48 hours — depending on the amount of added catalyst and on the temperature of the solution — a white, almost opaque, hardened resin is produced.

The treatment of waterlogged wood passes through the following stages :

1. The wood ought to be cleaned very thoroughly, first with tap-water and then in desalinated water for at least four days. This should eliminate as much as possible of the soluble extraneous substances which are likely to disturb the condensation process.

2. The wood is impregnated at room temperature in a 25 % aqueous solution of Arigal-C. The volume of the solution should be five times greater than that of the object. The wood remains in the bath until the exchange has been completed, which can be recognised by the sinking of the object. It is left in the bath for two additional days. The pH of the bath must not drop below 7.8 since at 7.2 the condensation process begins and thus the diffusion of the resin solution into the wood is made difficult. The shift towards the acid range by the absorption of carbon dioxide from the air can be prevented by making the treatment vessels airtight. The lowering of pH can be also caused by the wood extractives. This can be remedied only by replenishing the solution in due course.

3. We add now to the Arigal-C bath 10 % of the Arigal-C catalyst, after which the solution remains usable for 35 to 40 hours, depending on the ambient temperature. After this period has elapsed viscous-tacky condensation products form rapidly on the object and inside it. It is indispensable to remove them as soon as possible from the surface with hot water or, if already dried up, with diluted sulphuric acid. After the condensation process has been completed the objects should be removed from the bath, rinsed with hot water and laid into the sufficient quantity of moistened cellulose fleece. The cellulose envelope prevents the formation of new surface coatings from the resin which condenses after having oozed out.

4. The objects are then put into polyethylene bags which are knotted up and stored at 65 °C for 48 hours. At this stage the wood, while in the waterlogged condition, is already made firm. Following thorough rinsing the objects are slowly dried to constant weight at room temperature and a relative humidity of about 50 % (not less !).

Experience has taught us that objects of up to 500 g. (wet weight) require a repetition of the entire treatment following a drying-up lasting 24 hours. In this case, however, after the object has been dipped into the bath, the air from the wood is removed by applying vacuum, and only 5 % of the catalyst is added. Objects with a wet weight in excess of 500 g. require three to four repetitions of the process.

In the case of thick objects it is necessary to make several boreholes to enable the resin solution to better penetrate into the bulk of the wood [86].

The most important condition to be complied with in the Arigal-C process is a thorough cleansing, in Step 1 and a slow drying of the objects in Step 4. In the case of oak, silver fir and yew, likewise in the case of round timber with a diameter in excess of 10 cm, cracks often appear later if the objects are stored at a low degree of humidity.

As an alternative to the process described above the catalyst can be added to the impregnating solution right at the beginning but in this case it is recommended that the initial concentration of Arigal-C does not exceed 15 % and the temperature be maintained between 10 and 15 °C, while the amount of catalyst must be reduced to 2 to 5 % of that of the resin. In this case the process should be repeated several times.

The white colour of the condensed resin itself imparts to the wood a bright coloration. When the wood is not packed carefully into a sufficient quantity of cellulose, it can acquire a chalk-like appearance, which requires an after-treatment with brushes and a wax or resin varnish or staining with a suitable dye [85].

In view of the short period of condensation Arigal-C seems to be unsuitable for large objects. The Russian method by Grabar [44] described here below merits consideration owing to the fact that the impregnants used are low-molecular weight pre-condensate (resinoids) of urea and formaldehyde, or melamine and formaldehyde, which are soluble in water or acetone. Compared with Arigal-C, their period of condensation is longer. When the solid content is between 30 and 60 %, the viscosity of the solutions is low since the resin is in the initial condensation stage. Ammonium chloride is used as catalyst. A reaction between the polycondensates produced and the wood components is considered to be possible. Also in this case it is highly important that a thorough preliminary cleansing is carried out. The pH of the cleaning water must not be lower than 7.5 - 8.

The treatment is subdivided into the following stages :

Following thorough treatment of the wood with water the wood is subjected to further treatment, either directly or after previous dehydration, with alcohol. 100 parts by weight of formalin (formaldehyde content from 37 - 40 %) are neutralized with ammonia, to bind the ever present formic acid. To this solution 46 parts by weight of urea or 32 parts by weight of melamine are added in two portions. Next the mixture is heated for thirty minutes on a water-bath. In the case of melamine this takes place at 80 - 90 °C, until the solution becomes clear ; with urea the temperature is kept at 25 - 30 °C. Finally also 15 - 20 parts by weight of ethanol are added. From this stock solution, according to the diverse porosity of the wood, the impregnating solution proper can be prepared, viz. by diluting the stock solution with 1 - 3 parts of alcohol, acetone or water. Immediately before the actual impregnation of the wood, 2 % of ammonium chloride, in terms of the resin content of the solution is added. The impregnation of the wood is achieved by immersing the objects for 2 - 5 hours. In cases when the objects cannot be immersed, the solution is applied to them with a painting brush, viz. until 300 - 500 g. of the resin solution has been absorbed per 1 kg. of wood. The impregnated wood is dried to constant weight for two to three days at room temperature. The entire process is repeated as long as the resin solution can be absorbed.

The method proposed by Lehmann, National Museum, Poznan, Poland [45], presents many similarities to the one just described. Waterlogged archaeological wood, especially oak and pine, is impregnated by dipping in a 10 % solution of a carbamide resin (Polish designation KMC 121), using 0,1 % mercuric chloride ($HgCl_2$) as a catalyst. The solvent used is a mixture of 20 % water, 55 % ethanol and 25 % glycerol or ethylene glycol. The impregnation is achieved within a period from several days to several weeks. The objects dry up and harden at room temperature. The wood preserves the natural colour. The microscopic investigations conducted over cross-sections reveal a complete impregnation with resin. The amount of resin absorbed fluctuates between 38 and 78 % of the wet weight and depends on the species of the wood and the degree of its degradation. The achieved strengh is considerable, and no shrinkage or form changes have been observed.

The conservation of waterlogged archaeological timber with thermosetting resins yields good results when the pre-condensation products (resinoids) are of sufficiently low molecular weight and, consequently, the viscosity of the solution is sufficiently low to enable the diffusion into the submicroscopic cavities. In the course of setting due to catalysts or heat the pre-condensates irreversibly embedded supporting materials which impart a high strengh to the wood. The application is limited to a certain extent because the rate of condensation cannot be exactly controlled. Whenever there will be some improvement in the diffusion power of the resins and in the control of the setting process, the conservation of the waterlogged archaeological wood with low molecular weight condensation resins will be subject to further development.

c) The electrokinetic method [87,91]

In 1949 Cebertowicz and Jasienski carired out tests at the Technological University at Gdansk, Poland, with the purpose of solidifying the ground in the foundations of buildings. The soil was saturated with aqueous solutions of sodium silicate and calcium chloride, and a direct current was allowed to pass at the same time. The action of the current brings about a shift of the liquid phase towards the negative electrodes allowing the reaction of precipitation of calcium silicate to take place at some depth inside the ground which is so consolidated. This method has been used repeatedly with the waterlogged archaeological wood at Gdansk and at Biskupin, in the latter place even *in situ*. The results are reported as successful. When used on a laboratory scale in other places this method failed to justify expectations.

d) The method of Garrouste/Bouis [14,92]

This is a chemical hardening process by means of an aqueous solution of 2 - 10 % chromic anhydride. The solution can be used either as such, or with an addition of 10 - 20 % sodium bichromate. The wood must be preliminarily thoroughly washed and left for some time in a 1 % hydrochloric acid, to eliminate any calcium carbonate present. The concentrations aer modified depending on the kind and dimensions of the objects. In the case of objects removed from freshwater 10 % sodium chloride should be added to the solution.

The entire method is described in the French Patent No. 1 392 835 of 1965.

Garrouste, the inventor, reports, as a result of his research, that, in the case of heartwood and under atmospheric pressure, each centimetre (in the direction of the thickness) requires a two-months' impregnation to achieve complete penetration. For larger objects it is recommended to introduce the preserving solution by injections under a higher pressure at a number of spots, after which the objects should immediately be left in a conservation bath for a prolonged time. Next the objects are allowed to dry in the air. They acquire a rust-brown colour, are light, porous and do not change any longer their dimensions during variations of humidity ; however they are brittle and need a fruther strengthening by impregnation with any solidifying agent. Depending on the type of the object the author used wax melts, linseed oil or solutions of thermosetting synthetic resins.

e) The alcohol-ether-resin method

Brorson-Christensen reported in 1951 [16] about his experiments with the conservation of waterlogged wood, based on the microscopic techniques of wood preparation. Pieces of up to 50 cm. in length were dehydrated in a series of alcohol baths, next the alcohol was replaced with toluene, to the toluene bath a mixture was added, consisting of beeswax, carnauba wax, paraffin wax and dammar resin, and the whole mass was kept at a temperature of 115 °C until all of the toluene had disappeared. The observation that, following the complete dehydration of the wood with alcohol, the dimensions did not change any longer, became the starting-point of the development of the alcohol-ether-resin method used at present.

After two renewals of alcohol this solvent was replaced with ether, and the objects were — preferentially in a vacuum — dried rapidly, which mostly can be done without shrinkage, warping and radial fissures. In this way Brorson-Christensen disproved the statement thus far in vigour, viz. that the wood saturated with water is unable, when in an anhydrous state, to carry its own weight, and therefore that it must collapse upon drying. However, the pieces thus dried retained their original dimensions only until they had absorbed from the ambient air the moisture owing to the hygroscopicity of the wood, whereupon the capillary attraction forces gave rise to shrinkage and fissuring. An immediate treatment with a 3 % polyvinyl-acetate solution and vacuum drying counteracts this sensitivity to moisture, and the product is finally strengthened mechanically with a 10 % solution of dammar resin. Later polyvinyl acetate was replaced by a solution of sandarac gum in ether, followed by vacuum drying. For strengthening Brorson-Christensen uses a 10 % solution of an acrylic resin in benzene and, after the final vacuum drying, he applies a protective coating of a synthetic oil lacquer.

This method is used with complete success for valuable and sensitive objects of a small size.

Proceeding from the experience gained by Brorson-Christensen, Kramer [93] has been developing since 1952 at the Schweizerisches Landesmuseum in Zurich improvements of the above method for the purpose of preserving waterlogged archaeological wood from the Stone Age settlements in such a way as to achieve not only the preservation of the form and volume, but also, as far as feasible, the natural appearance of the objects. For this end it was necessary to pre-treat the pieces in a cleaning bath containing 4 ml. concentrated ammonia and 4 ml. 30 % hydrogen peroxide per litre of water, viz. until the bath liquid is no longer coloured by the dissolved wood extractives. Next the items are thoroughly soaked in water, after which the dehydration of the wood is started by placing the pieces in ethanol of 70 to 90 % by volume. The alcohol is renewed until the density measurements demonstrate that no more water is removed from the wood. In the following stage ether is substituted for ethanol in a series of baths. The end-point of this exchange is determined by a test with the alcohol-soluble rhodamine B dye. Next the objects are placed in a conserving solution having the following composition : 500 g dammar resin (selected bright grade), 200 g palest rosin, 100 ml castor oil blown 4 000 cP (viscosity number), 100 ml stand oil, 3 000 ml ether, and left there until the density of the ether-resin solution has ceased to change.

Finally the pieces were vacuum-dried, and obtained as the final treatment a surface layer of plastic micro-waxes, which was applied with a brush in the form of a melt.

This methold is perfectly suitable for small objects made of broad-leaved woods, ash, sycamore, elm, linden, beech and oak sapwood. It is not suitable for coniferous woods, especially yew and silver fir. Objects exceeding 1/2 m. in length and 20 cm. in diameter have not so far been treated because of the danger involved in the use of the greater amounts of ether that would be required.

f) The polybutymethacrylate method, the Hermitage Museum, Leningrad [94]

I. Nogid and A. Pozdnyak dehydrate waterlogged archaeological wood in a series of three acetone baths. Immediately afterwards acetone is replaced with butyl methacrylate to which 0.3 — 1 % benzoyl peroxide has been added as a catalyst. After the wood has been saturated with the monomer the polymerization is carried out during 8 — 9 hours in a stove at 65 - 95 °C. Provided the impregnation has been satisfactory, one obtains by this method excellent dimensional stabilization.

Numerous finds from the Neolithic period and from the 12th century have been conserved with success, and the wood has a natural appearance.

g) The method of radiation-induced polymerization [95]

For the improvement of timber there are used in the U.S.A. on an industrial scale high-energy gamma rays to polymerize the introduced monomers. These monomers are introduced into the wood by way of solvent exchange following the removal of water with methanol. The Schweizerisches Landesmuseum in conjunction with the Departement of Physical Chemistry, Ecole Polytechnique de l'Université de Lausanne, has carried out preliminary tests with neolithic ash and fir wood specimens. Aqueous emulsions of styrene, methyl acrylate and methyl methacrylate, as well as their alcoholic solutions, were used to impregnate small wood cubes. These were then treated at room temperature with the radiation from a cobalt 60 radiation source. The radiation intensity of the source amounted to 0.6 Megarad/hour. In the case of emulsions the results were unsatisfactory ; the wood absorbed an insufficient quantity of the monomeric substances. However, the tests with pure monomers brought about an excellent strength and dimensional stabilization [37].

Further work was undertaken in the meantime by Munnikendam at the Central Laboratory for the Examination of Works of Art in Amsterdam. This research has resulted in new practical possibilities in the field of conservation of waterlogged wood [39, 95].

Monomers were introduced into the wood by a solvent-exchange process, replacing water with methanol and the latter with a monomer. In the case of the water-soluble monomer 2-hydroxyethylmethacrylate only one exchange process would be needed.

After complete diffusion the wood-monomer combination was irradiated by gamma radiation from a Co 60 — source of the Reactor Instituut of the Technische Hogeschool in Delft.

The advantage of this method are obvious :

1. Due to their lower molecular weights the monomers will have far greater diffusion constants.

According to Graham's law [72] the diffusion constant of a compound is approximately inversely proportional to its molecular weight whereas the time required for any point in the wood to reach a given concentration varies inversely as the diffusion coefficient [96].

Thus as a first approximation it can be stated that the diffusion time of a certain substance will be proportional to its molecular weight. Methanol having a molecular weight of 32 will diffuse about 30 times as fast as PEG 1 000, whereas methyl methacrylate, with a molecular weight of 100, will differ from PEG 1 000 by a factor 10.

2. Working with undiluted methanol and monomers which will enhance the speed of the process is not expected to be hazardous.

This is due to the diffusion constants of water and of impregnating fluids being more comparable to each other.

3. Due to their smaller dimensions the monomers are able to penetrate more easily into the intermicellar spaces of the cell wall.

From what is said in Chapters 2 and 3 of this book it follows that any molecule having larger dimensions than the pore size of the intermicellar space is mechanically prevented from entering it and will not exert any stabilizing effect. Tarkow et al. [97] showed that the limiting size for the penetration of a water soluble material into green sitka spruce wood substance is that of a PEG 3 000 molecule.

4. Unlike PEG the formed polymer is a hard substance and will give the wood considerable increase in strength.

5. The resin is cured without the need of introducing a catalyst after the impregnation, which in certain cases will be necessary, as for instance the treatment with melamine-formaldehyde resin [40, 46].

The γ -radiations in view of their penetrating power will start polymerization in every part of the wood to the same extent.

The effect of high-energy radiations on wood has been described by various authors [98, 99]. It mainly consists in the cross-linking and scission of the lignin carbohydrate of the wood. The hemicelluloses are most susceptible to radiolysis ; cellulose comes next. Lignin is the most radiation-resistant component, due to its aromatic groups which protect carbohydrates from radiolysis [100].

It has been shown that little deterioration of wood qualities is caused by doses less than 10 Mrad. For the polymerization of methylmethacrylate in wood a dose of about 5 Mrad will be sufficient in most cases, moreover most of the radiation energy is in this case absorbed by the monomer. The process of γ-ray-induced polymerization in wood has been described by various authors [100, 106].

Munnikendam carried out tests on cross sections of oak wood, 1 cm. in the fibre direction and 3 cm. in the other direction.

The specimens were dressed so that the growth rings were as parallel as possible to two opposite faces.

The wood was cut from a plank belonging to the wood finds of the Zuyder Sea reclamation, which was representative for most of those finds.

The length of the plank was about 80 cm., the width about 20 cm. and the thickness about 7 cm. Most samples were cut from the heart.

After additional soaking in tap-water during a few months its water content and shrinkage were determined by drying at 103 °C during 24 hours. The percentage of water was 62 % of the wet weight (160 % of the oven dry weight). There was a shrinkage of 15.2 % of the wet dimensions in tangential direction (18 % of the oven dry dimensions) and 8.1 % of the wet dimensions in radial direction (8.9 % of the oven dry dimensions).

No shrinkage occurred in the fibre direction. For fresh oak these figures amount to 40-45 % for the maximum water content, 8.2 % for the tangential shrinkage and 4.0 % for the radial shrinkage. (All percentages relate to the wet state) [106]. A number of samples were treated by ammonia + H_20_2. After weighing and measuring the specimens were treated with the monomers methylmethacrylate and 2-hydroxyethylmethacrylate.

The latter is a water-soluble monomer and can be used to replace the water directly. In the case of methylmethacrylate the water has first to be exchanged for methanol.

The time needed for one exchange process varied from 3-5 days ; each day the treating liquid was renewed.

After this process the samples were sealed in Melinex polyester film to prevent evaporation, and irradiated with a Co 60 — source. They were given a dose of 5 Mrad at a dose rate of approximately 0.1 Mrad/hr. After irradiation they were dried at 60 °C for eight hours and overnight at 103 °C. Dimensions and weights were then measured again. The percentage of shrinkage in three directions was calculated and compared with untreated blocks of similar dimensions which were dried under the same circumstances.

The extent of impregnation was calculated from the known water content assuming a 100 % impregnation in the case when all the water was replaced by an equal volume of methylmethacrylate.

TABLE 7

weight		% impregnation	tangential dimensions		% shrinkage	radial dimensions		% shrinkage	longitudinal dimensions		% shrinkage
before	after		before	after		before	after		before	after	
12,24	12,40	109	3,22	3,20	0,6	3,10	3,11	—0,3	1,26	1,31	—3,8
9,01	9,17	110	2,66	2,65	0,4	2,86	2,83	1,0	1,23	1,29	—4,6
8,34	7,95	98,5	3,09	3,10	—0,3	2,46	2,40	2,0	1,09	1,11	—1,8
10,29	10,54	111	3,20	3,17	1,0	3,00	3,00	0,0	1,07	1,14	—6,1
10,78	11,09	111,5	3,08	3,12	—1,3	3,03	3,05	—0,6	1,16	1,18	—1,7
9,68	9,68	107	3,27	3,24	0,9	2,85	2,84	0,3	1,02	1,08	—5,6
15,8	14,8	93,5	3,42	3,30	3,5	3,32	3,25	2,1	1,24	1,24	0,0
12,7	10,9	77,5	3,06	2,90	5,2	3,00	2,91	3,0	1,24	1,25	—0,8
12,1	11,2	91,5	2,91	2,83	2,7	3,03	2,96	2,3	1,23	1,24	—0,8
13,4	11,4	76,0	2,96	2,83	4,3	3,25	3,21	1,2	1,21	1,20	0,8
14,4	11,9	70,0	3,07	2,97	6,5	3,13	3,01	3,8	1,35	1,32	2,3
13,7	11,6	75,0	3,16	2,95	6,6	3,14	3,01	4,1	1,24	1,21	2,5
14,4	12,4	77,5	3,20	3,07	4,1	3,25	3,12	4,0	1,24	1,23	0,8
12,9	11,0	76,0	3,22	3,05	5,3	3,08	2,97	3,5	1,17	1,17	0,0

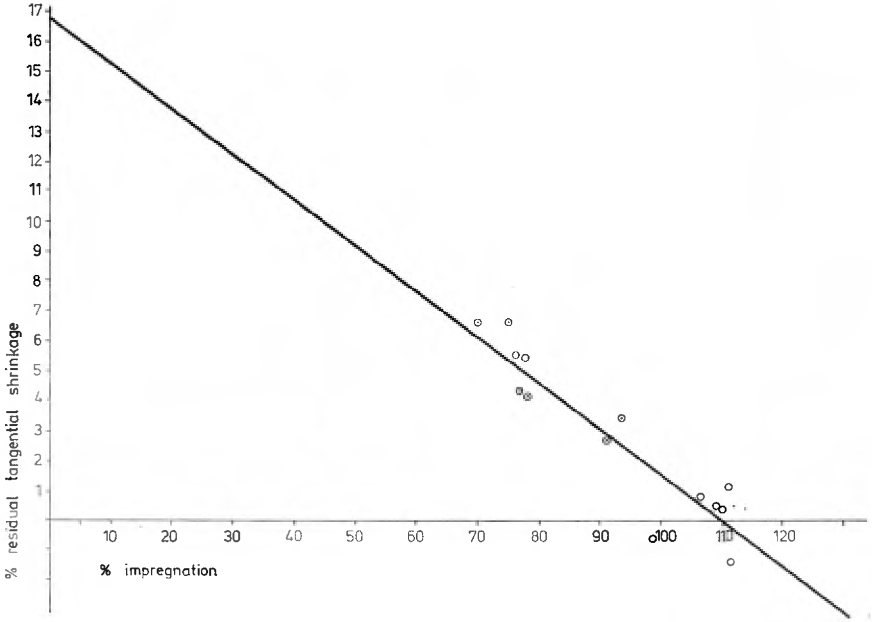


FIG. 8. — Percentage of residual tangential shrinkage vs. Percentage of impregnation with methylmethacrylate.

When this percentage was plotted against the residual tangential shrinkage a straight line was obtained (fig. 8, table 7).

From this graph it may be seen that a 100 % dimensional stabilization is achieved only at 110 % impregnation with methylmethacrylate. This is probably due to the shrinkage during polymerization, the loss of volume being compensated by the diffusion of additional monomer into the sample which had not been wiped with blotting paper so that an excess monomer was always present.

7

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8

THE CONSERVATION OF WET LEATHER

1) Description of wet leather

Waterlogged leather is considered to be the result of a processus of alteration under anaerobic conditions. The extent to which the alteration has progressed depends mainly on the environmental conditions, pH value and microorganisms present. In such leather the bundles of collagen fibres and other protein fibres constituting the leather will be found to be converted to a more or less advanced glutinous state. On drying, these fibre bundles will no longer be able to slip over each other. Therefore a horny and brittle material is obtained. Presumably the original compactness of the *weave,* the amount of the break-up of bundles into fibres and the kind of processing which the leather once had undergone, will also affect the rate of decay. Vegetable tanned leather is most permanent, whereas, e. g., alum dressing imparts to the skin the properties of leather only as long as the alum is present [1-3].

2) Methods of conservation

The methods will be discussed under two headings : Replacement of water by a non-volatile material and replacement of water by a less polar solvent.

a) *Replacement of water by a non-volatile material*

The mateiral replaces water by diffusion and fills the voids between the fibre bundles, restoring to a certain extent the mechanical strength of the leather.

In earlier references are mentioned the use of Turkey red oil and linseed oil to restore flexibility to ancient leather which has become brittle and desiccated. In museum collections one comes across leather objects from excavations, which have been treated with linseed oil and glycerol becomes somewhat flexible. However due to its hygroscopicity such objects take on a such conditions can only be overcome by incorporating a fungicide. Phenol and the water-soluble sodium salt of its chlorinated compounds are often used. Polyvinyl alcohol, that is widely used for the impregnation of modern leather [4], is mentioned for the treatment of wet leather by Rumyantsev [7] who uses with quite good results an aqueous solution containing 0,7 - 2,5 % PVA and 40 - 42 Vol-% of glycerol. Experiments carried out in our laboratory yielded unsatisfactory results, when fragments of eighth century belts recovered from a coarse, gravelly soil were treated with PVA. The samples become strongly distorted and brittle. According to Plenderleith [2-3] leather from bogs or damp ground is immersed after cleaning in molten vaseline. Given favourable circumstances this enabled the object to be moulded back in to shape. The vaseline was then replaced with paraffin wax.

More recent experiments by Werner [6], carried out on the use of hydrophilic polyethylene glycols for the purpose of restoring the flexibility to desiccated and brittle ancient leather, have turned out to be also applicable to we leather.

Lefève [5] has described the treatment of several pieces of Roman and medieval leather, using Carbowax 750, a methoxy-polyethylene glycol, having a metting point of 30 °C. The objects, after careful cleaning, aer placed between glass-plates, then immersed into molten Carbowax. The wax is replaced several times with fresh material, each time for a prolonged period. Finally air-drying is allowed for two months approximately. The excess of wax is removed by wiping off (or by dissolving it with xylene).

A similar method was reported by Mrs. Blomberg [8]. After cleaning, the objects were spread out and the wax (polyethylene glycol

600) applied by brushing and painting with a 50 % aqueous solution. After air-drying the treatment was repeated at least three times, if necessary locally. Finally the objects were stored in polyethylene bags.

At the British Museum Laboratory (private communication by A. Werner) leather is immersed at 40 °C in molten polyethylene glycol, the particular grade used is Carbowax 1500, i. e. a mixture of equal parts of Carbowax 300 and 1540. The leather is left immersed in molten wax until the water has been replaced with the wax. Finally any excess of wax is removed from the surface with toluene and the leather then allowed to dry.

According to Wihr [10] Roman wet leather was kept either in Polydiol 400 at room temperature during 6 weeks or soaked in a 50 % aqueous solution of Polywachs 550 MG during 6 weeks and the temperature of the bath gradually raised to 60 °C. The excess of consolidant in both cases wases wiped off and the object left at normal temperature. Elasticity and softness were greasy to the touch. The former treatment had, on the contrary, a tendency to sink in.

A general drawback of all these methods is that although polyethylene glycol is much less hygroscopic than glycerol the objects tend to become moist on porlonged exposure to a humid atmosphere.

b) *Replacement of water by a solvent*

Water can be replaced by a less polar solvent, using a sequence of solvents of decreasing polarity. The glutinous collagen fibres are so desiccated, thus rendering their surface less sticky, before they approach each other again as a result of capillary forces occurring between them on evaporation of the solvent.

At the National Museum of Copenhagen (private communication) acetone is used to replace water. A detailed description of the process is not yet available.

The method used in the laboratory of the Swiss National Museum is as follows : 1. Thorough cleaning from soil deposits, among which clay particles are the most resistant. Removal of dark iron tannates by immersion for instance in a solution of disodium ethylene-diamine-tetraacetate ; the objects are surrounded by wire gauze and treated for 30 minutes with ultrasound, then carefully rinsed with pure water. 2. The objects are immersed in acetone and this is repeated several times. Methylethylketone is sometimes preferred in view of its lower volatility. 3. The leather is soaked for some minutes in carbon tetrachloride containing a fungicide, e. g. tributyltin oxide or tributyltin naphthenate and then allowed to dry between sheets of blotting paper and glasse-plates. In most cases a light-coloured leather of good flexibility wa obtained. The treatment of several medieval shoes by this method was described in reference [9]. The sole leather was less flexible than the top leather, as might be expected from its original function.

Objects consisting of both wood and leather

A. Werner (private communication) has developed the following method for a leather covered wooden shield. The whole is immersed in a 10 % solution of Carbowax 1540 at 45 C. More Carbowax solution is gradually added, giving the solution the strength of 20 %, 40 %, 60 % and finally enough solid wax is added, so that the object will be covered completely with the molten wax at the end of the process.

Fungicides

In all cases concerned with leather a fungicide should be incorporated at least in the final stage of the process. Some suitable types are listed below :

Types soluble in water :	Sorbic acid, solium salt of chlorinated phenols (Preventol 1, Santobrite, Cryptogil Na), sodium o-phenylphenate (Dowicide A), quaternary ammonium bases (Desogen).
Water insoluble types :	Cedarwood oil, pine oil, o-phenyl-phenol (Dowicide 1), salicylanilide, 2-mercaptobenzothiazole, tetrachloro-p-benzoquinone, octachlorocyclohexanone, organo tin compounds (tributyltin naphtenate and tributyltin oxide).

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APPENDIX

List of chemical products mentioned in the text and their source of supply. For further information the reader is referred to the pamphlet « Synthetic Materials used in the Conservation of Cultural Property » edited by the International Centre for the Study of the Preservation and the Restoration of Cultural Property and reprinted, in a revised form, as an appendix to the handbook *The Conservation of Cultural Property* UNESCO, 1968 (French and Spanish translations are also available at UNESCO).

Product	*Composition*	*Properties*	*Source of Supply*
Arigal C	Melamine-Formaldehyde pre-condensate	Thermosetting resin	CIBA, P. O., Box 4000, Basle 7, Switzerland.
Carbowax	Poylethylene glycol	Water soluble	Union Carbide Corp., 30 East 42nd Street, New York, U. S. A.
Criptogil Na	Sodium pentachlorophenate Isocyanate	Fungicide, water soluble	Xylochimie, Progil-Pechiney, 5, rue de Berry, Paris-8^e, France.
Desmodur D	Isocyanate	Component of thermosetting resins	Badische Anilin & Soda Fabrik, Ludwigshafen, W. Germany.
Desogen	Quaternary ammonium base	Water soluble	J.R. Geigy S.A., Schwarzwadallee 215, Basle, Switzerland.
Dowicide A	Sodium o-phenyl phenate	Fungicide, water soluble	Dow Chemical Co., Midland, Michigan, U. S. A.
Dowicide 1	O-phenyl phenol	Fungicide, soluble in organic solvents	» »
Polydiol Polywachs	Polyethylene glycol	Water soluble	Chemische Werke Hüls A.G., Marl, Kreis Recklinghausen, W. Germany.

Product	*Composition*	*Properties*	*Source of Supply*
Preventol	Sodium trichlorophenate	Water soluble. Fungicide for leather	Bayer A.G., 509 Leverkusen, W. Germany.
Rhodoviol	Polyvinylalcohol	Water soluble	Soc. des Usines Chimiques, Rhône - Poulenc, 21, rue Jean-Goujon, Paris-8^e, Fr.
Santobrite	Sodium pentachlorophenate	Fungicide. Water soluble	Monsanto Co., International Div., 800 N Lindbergh Blvd, St. Louis, Missouri 63166, U. S. A.
Tego 51 B	Alcalyl-(amino ethyl)-glycin hydrochloride	Water soluble. Surface active disinfectant	Theodor Goldschmidt A.G., Chemische Fabriken, Essen, W. Germany.
Tertiary butyl alcohol	Trimethyl carbinol	Solvent	Shell Chemical Co., 113 West 52nd Street, New York, N. Y. 10019, U.S.A.
Thymol	3-p-cymenol	Fungicide. Insecticide	Eastman Organic Chemicals Dept., Rochester 3, N. Y., U. S. A. or The British Drug Houses Ltd., Poole, England.
Elvanol	Polyvinylalcohol	Soluble in water	E.I. du Pont de Nemours Inc., Wlmington 98, Delaware, U. S. A.
Fluralsil BS	Combined organic and organic salts. Free of fluorine	Soluble in water	Desowag-Chemie GmbH, Bismarckstrasse 83, Düsseldorf, W. Germany.
Gelvatol	Polyvinylalcohol	Soluble in water	Shawinigan Products Corp., Shawinigan Falls, P. Q., Canada.
2-Hydroxy-ethyl-methacrylate	Hydroxethyl ester of methacrylic acid	Monomer. Soluble in water	Rohm & Haas Co., Independence Mall West, Philadelphia 5, Pa., U. S. A. also Rohm & Haas GmbH, Weiterstadtstrasse 42, Darmstadt, West Germany.
Melamine	2,4,6-triaminotriazine	Component of thermosetting resins	Shell Chemical Co., Plastics and Resins Division, 113 West 52nd Street, New York, N. Y. 10010, U.S.A.

Product	*Composition*	*Properties*	*Source of Supply*
Modolog antiqua	Polyethylene glycol	Water soluble granulate combined with fungicides	Mo och Domsjö A B, Strandvägen 1, Stockholm.
Modopeg	Polyethylene glycol	Water soluble	Mo och Domsjö A B, Strandvägen 1, Stockholm, Sweden.
Mowiol	Polyvinylalcohol	Water soluble	Farbwerke Hoechst A.G., Postfach 70, Frankfurt am Main, Germany.
Peg (PEG)	Polyethylene glycol	Water soluble	Shell Chemical Co., Plastics and Resins Division, 113 West 52nd Street, New York, N. Y. 10019, U.S.A.
Tributyltin naphtenate Tributyltin oxide	Organic tin compounds	Insoluble in water. Fungicides	Metal & Termite Corp., 200 Park Ave., New York 17, U. S. A.
Vinavilol	Polyvinylalcohol	Water soluble	Montedison Spa Largo G. Donegani, Milan 20121, Italy.

Dépôt légal : 4e trimestre 1972. **N° d'Editeur : 2 699**

IMPRIMERIE LABOUREUR ET CIE, 5-7 RUE DE ROME, 36 - ISSOUDUN

8456