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Conservation of Wood Artifacts

A Handbook



Springer

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*We owed to wood so very much. We wasted nothing of it.
It held up our houses and fueled our fires. We made our tools
from it, we made our vessels from it.*

*When we brought down a tree, it was long work to make it
fit into our world of useful things. But it brought us beauty.*

Early People Exhibition
Museum of Scotland, Edinburgh

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Preface

The impetus for this book was the desire to systematically organize the extant literature on the conservation of cultural property made of wood, from its beginnings before the Christian Era to the year 2000. Various published reviews and monographs, including *Holzkonservierung* (Wood Conservation) published by the senior author in 1988, have appeared over the years, especially in English and in German. They have provided exemplary treatment of individual areas or aspects of wood conservation, but a comprehensive, up-to-date exposition of historic and current developments has been lacking. The diverse professional fields of the authors, as well as their insights into methods of conservation and restoration of wood artifacts in Europe, North America, and Asia provided a solid basis for the success of this undertaking. One of the goals during the examination of the literature was that not only well-known conservators and scientists from countries that are leaders in wood conservation should be represented, but that less well-known, often not as readily accessible contributions should also be included. Only in this manner was it possible to draw a comprehensive picture of the national and international state of wood conservation. The Art and Archaeology Technical Abstracts (AATA) of the Getty Institute were very helpful in our efforts to evaluate as many publications as possible.

This book is not to be understood as a collection of recipes, although there are many instances where techniques of conservation are described in some detail. The use of conservation materials should take place only when all other possibilities have been exhausted. Conservators/restorers must understand very clearly that the preservation of an object by the application of conservation materials and methods is accompanied by a loss of originality. Any treatment should be based on the premise "as little as possible, as much as necessary." Unfortunately, objective criteria and methods for determining how much intervention is really necessary are rarely at hand. One essential question is whether the original properties of the native wood of a damaged object should be reestablished, or whether only a condition permitting safe presentation of the object is required. The number of cases where former restorations are being removed again is increasing continually, and the choice of conservation materials and methods must therefore be made especially carefully and responsibly. There are all too many examples of cases where the application, with the best of intentions, of conservation materials

and methods resulted in a noticeable worsening of the condition of treated objects with the passage of time. The inevitable, gradual deterioration of objects should be slowed down and should not be accelerated by ill-considered conservation measures.

The authors proceed from the premise that nothing is perfect and that everything is in need of continual improvement. They would therefore be grateful for comments on the book that would eradicate errors, replenish the missing, and rescue the forgotten from anonymity.

Many colleagues and associates have supported the development of this book and have been of great help in its realization. We are especially indebted to Professor Frank C. Beall, Professor W. Wayne Wilcox, Ms. Gail Getty, Dr. Harald Berndt, Dr. Rod Eaton, Mr. Oskar Dietterle, Mr. Klaus Pelz and Mr. Hans-Peter Wunderlich. Special thanks go to Mrs. Edith Boche for her continual assistance and patience during the preparation of this book.

Last, not least, the authors would like to thank Mrs. Christiane Glier of Springer-Verlag for her cooperation and helpful support.

Berlin, Berkeley and Eberswalde,
June 2001

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Introduction

This book is intended to be a comprehensive source on the history of wood conservation, on the structure and properties of wood, on organisms causing deterioration, on methods of diagnosis of wood condition, on materials and methods of wood preservation, on consolidation of deteriorated wood, and on adhesives for wood. An overview of the use of particular conservation materials and methods is presented as they apply to dry wood as well as to wet or waterlogged wood, the division being based roughly on the fiber saturation point.

Access to the information is facilitated by separate indexes for conservation materials, trade names, and pests. The core chapters contain a general introduction followed by more specific exposition. Conservation materials and methods gathered from the voluminous literature are organized chronologically, since dates of first use and the periods of use are important to present-day conservators/restorers. For liquid preservatives, fumigants, and consolidants, these listings are preceded by important data on each of the materials.

Trade names of old products no longer used or no longer available are included in addition to materials used now. The assortment of trade names is based on their appearance in the original literature on wood conservation and its references, but no claim for completeness can be made. Data cited on composition of commercial products and the data on material properties are intended as an aid to conservators for their use on particular objects and for removal of old conservation treatments. In the case of older commercial products precise information on composition was often lacking. It was also difficult to determine the composition of products which kept the same trade name while changing the formulation repeatedly over the course of time. Material data in the great majority of cases is based on the chemical dictionary *Römp-lexikon*.

Conservation materials often have significant toxicological effects, and their description seemed to be desirable. For wood preservatives and fumigants, their biological effects are also listed, because conservators may not always be able to determine at first glance whether it is a fungicide, an insecticide, or bactericide, etc., or whether the materials can be used against several types of pests. Directions for the use of wood preservatives and fumigants only apply to dry wood, and variations of the listed concentrations are possi-

ble. Data on the actual effective amounts of pesticide in terms of g/m^2 or kg/m^3 have not been included, since each relevant pest organism and its developmental stages would have had to be considered separately.

Originally, a chapter on chemical analysis of wood and of conservation materials had been considered. In view of the somewhat secondary importance of the subject to conservators and because of limitations of space, this had to be abandoned. However, descriptions of each of the conservation materials include a listing of possible chemical analysis methods.

Information on the use of conservation materials is divided into historical and present-day uses. This emphasizes active or restricted use of certain materials, which in turn can often be deduced from the listed advantages and disadvantages. The discussion of advantages and disadvantages is based mainly on information in the original literature, but the authors' own experience has also been drawn upon. A sharp division between advantages and disadvantages did not appear to be meaningful, since such distinctions are sometimes a matter of judgment and may also depend on the specific application being considered. The chapters "Liquid Wood Preservatives," "Fumigants," and "Consolidants" contain special sections dealing with potential or previous damage caused to objects and suggestions on how to avoid or remedy these, so that the behavior of these conservation materials can be more effectively evaluated. The resistance of consolidants to biological deterioration, which to date has received scant attention, has been especially considered. In the chapter "Adhesives and Gap Fillers" descriptions of gluing technology and particular adhesive joints have been purposely omitted, since comprehensive publications on those subjects are already available.

Extensive listings of literature are appended to each chapter which should facilitate access to primary and secondary sources. In many cases the reference to the AATA abstract is also given, in case the original publications are difficult to obtain.

1 History of Wood Conservation

Wood is one of the oldest materials used by people for making tools, utensils, shelter, ships and vehicles because it can be easily worked with simple tools. It soon became apparent that wood is susceptible to the effects of fire, weathering, and various organisms. The Bible referred to decay fungi and wood borers as pests. Thus, it is not surprising that people attempted to improve the durability of wood by various means.

People observed from nature that the wood of certain trees was either less susceptible to pests or even avoided by them altogether. Australian aborigines used the termite and fungus resistant bloodwood for their graves about 5000 B.C., the Mayas built a temple in Guatemala about 700 A.D. with a termite-resistant wood, and Theophrastos (371–287 B.C.) made a list of durable woods. It was also believed that the season when trees were felled influenced the natural durability of wood. Ancient literature has many references to the most suitable season and phases of the moon for felling trees (Indian Rig-Veda, 1000–400 B.C.; Hesiodos, about 700 B.C.; and Confucius, 551–479 B.C.), and even Napoleon demanded in 1810 that warships be built of winter felled timber, but present-day insights do not attach any importance to these criteria. Recommendations for debarking and careful storage in air or water in order to minimize attack by pests and to prevent checking and splitting of the wood have also been handed down.

Large quantities of wood have been used for building ships and houses, and it is apparent from many structural details that there were attempts to guard wood members against destructive agents in order to prolong their useful life. The buildings on stilts of the stone age, the temples of the Mayas, and the Norwegian stave churches which lasted for 800 years are telling examples of the continuing development of methods to preserve wood in structures.

Attempts were made to increase the durability of wood, even before working it, by treatment with preservatives. Early beginnings of chemical preservation included charring, storage in salt water, and brushing with oil, tar, or pitch (Appendix Table 1). Decay fungi, wood borers, shipworms, and termites as persistent pests threatening wood in use forced people to search for ways to preserve it. Columbus' report on his fourth journey shows how serious the situation could be: "the shipworms have attacked the ships so severely that they look like honeycombs" and "there is no remedy against the

scourge of the worms." In the eighteenth century the dikes in Holland were hit by a catastrophic attack of shipworms, which led to the proverbial expression "Holland in need." In 1784 the Royal Society of Arts resolved to award a gold medal to the person who could discover the origin of wood decay in houses and control it effectively.

During the Middle Ages, the recipes of antiquity were by and large adopted, but new chemical substances also found their way into wood preservation. It is known that Leonardo da Vinci (1452–1519) coated the wood panels for his paintings with mercury(II) chloride and arsenic(III) oxide. The physician and chemist Homberg (1652–1715) in 1705 also recommended mercury(II) chloride to control wood borers. The substance attributed to him, *sal sedativum Hombergi* or boric acid, is today one of the most important preventive wood preservatives. In 1718 a "Holtz-Balsam" (wood balm) was patented, and at the beginning of the nineteenth century the *Encyclopedia Britannica* already contained lists of wood preservatives. The English chemist Kyan, after years of experimentation, was awarded a patent for the soaking treatment of wood with mercury(II) chloride in 1832, thus marking the beginning of modern wood preservation. Other substances and processes soon arrived into a developing market. In 1874, the work of R. Hartig on the principal decay fungus attacking buildings in Europe was published, which recognized the origin of the attack as being due to invasion of fungi. This book stimulated further search for suitable wood preservatives, which culminated around the turn of the century in many new preparations.

The rapid advances in industrial wood preservation had virtually no impact on practices in the conservation of wood artifacts. As late as 1852–1855, A. Stifter treated the Kefermarkt altar in Austria (Fig. 1.1) with table salt which is completely ineffective against insects. Councillor Bolle's attempts to drive off the altar's wood borers by brushing with petroleum and hexachloroethane during 1916–1918 were equally unsuccessful. It was not until 1929 that the use of hydrogen cyanide, which had been in use in America against pests in plants and stored products since 1880, brought the desired success (Appendix Table 2). Since then, fumigants have played an important role in freeing cultural property of wood-destroying pests. Most recently, attempts have been made to replace such highly toxic, environmentally unfriendly substances as hydrogen cyanide, bromomethane, and ethylene oxide with inert gases such as carbon dioxide, nitrogen, or argon. The destruction of insects by reduction or replacement of vital oxygen with these gases goes back to a method practiced in antiquity, where grains were stored in hermetically sealed containers which caused the oxygen content to be reduced so much that insect pests had no chance of survival.

Control of wood-destroying insects and fungi by heat application is also not new (Appendix Table 3). Statements in the older literature, however, often do not make it clear whether the treatment is a matter of drying of the wood or a destruction of the causative pests, or both. The environmentally friendly hot air treatment has been an important method for controlling the

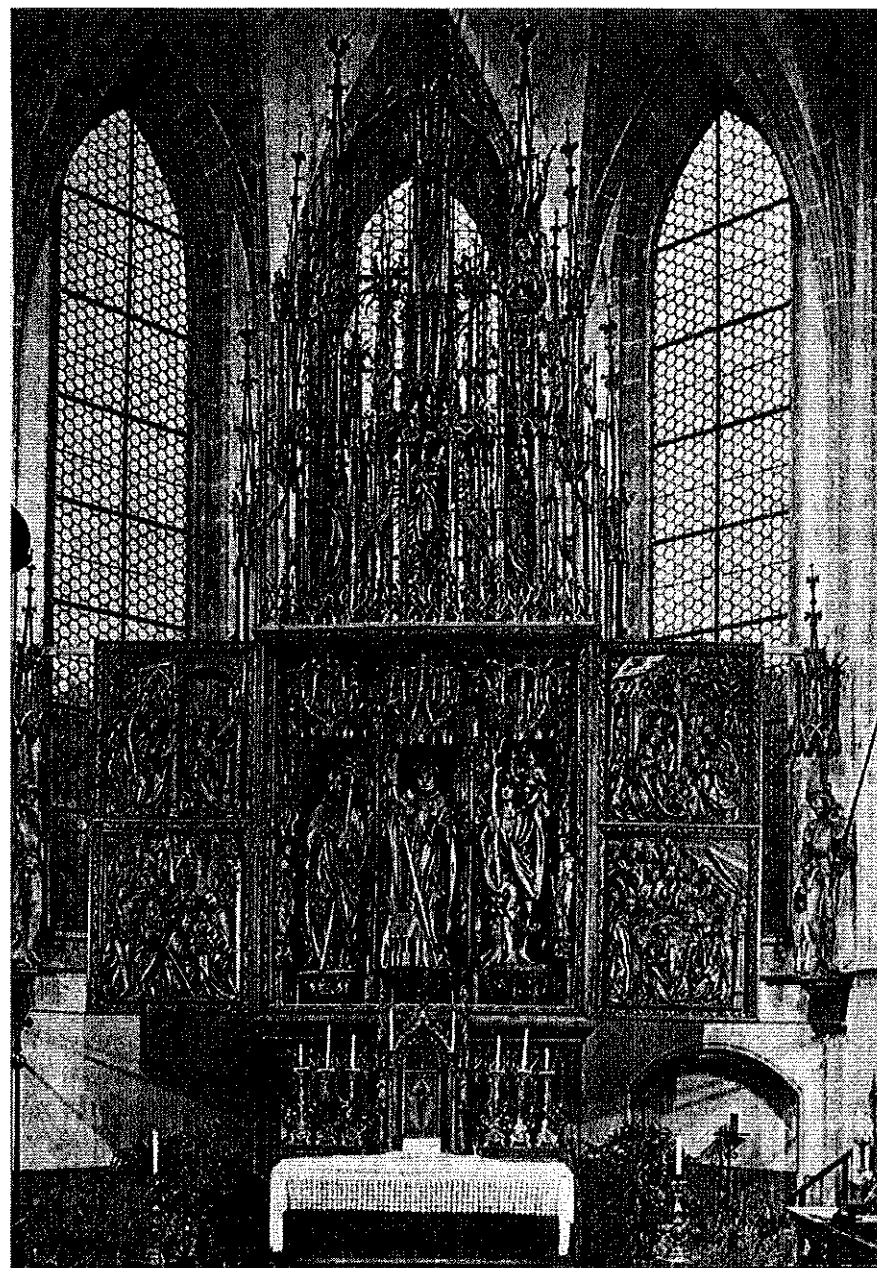


Fig. 1.1. The Kefermarkt altar in Austria

larvae of wood borers in registered historical buildings. Museum objects attacked by insects can also be treated with low temperatures, microwaves, or gamma radiation, while other electromagnetic waves are used comparatively seldom.

With regard to consolidation of deteriorated wood, moisture content is very important. Accordingly, we can make a fundamental distinction between consolidation methods for deteriorated dry wood in structures, monuments, and museum objects, on the one hand, and wet or waterlogged wood finds from archaeological excavations, on the other.

During the eighteenth and nineteenth centuries, stabilization of valuable cultural property such as wood carvings of altars which had been severely damaged by insects was carried out primarily by impregnation with glue (Appendix Table 4). Approaching the twentieth century, oil, varnish, and natural resins and waxes were added which were used either alone or, more commonly, as mixtures. New products based on cellulose nitrate or cellulose acetate also came into use as wood consolidants at that time. The development by D. Rosen of the wax immersion method for consolidating biologically deteriorated sculptures was the outstanding event in wood consolidation in the 1930s. Following World War II, the plastics industry underwent rapid development, and its products were also tested by conservators for their suitability for the stabilization of deteriorated wood artifacts. About 10 years after the industrial production of wood-plastic combinations by impregnation with monomers and polymerization in situ, this method was first applied to cultural property. During the second half of the 1980s, a number of publications appeared which contained long overdue critical evaluations of the properties of various wood consolidants.

The recovery of the first large objects of waterlogged wood in Scandinavia in the middle of the nineteenth century created an urgent need for a suitable conservation method. Thanks to the Danish restorer C.F. Herbst, many threatened objects could maintain their external form and be stabilized by exchanging the water in the wood with alum (aluminum potassium sulfate; Appendix Table 5). In this manner, between 1858 and 1958 about 100,000 individual objects could be stabilized and preserved for future generations at the Denmark National Museum. Beginning in the 1930s, extensive research was conducted at the United States Forest Products Laboratory in Madison, notably by A.J. Stamm, on various methods for modifying wood to minimize its shrinkage. One of these was treatment with poly(ethylene glycol), PEG, which replaced the alum treatment. PEG was used for treating the Swedish warship *Wasa* recovered in 1961. PEG was also selected for the stabilization of the remains of the *Mary Rose*, the flagship of Henry VIII of England. Smaller wood objects have been pretreated with low molecular mass PEG and freeze-dried. W. Powell was awarded a US patent in 1904 for treating wood with sugar to minimize shrinkage. This treatment was not a commercial success, but most recently there is growing interest in using beet or cane sugar or sugar alcohols for the stabilization of waterlogged wood finds.

Overviews relating to the history of wood conservation have been published by Broese van Groenou et al. (1952), Lohwag (1967), Brorson Christensen (1970), Graham (1973), Bill and Mühlethaler (1979), Schiessl (1984), Grattan and Clarke (1987), Clausnitzer (1990), Richardson (1993), Tsoumis (1995) and Schiessl (1998).

References

- Bill J, Mühlethaler B (1979) Zum Holzaufbau und zur Entwicklung der Holzkonservierung. *Z Schweiz Archäol Kunstgesch* 36(2):99–102
- Broese van Groenou H, Rischen HWL, van den Berge J (1952) Wood preservation during the last 50 years, 2nd edn. AW Sijthoff's Uitgevers – Maatschappij NV, Leiden
- Brorson Christensen B (1970) The conservation of waterlogged wood in the National Museum of Denmark. *Museumstekniske Studier* 1. The National Museum of Denmark, Copenhagen
- Clausnitzer K-D (1990) Historischer Holzschutz. *ökobuch*, Staufen bei Freiburg
- Graham RD (1973) The history of wood preservation. In: Nicholas DD (ed) *Wood deterioration and its prevention by preservative treatments*. Syracuse University Press, Syracuse, pp 1–30
- Grattan DW, Clarke RW (1987) Conservation of waterlogged wood. In: Pearson C (ed) *Conservation of marine archaeological objects*. Butterworths, London, pp 164–206
- Lohwag K (1967) Zeittafel zur Geschichte des Holzschutzes. *Int Holzmarkt* 58(16/17):45–54
- Richardson BA (1993) *Wood preservation*, 2nd edn. E & FN SPON, London
- Schiessl U (1984) Historischer Überblick über die Werkstoffe der schädlingsbekämpfenden und festigkeitserhöhenden Holzkonservierung. *Maltechnik Restauro* 90(2):9–40
- Schiessl U (1998) History of structural panel painting conservation in Austria, Germany, and Switzerland. In: Dardes K, Rothe A (eds) *The structural conservation of panel paintings. Proceedings of a Symposium at the J. Paul Getty Museum, 24–28 April 1995*, The Getty Conservation Institute, Los Angeles
- Tsoumis G (1995) The beginning of wood science. *J Inst Wood Sci* 13(6):535–538

2 Wood Structure

2.1

Macroscopic Structure

2.1.1

Recent Wood

Wood is the secondary, permanent tissue of woody plants, i.e., trees and shrubs. It is made up of interconnected cells which vary in appearance, size, number, type, and arrangement. Tissues are formed by agglomeration of like cells. The various types of tissues fulfill the functions of mechanical support, conduction of liquids, and storage.

The wood of trees and shrubs is surrounded by bark, which is divided into inner and outer bark (Fig. 2.1). Between wood and bark is the macroscopically not discernible cambium.

Many wood species have a darker, inner zone of heartwood and an outer zone of lighter sapwood. The sapwood contains some living cells, but the heartwood is composed entirely of dead cells. The rays are ribbons of radially aligned cells extending from the bark toward the pith. On a cross section they usually appear as fine lines but in many cases are not apparent to the naked eye.

In the temperate zones of the world, trees form concentric annual rings as a result of seasonal climatic variations. Broad-leaved trees of the subtropics and tropics may show growth zones formed by alternating dry and rainy periods, but there are also tropical woods where growth zones are completely absent.

Annual rings of temperate zone trees consist of earlywood and latewood. Earlywood serves for the fast transport of water and nutrients in the early part of the growing season, whereas the latewood is primarily designed for mechanical support.

The wood of broad-leaved trees (hardwood) can be distinguished macroscopically from coniferous wood (softwood) by the pores distributed over the growth rings of the former. According to size and distribution of the pores, they are divided into ring-porous, diffuse-porous, and semi-ring-porous woods.

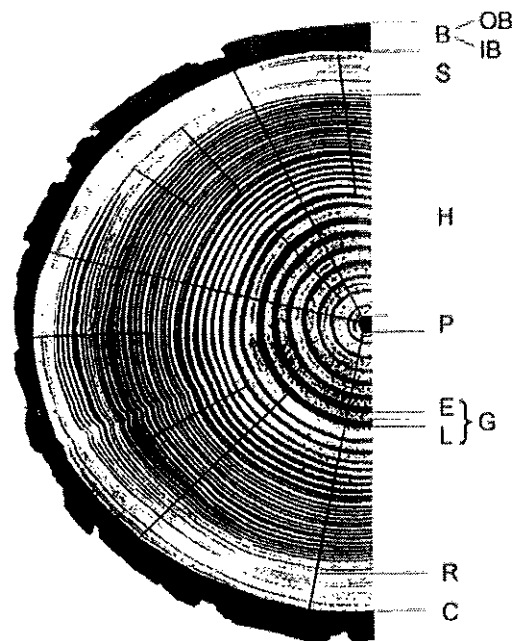


Fig. 2.1. Cross-section through the trunk of a conifer (Douglas-fir). *B* bark, *IB* inner bark, *OB* outer bark, *C* cambium (macroscopically not visible), *S* sapwood, *H* heartwood, *E* earlywood, *L* latewood, *G* growth ring, *R* wood ray (macroscopically barely visible), *P* pith. (After Grosser 1977)

The width of growth rings is determined by climate and growth site. Using the ring width patterns of a given species and a given growth region, it is possible to date cultural property made of wood.

2.1.2 Historical Wood

Wood ages with the passage of time and deteriorates through environmental influences. Deterioration may occur because of climatic factors (weathering), through wood-destroying organisms (insects, fungi, bacteria, and marine borers), or because of burial in a terrestrial or marine environment. It is significant whether the deterioration takes place under aerobic or anaerobic conditions.

Openly placed, dry wood under aerobic conditions will usually darken and may form checks and splits. The influence of aging alone, however, is minimal even with objects as old as 4000 years (Nilsson and Daniel 1990).

Weathering of wood leads to decomposition of the surface layers of wood, as for instance evidenced by the silvery, gray surfaces of unpainted fences and farm buildings.

Objects attacked by wood-destroying organisms often show typical patterns of decomposition or destruction. Insect pests, for instance, may alter the macroscopic structure of sapwood or earlywood. They leave behind a system of bore and exit holes that is characteristic for the attacking species (cf. Chap. 5).

Wood-destroying fungi also effect characteristic changes in wood. Staining fungi may cause discoloration that can extend well into the wood interior, white-rot fungi make wood appear lighter, and brown-rot or soft-rot fungi will not only cause the wood to darken but also produces cubical or clamshell-shaped cracks (cf. Chap. 5).

Wet wood buried in soil or waterlogged wood under anaerobic conditions decomposes progressively from the surface to the inside. In many cases, especially in oak, a sharp transition develops parallel to the original surface between a severely decomposed outer zone and a largely unaffected core (Hoffmann et al. 1986). The outer zone can then be soft and spongy while the core is still solid and hard. Under aerobic conditions, archaeological wet wood can be attacked by soft rot or marine borers (cf. Chap. 5). In anaerobic situations, chemical decomposition by hydrolysis and structural changes by bacteria (or certain soft rots) can occur in wet or waterlogged wood.

Many prehistoric woods that have been buried in the earth for thousands of years will have taken up silicates, phosphates, or calcium compounds and thus become petrified.

2.2 Microscopic Structure

2.2.1 Recent Wood

Between wood (xylem) and bark (phloem) is the cambium, a thin layer of formative cells. These cells divide either toward the outside to form phloem cells or to the inside to form xylem cells. In the temperate zones, the conducting cells formed at the beginning of the growth period – tracheids in softwoods and vessel elements in ring-porous hardwoods – are relatively large in diameter and have thin walls, whereas the cells formed later in the season are thick-walled and have small lumina. In diffuse-porous and semi-diffuse-porous woods these differences are less pronounced.

Following division, the cells differentiate into various types with specialized functions. The presence, form, frequency, and distribution of the various cell types can be used to distinguish between softwoods and hardwoods and to identify individual wood species. Coniferous woods of the temperate zones consist of 90–95% tracheids (predominantly longitudinal tracheids) and 5–10% ray tissue and longitudinal parenchyma. Some softwoods also have resin canals; these are lined with epithelial cells which produce resinous secre-

tions. Broad-leaved woods of the temperate zones are composed of 40–65% fibers (libriform fibers and fiber tracheids), 20–40% vessel elements, and 5–30% ray tissue and longitudinal parenchyma (where the latter may predominate).

The longitudinal tracheids of softwoods function as conduits for liquids (earlywood tracheid, Fig. 2.2A) and for mechanical support (latewood tracheid, Fig. 2.2B). They are 2–5mm long and have a diameter of 0.01–0.06mm. The fibers of hardwoods are 0.6–1.6mm in length and 0.01–0.04mm in diameter, and serve for mechanical support. Vessel elements (Fig. 2.2C) specialize in conduction of liquids. They are connected with each other through perforated end walls (perforation plates) to form conduits which may range from several centimeters to several meters in length. As seen in cross-section, they are referred to as pores, with diameters of 0.01–0.4mm. The size and arrangement of the pores divide hardwoods into ring-porous, semi-ring-porous, and diffuse-porous. Longitudinal parenchyma cells which serve as storage elements are more numerous in broad-leaved than in coniferous woods.

Exchange of substances between adjacent cells occurs via openings in the cell wall, the pits. We can distinguish between simple, bordered, and half-

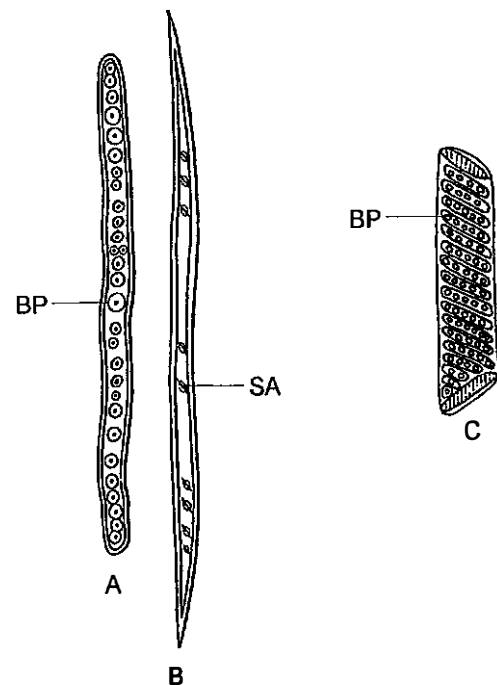


Fig. 2.2. Tracheids of pine (A earlywood tracheid, B latewood tracheid) and vessel element of limewood (C) with bordered pits. BP Bordered pit, SA bordered pit with slitlike aperture. (After Kollmann and Côté 1968)

bordered pits. Simple pits are canals through the cell wall from the lumen to the middle lamella, which serves as a closing, but porous membrane. Simple pits occur only in parenchyma and in libriform fibers. Half-bordered pits connect parenchyma to tracheids. Vessel elements, tracheids, and fiber tracheids have bordered pits (Fig. 2.3) which can vary greatly in form depending on species and cell type.

Cells in wood consist of a cell wall surrounding a cell cavity (lumen). With the aid of an electron microscope we can distinguish a layered structure of the cell wall (Fig. 2.4). The outermost layer is the primary wall (P), which is the first solid covering of a new cell. It contains cellulose microfibrils in thin aggregates which cross each other, facilitating diameter growth of the cell. The average thickness of the primary wall is 0.06–0.09 μm (Fengel and Wegener 1984). The secondary wall, which adjoins the primary wall, is divided into three layers, the outer layer being the S1 layer, followed by the S2 and S3 layers. The S1 layer is 0.25–0.50 μm thick and consists of several lamellae with microfibrils arranged in a flat helix. The sense of the helix changes from one lamella to the next, resulting in a crossed structure. The configuration of the S1 layer contributes significantly to the compression strength of cells. The S2 layer is the thickest at 0.50–4.4 μm and also has a lamellar structure. Here, the microfibrils follow a steep, helical angle which accounts for the high strength of wood in the longitudinal direction, particularly its tensile strength. Recent investigations by means of high resolution scanning electron microscopy with field emission cathode (FE-SEM) have shown that the lamellae of the S2 layer are not concentric to the long axis of the cell, but that they are oriented perpendicular to the S1 and S3 layers, resulting in a kind of sandwich structure of the secondary wall (Sell and Zimmermann 1993; Booker and Sell 1998). The S3 layer is 0.30–0.40 μm thick and has microfibrils arranged in a flat helix.

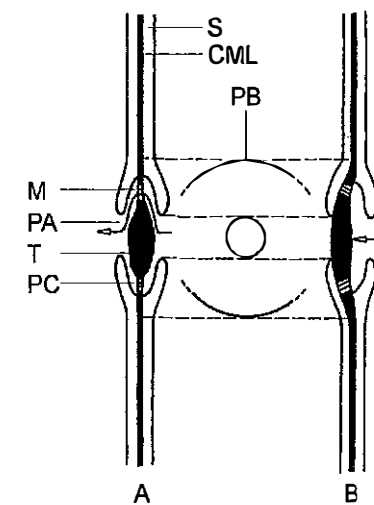


Fig. 2.3. Sectional view of bordered pit (A open, B closed, CML Compound middle lamella (middle lamella plus two primary walls), M margo (thin part of the pit membrane, permeable to fluids), PA pit aperture, PB pit border, PC pit chamber, S secondary wall, T torus (thickened part of the pit membrane)). (After Grosser 1985)

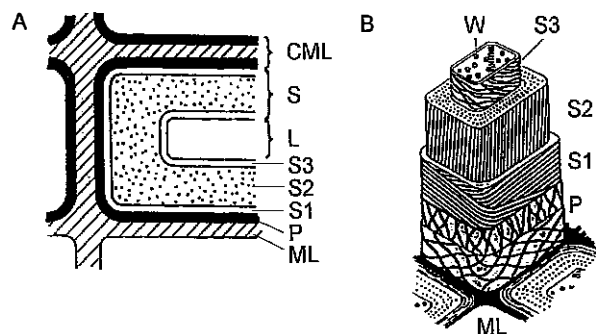


Fig. 2.4. A Cross section of a wood cell. B Model of cell wall structure of conifer tracheids and hardwood libriform fibers. L Lumen, CML compound middle lamella, ML middle lamella, P primary wall, S secondary wall, S1 outer, S2 central, and S3 inner layer of the secondary wall, W warty layer. (After Fengel and Wegener 1984)

Some authors have recognized a tertiary layer, either in addition to the S3 layer in parenchyma cells or instead of it in all other cells, but this concept is no longer generally accepted. Some species have a layer on the lumen side of the cell wall with protrusions which resemble warts.

The middle lamella, which is in principle free of cellulose, is located between neighboring cells and combines them into tissue. Since the middle lamella and the primary wall are difficult to distinguish, the primary walls of two adjacent cells and the middle lamella between them are collectively known as the compound middle lamella.

Formation and growth of the cell wall proceed from the sugars contained in the protoplasm. Cellulose and hemicelluloses (polyoses) are formed from these sugars by enzymatic synthesis. The cellulose aggregates into microfibrils, which in turn are organized into coherent lamellae.

2.2.2

Historical Wood

Dry wood in historical buildings, in panel paintings, and in sculptures often shows fine cracks under the microscope, and in the case of very old archaeological objects a weakened ultrastructure, especially in the area of the middle lamella has been observed. Also, in the secondary wall, a recognizable separation between lamellae can occur (Nilsson and Daniel 1990).

Insects, and brown-rot and white-rot fungi, can attack wood only under aerobic conditions and will leave macroscopically or microscopically recognizable marks of their activity on the wood surface and in its interior, such as frass and fecal pellets in the bore holes or hyphae in the cells (cf. Chap. 5). Aerobic soft-rot fungi were found in the wood of an Egyptian mummy coffin (1000–2000 BC) which had created cavities specifically in the S2 layer (Nilsson and Daniel 1990).

In waterlogged oak wood from archaeological digs, the abiotic, hydrolytic decomposition in the firm inner parts begins with a loosening of the cell wall structure in the rays and longitudinal parenchyma, or takes place simultaneously with the decomposition of fiber tracheids (Hoffmann et al. 1986). With increasing decomposition, swelling of the thick-walled fibers with narrow lumens is observed, followed by progressive loosening of wall structure from lumen to middle lamella and the development of folds into the lumen. The actual destruction of the cell wall also proceeds from the lumen (Bednar and Fengel 1974) and occurs to the greatest extent in the swollen secondary wall (Hoffmann and Parameswaran 1982). In the final stages only the middle lamella remains.

Biological deterioration of archaeological wet and waterlogged wood by soft-rot fungi (cf. Chap. 5) manifests itself by the formation of chained cavities within and erosion of the cell wall. The cavities develop mainly in the S2 layer, the attack proceeding from hyphae in the lumen. Simultaneously, erosion of the cell wall takes place, but this is not observed as often in softwoods or hardwoods with a high lignin content (Blanchette et al. 1990). The middle lamella is resistant to erosion.

Certain types of bacteria preferentially attack the pit membranes of softwoods while other types destroy the cell wall (cf. Chap. 5). The former type of attack occurs mainly in the pits of tracheids and ray parenchyma of softwoods, leading to a marked increase in liquid permeability of the wood. When bacteria attack the cell wall, three main types of deterioration can be distinguished, namely erosion, tunneling, and cavity formation. There are differences between the erosion and cavity formation caused by bacteria and by soft-rot fungi.

2.3

Chemical Composition of Wood

2.3.1

Recent Wood

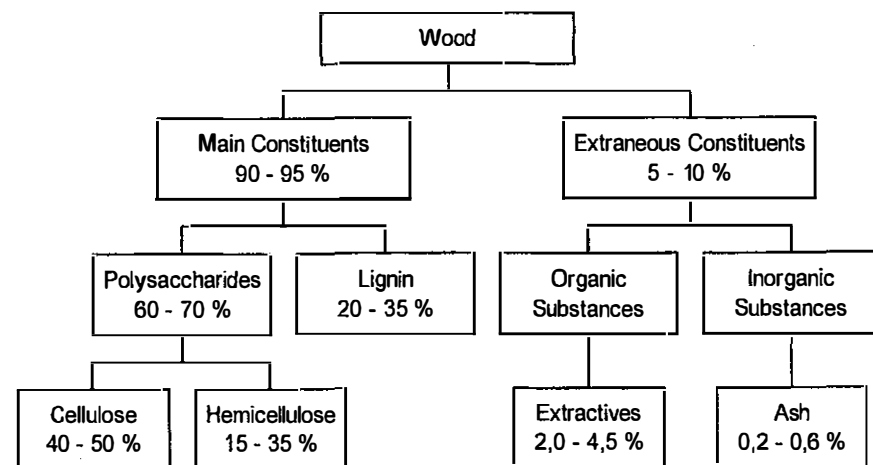
2.3.1.1

Elementary Composition

In principle there are no differences in elementary composition between softwoods and hardwoods or between individual wood species. Wood is composed mainly of carbon, oxygen, and hydrogen (Table 2.1). In addition, it contains nitrogen and in the ash, calcium, potassium, magnesium, manganese, sodium, aluminum, and iron as cations plus carbonate, chloride, phosphate, and sulfate as anions. Small quantities of protein compounds containing nitrogen serve as nutrients for certain wood destroying insects.

Table 2.1. Elementary composition of wood

Element	Percentage (%)
Carbon (C)	49–51
Oxygen (O)	43–44
Hydrogen (H)	6–7
Nitrogen (N)	0.1–0.3
Ash (Ca, K, Mg, Mn etc.)	0.2–0.6

**Fig.2.5.** Main and extraneous constituents of wood

2.3.1.2

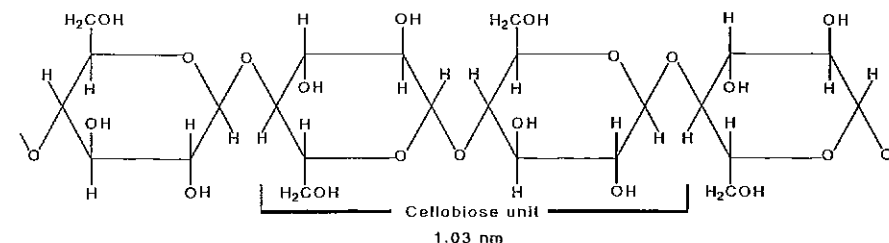
Chemical Components

The main constituents of wood are the macromolecular components, namely cellulose, hemicelluloses, and lignin (Fig. 2.5). Cellulose and the hemicelluloses are polysaccharides and are known collectively as holocellulose. Lignin is aromatic in nature. In addition, small quantities of polymeric substances such as starch, pectins, gums, and proteins may occur in wood. The extraneous substances are generally of relatively low relative molecular mass, and may be organic or inorganic. The organic extractives may include phenolics, terpenes, aliphatic acids and alcohols (as esters) as well as water soluble mono- and disaccharides. Softwoods and hardwoods of the temperate zones vary in cellulose, hemicellulose, and lignin content (Table 2.2), the most marked differences being found in the hemicelluloses.

Cellulose is the principal constituent of the cell wall. It is built up of cellobiose units which are formed by the reaction of two glucose molecules and the liberation of water. The cellobiose units are connected into long chain molecules of cellulose (Fig. 2.6) which in plants consist of 7000–15,000 glucose units and have a length of 3–8 μm . On the surface of the cellulose molecule

Table 2.2. Polysaccharide and lignin content in softwoods and hardwoods of temperate zones

Constituent	Softwood (%)	Hardwood (%)
Cellulose	45–50	40–45
Hemicelluloses	15–20	20–30
Lignin	25–30	20–25

**Fig. 2.6.** Structural formula of cellulose (interior segment of the molecular chain)

are hydroxyl groups, three from each glucose unit. These hydroxyl groups account for the particular chemical reactivity, the physical behavior, and the supramolecular structure of the cellulose. Hydroxyl groups form hydrogen bonds with each other, both within and between neighboring molecules (intra and intermolecular bonds), and water is adsorbed to cellulose in the same manner. X-ray diffraction shows that cellulose is ordered into crystal lattices. At the next level of order cellulose molecules aggregate into elementary or proto fibrils which can be made visible in the electron microscope. They have a diameter of 2–4 nm (Fengel and Wegener 1984) and consist of about 40 cellulose chains. Elementary fibrils together form higher units with a diameter of 10–30 nm which are called microfibrils.

Hemicelluloses, unlike cellulose, are made up of a variety of sugar units which may have side chains. The molecules, which consist of 100–200 sugar units, are shorter than cellulose and are usually branched. The sugar units can be divided into pentoses, hexoses, hexuronic acids and deoxy-hexoses. The backbone of hemicelluloses may be composed entirely of the same sugar units (e.g., xylans) or of two or more kinds of sugar units (e.g., glucomannans). The most important hemicellulose in softwoods is glucomannan, which contains acetyl groups and galactose residuals. The structure of such an *O*-acetyl-galactoglucomannan is shown in Fig. 2.7. Arabinoglucuronoxylan is also found in softwoods, but in hardwoods glucuronoxylan is the dominant hemicellulose constituent. Compared with cellulose, hemicelluloses are more readily hydrolyzed by acids and are more soluble in dilute alkali. Hemicellulose chains form fibrillar subunits, which serve as building blocks for microfibrils.

Lignin is the phenolic component which imparts rigidity to wood, and is generally resistant to hydrolysis by acids. Within the cell wall it forms a three-

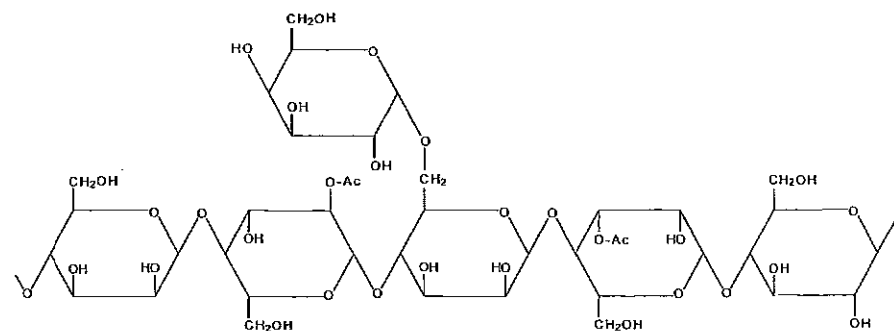


Fig. 2.7. Structure of *O*-acetyl-galactoglucomannan of softwood (section)

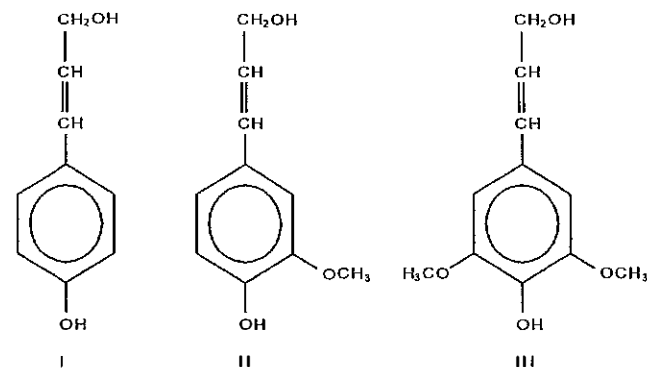


Fig. 2.8. Building blocks of lignin: 4-coumaryl alcohol (I), coniferyl alcohol (II), sinapyl alcohol (III)

dimensional network with bonding to the polysaccharide fraction. After acid decomposition of the polysaccharides, lignin remains as an amorphous brown powder. Lignin is susceptible to oxidants, and therefore can be removed easily from pulps by bleaching agents. Three cinnamyl alcohols, namely 4-coumaryl alcohol (I), coniferyl alcohol (II), and sinapyl alcohol (III), are the basic building blocks of lignin (Fig. 2.8). According to Hedges (1990), these monomers form radicals which react randomly to form a three-dimensional polymer. Softwoods contain primarily guaiacyl lignin which is produced by polymerization of coniferyl alcohol, while hardwoods contain guaiacyl-syringyl lignin which is formed by copolymerization of coniferyl and sinapyl alcohol.

2.3.2

Historical Wood

2.3.2.1

Elementary Composition

Changes in the elementary composition of dry archaeological wood are probably no greater than the natural variability in composition of recent wood.

Buried alder and oak wood, however, have lower hydrogen and oxygen contents compared with recent wood (Hedges 1990). The nitrogen content is higher in these deteriorated woods and indicates the occurrence of diagenesis. Unearthed woods are almost invariably found to have higher ash contents. Whereas recent wood generally has an ash content of less than 1% (Table 2.1), this can be 10% or more in archaeological wood found in a wet environment. The iron content of archaeological wood is important in regard to subsequent conservation treatments. Iron may occur in the form of reducing minerals such as pyrite (iron (II) sulfide, FeS_2). If these are exposed to oxidizing agents, sulfuric acid may be formed which could possibly lead to hydrolysis of the polysaccharides in wood.

2.3.2.2

Chemical Components

Specimens of old dry wood exhibit less birefringence when examined under polarized light, indicating reduced crystallinity of the cellulose (Borgin et al. 1975b). The holocellulose content is higher than in recent wood (Van Zyl et al. 1973), the apparent cause being reduced lignin content due to its oxidative decomposition (Borgin et al. 1975a). Hinoki wood in Japanese temples was found to be subject to two simultaneous aging processes: increases in cellulose crystallinity and cellulose decomposition (Kohara 1958; Schniewind 1989). Changes in crystallinity cease after about 350 years. Together, these two processes bring about an initial increase in certain strength properties, but after 350 years there is a steady decrease in strength with age.

Recent research has shown that in waterlogged wood decomposition generally begins with the hemicelluloses, followed by cellulose. Lignin is most resistant (Fengel and Wegener 1984), and therefore the proportion of lignin increases during decomposition. However, if wood composition is expressed on the basis of volume percentage, the lignin content remains relatively constant with increasing decomposition as indicated by increasing values of maximum moisture content (Hoffmann et al. 1986). There appears to be no correlation between mass-based lignin content and age of wood specimens.

Within the wood cells, following the acid hydrolysis of the hemicelluloses, the cellulose of the S2 and S3 layers is attacked either from the lumen or the borders between the S1 and S2 layers (Hoffmann and Jones 1990). After a breakup of the crystalline structure, the cellulose chain molecules are depolymerized and dissolved. The remaining lignin skeleton of the S2 layer decomposes into a granular mass which shrinks and becomes detached from the S1 layer. Later, the S1 layer also decomposes, so that only a network of middle lamellas remains.

Whereas acid hydrolysis of polysaccharides does not require molecular oxygen, the latter is necessary for the decomposition of lignin. Oxygen is not available to wood buried deeply in soil or under water, and thus lignin remains (Hedges 1990). Contrary to the sequence of decomposition described so far,

Iiyama et al. (1988) found that in buried wood hemicelluloses were more stable than cellulose, which decomposed first. Further comparative research is necessary to clarify this point (Hedges 1990).

2.4

Ultrastructure of the Cell Wall

Cellulose, hemicelluloses, and lignin are not uniformly distributed through the different cell wall layers or the cell wall as a whole. Many analytical investigations of the distribution of the three main constituents form the basis for models of cell wall ultrastructure. Hydrogen bonds formed by hydroxyl groups on the cellulose and hemicellulose chains lead to fibrillar units. Such fibrillar units of hemicelluloses can associate with cellulose and possibly form more or less well-defined layers which surround the cellulose microfibrils. The hemicellulose units also form the bridge to the lignin, which surrounds the polysaccharide structural elements. Figure 2.9 shows the Kerr and Goring (1975) model of cell wall structure, which illustrates the embedding of cellulose and hemicelluloses within the lignin particularly well. It resembles the structure of reinforced concrete, where the polysaccharides represent the steel and lignin the concrete.

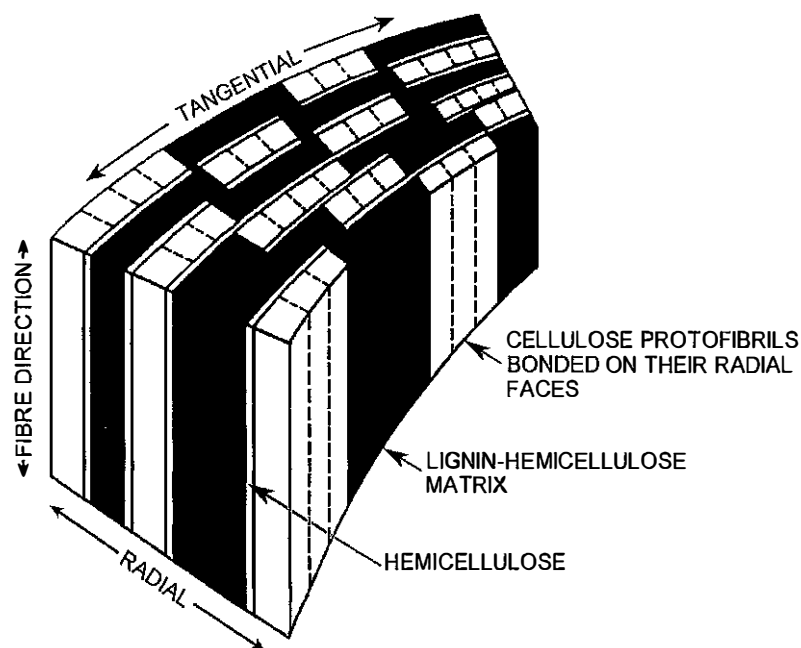


Fig. 2.9. Model of the structural arrangement of cellulose, hemicelluloses and lignin in the cell wall. (Kerr and Goring 1975)

Table 2.3. Diameter of void spaces within the cell wall

Structural element	Diameter (nm)	Reference
Transient cell wall capillaries	~0.4	Seifert (1960)
Interfibrillar void spaces:		
Dry:	~1	
Swollen:	~1.2–5	Fengel and Wegener (1984)
Interfibrillar void spaces	~10	Niemz (1993)
Pit membrane pores (margo)	20–100	Kollmann (1987)

Wood cell walls contain numerous void spaces which are of critical importance to the entrance of water and the impregnation of wood with chemical substances. To what extent water and other fluids can enter into the cell wall depends on the size of the void spaces. According to Table 2.3, water molecules with their diameter of 0.3 nm can readily penetrate the transient cell wall capillaries and the dry interfibrillar spaces and swell these by their interaction with the hydroxyl groups of cellulose and hemicelluloses. The accessibility of these hydroxyl groups to water and other chemical compounds can be determined by an exchange with deuterium oxide (Unger and Poller 1983). Materials used to stabilize wood such as sucrose (ca. 0.6 nm diameter) or monomers like methyl methacrylate can also penetrate the interfibrillar spaces. However, the pores of the pit membranes already act as filters for many polymers in solution, so that they can merely be deposited longitudinally into the lumens of the various cells. The accessibility of the waterlogged wood cell wall to water-soluble agents can be determined by measuring relative swelling of dry wood by water-free organic solvents (Jensen 1997). The results indicate that molecules with a diameter of up to 0.55 nm can penetrate into areas within the cell wall which are normally occupied by adsorbed water. Water is adsorbed selectively from aqueous solutions resulting in low concentrations of the solutes in the cell wall. Thus, it seems to be better to use impregnation agents with high affinity for wood substance or agents which can enter areas not accessible to water such as those used in the Cellosolve-petroleum method (cf. Chap. 11, paraffin).

References

- Bednar H, Fengel D (1974) Physikalische, chemische und strukturelle Eigenschaften von rezentem und subfossilem Eichenholz. *Holz Roh Werkst* 32:99–107
- Blanchette RA, Nilsson T, Daniel G, Abad A (1990) Biological degradation of wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington, DC. *Adv Chem Ser* 225:141–174
- Booker RE, Sell J (1998) The nanostructure of the cell wall of softwoods and its functions in a living tree. *Holz Roh Werkst* 56:1–8
- Borgin K, Faix O, Schweers W (1975a) The effect of aging on lignins of wood. *Wood Sci Technol* 9:207–211

- Borgin K, Parameswaran N, Liese W (1975b) The effect of aging on the ultrastructure of wood. *Wood Sci Technol* 9:87–98
- Fengel D, Wegener G (1984) *Wood. Chemistry, ultrastructure, reactions*. De Gruyter, Berlin
- Grosser D (1977) *Die Hölzer Mitteleuropas*, Springer, Berlin Heidelberg New York
- Grosser D (1985) *Pflanzliche und tierische Bau- und Werkholzschildlinge*. DRW-Verlag Weinbrenner, Leinfelden-Echterdingen
- Hedges JI (1990) The chemistry of archaeological wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington, DC. *Adv Chem Ser* 225:111–140
- Hoffmann P, Jones MA (1990) Structure and degradation process for waterlogged archaeological wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington, DC. *Adv Chem Ser* 225:35–65
- Hoffmann P, Parameswaran N (1982) Chemische und ultrastrukturelle Untersuchungen an wassergesättigten Eichenhölzern aus archäologischen Funden. *Berl Beitr Archäometrie* 7:273–285
- Hoffmann P, Peek R-D, Puls J, Schwab E (1986) Das Holz der Archäologen. *Holz Roh Werkst* 44:241–247
- Iiyama K, Kasuya N, Tuyet LTB, Nakano J, Sakaguchi H (1988) Chemical characterization of ancient buried wood. *Holzforschung* 42:5–10
- Jensen P (1997) Sorption of water and water soluble agents in the waterlogged wooden cell wall. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997*, pp 399–434
- Kerr AJ, Goring DAI (1975) The ultrastructural arrangement of the wood cell wall. *Cell Chem Technol* 9:563–573
- Kohara J (1958) Study on the old timber. *Res Rep Fac Technol Chiba Univ* 9(15):1–55; 9(16):23–65
- Kollmann F (1987) Poren und Porigkeit in Hölzern. *Holz Roh Werkst* 45:1–9
- Kollmann FFP, Côté WA Jr (1968) *Principles of wood science and technology*. Springer, Berlin Heidelberg New York
- Niemz P (1993) *Physik des Holzes und der Holzwerkstoffe*. DRW-Verlag Weinbrenner, Leinfelden-Echterdingen
- Nilsson T, Daniel G (1990) Structure and the aging process of dry archaeological wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington, DC. *Adv Chem Ser* 225:67–86
- Schniewind AP (1989) *Archaeological wood*. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. Pergamon Press, Oxford / MIT Press, Cambridge, Massachusetts, pp 14–18
- Seifert K (1960) *Angewandte Chemie und Physikochemie der Holztechnik*. Fachbuchverlag, Leipzig
- Sell J, Zimmermann T (1993) Radial fibril agglomerations of the S2 on transverse fracture surfaces of tracheids of tension-loaded spruce and white fir. *Holz Roh Werkst* 51:384
- Unger A, Poller S (1983) Methode zur Bestimmung von accessiblen Hydroxylgruppen im Holz durch Deuteriumaustausch. *Holztechnologie* 24:108–113
- Van Zyl JD, Van Wyk WJ, Heunis CM (1973) The effect of aging on the mechanical and chemical properties of wood. In: *Proceedings of the IUFRO-5 meeting, vol 2*. International Union of Forestry Research Organizations, Vienna

3 Wood Properties

3.1

Wood-Moisture Relations

3.1.1

Recent Wood

Wood is a porous, hygroscopic material that can take up moisture from the atmosphere or directly in liquid form. Moisture content refers to water which is adsorbed on the interior wood surfaces or present as liquid, free water within the porous structure. Moisture content affects (1) physical properties such as shrinking and swelling; density; electrical, thermal, and acoustic properties; weathering; and mechanical properties; (2) reaction to biological agents such as decay fungi, insects, bacteria, and marine borers; and (3) technological properties and processes such as machinability, drying, preservative treatment, gluing, coating, and consolidation.

Moisture content, u , is usually based on the mass of oven-dry, i.e., water-free, wood:

$$u = \{(m_u - m_o) / m_o\} \times 100 [\%],$$

where u is the moisture content, m_u is the mass of moist wood, and m_o is the mass of oven-dry wood.

An alternative, but rarely used, method expresses moisture content based on the mass of moist wood:

$$f = \{(m_u - m_o) / m_u\} \times 100 [\%],$$

where f is the moisture content based on the mass of moist wood. Methods of measuring moisture content are discussed in Chapter 6.

In the wood of a freshly cut tree, moisture is present in the cell cavities as free water, and within the cell walls as bound water. As this wood is exposed to the atmosphere, it will begin to dry, initially losing mainly free water. The state in which all of the free water has been lost, but the entire bound water remains, is referred to as the fiber saturation point. This is a very important concept, because changes in moisture content below the fiber saturation point will affect virtually all wood properties, while changes above this point will

have little or no effect on most properties. Accordingly, we can distinguish between three limit states with respect to moisture content:

1. $u = 0\%$, oven-dry wood. This state can be achieved by drying wood in an oven at 103°C until it reaches constant mass, and all of the adsorbed water has been removed,
2. $u \approx 25\text{--}30\%$, the fiber saturation point, the particular value depending on the wood species, and
3. u_{max} , the maximum moisture content, when all of the pore volume in wood is completely filled with water. This state occurs only rarely in living trees, but is often found in archaeological wood which is then referred to as waterlogged wood.

If oven-dry wood is exposed to a humid atmosphere, it will adsorb moisture on and within its cell walls. Initially, water molecules will be adsorbed directly on primary sorption sites in the wood, and these will be held most strongly. Most of these primary sorption sites will be occupied when the moisture content reaches about 6%, which corresponds to a relative humidity of about 30%. Additional sorption takes place either on primary sorption sites already occupied by one or more water molecules, or on secondary sorption sites. This water is not held as strongly. As the relative humidity approaches 100%, capillary condensation takes place in the cell wall structure (Skaar 1989a).

Since wood is hygroscopic, it may either gain moisture or lose it to the air. At constant temperature and relative humidity, wood will reach an equilibrium moisture content, which may vary somewhat from species to species. The relationship between moisture content and relative humidity can be shown in the form of sorption isotherms (Fig. 3.1). On desorption the moisture content will be higher than on adsorption, the difference owing to sorption hysteresis. In theory, wood will equilibrate to the fiber saturation point at 100% relative humidity, but in practice such a state cannot be achieved because at a humidity level close to saturation even very small temperature variations can cause significant amounts of condensation.

Adsorption and desorption below the fiber saturation point are accompanied by swelling and shrinking, respectively, but above the fiber saturation point the dimensions of wood are not affected by changes in moisture content. Shrinking and swelling differ depending on direction in wood. Shrinkage is least in the longitudinal (fiber) direction, and greatest in the tangential direction. Average shrinkage values of European woods from green to oven-dry, based on the green dimensions, are 0.4% longitudinally, 4.0% radially, and 8.3% tangentially (Knigge and Schulz 1966). Very dense hardwoods may shrink 12% or more in the tangential direction, and in most woods the radial shrinkage is approximately one half of the tangential shrinkage (Skaar 1989b). Dimensional movement in the longitudinal direction can usually be neglected, but the large difference between radial and tangential shrinkage leads to warping and changes in shape (Fig. 3.2). In general, shrinkage of wood tends to be directly proportional to density, so that tropical woods of very high density present the greatest problems, teak being a notable exception.

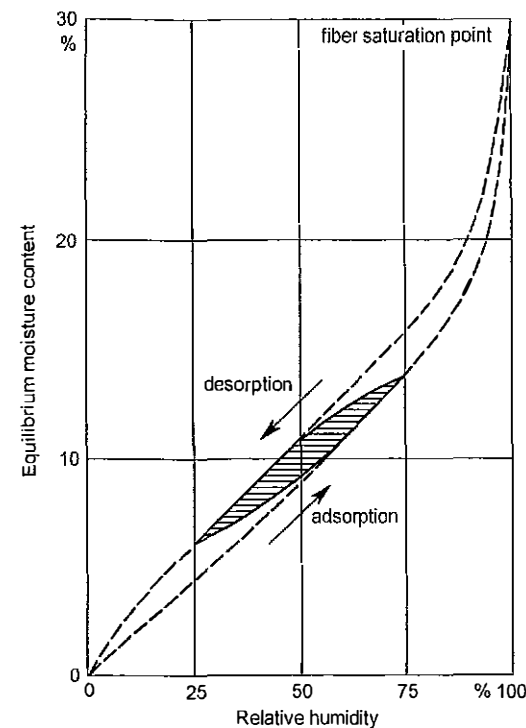


Fig. 3.1. Sorption isotherms for wood. (After Sutter 1986)

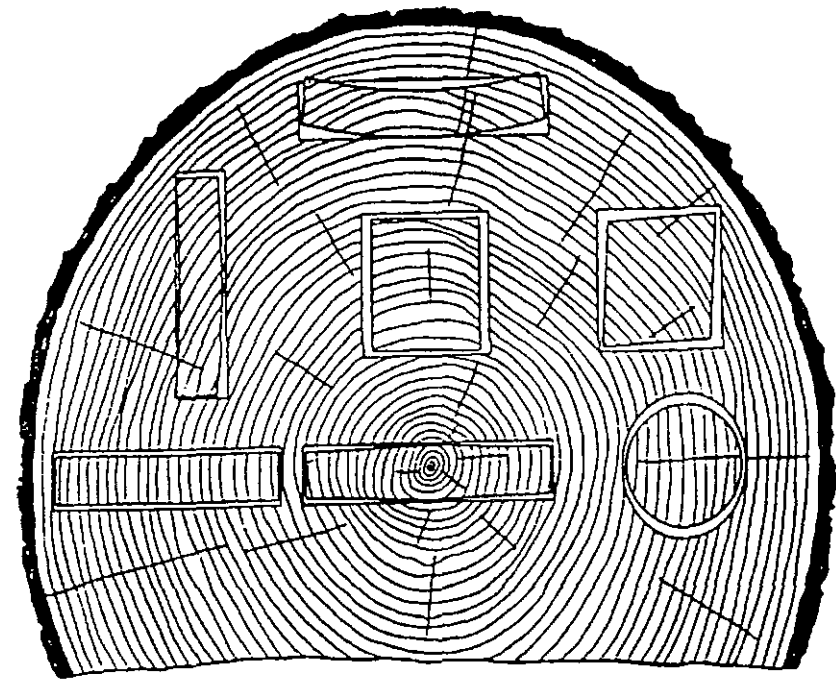


Fig. 3.2. Shrinkage effects of variously shaped wood members according to their location in the log cross section. (Forest Products Laboratory 1987)

The shrinkage of wood from green to oven-dry is approximately linear, so that dimensional changes accompanying changes in moisture content can be estimated by calculation. It is possible to distinguish between shrinkage, expressed as a percentage based on original dimension in the green state, and swelling expressed as a percentage based on the oven-dry dimension. Data on total shrinkage from green to oven-dry are useful in comparing shrinkage behavior of different species of wood, but in practical situations such a drastic change would not ordinarily be encountered. A more practical concern would be the expected dimensional change when moisture content changes in smaller increments within the hygroscopic range, i.e., below the fiber saturation point. Dimensional changes in the range of 6–14% moisture content, corresponding to a relative humidity ranging from about 30 to 75%, can be estimated according to:

$$\Delta D = D_i [C_T(u_f - u_i)],$$

where ΔD is the change in dimension; D_i is the initial dimension; C_T is the dimensional change coefficient in the tangential direction (for the radial direction, C_R must be substituted), which gives the change in dimension for a change in moisture content of 1%; u_i is the initial moisture content, in percent; and u_f is the final moisture content, in percent.

If the final moisture content is less than the initial one, ΔD will be negative, indicating a decrease in dimension. Values of total shrinkage and the dimensional change coefficients C_T and C_R are shown in Table 3.1 (Forest Products Laboratory 1987).

Table 3.1. Shrinkage and dimensional change coefficients of some wood species. (From Forest Products Laboratory 1987)

Species	Shrinkage, green to oven-dry		Dimensional change coefficient	
	Radial (%)	Tangential (%)	Radial, C_R	Tangential, C_T
White ash	4.9	7.9	0.00169	0.00274
American beech	5.5	11.9	0.00190	0.00431
Yellow birch	7.3	9.5	0.00256	0.00338
American elm	4.2	9.5	0.00144	0.00338
Red oak	4.0	8.6	0.00158	0.00369
Sugar maple	4.8	9.9	0.00165	0.00353
Walnut	5.5	7.8	0.00190	0.00274
Douglas-fir	4.8	7.6	0.00165	0.00267
Eastern white pine	2.1	6.1	0.00071	0.00212
Longleaf pine	5.1	7.5	0.00176	0.00263
Red spruce	3.8	7.8	0.00130	0.00274
Balsa	3.0	7.6	0.00102	0.00267
Greenheart	8.8	9.6	0.00390	0.00430
Limba	4.5	6.2	0.00151	0.00187
Mahogany, true	3.0	4.1	0.00172	0.00238
Teak	2.5	5.8	0.00101	0.00186

Whether wood can be treated with liquids depends greatly on its moisture content, but also on species, the presence of sapwood or heartwood, and structural factors such as pit aspiration in softwoods and tyloses in hardwoods. Wood can be classified on the basis of its resistance to impregnation into four classes ranging from readily treatable to refractory (European standard EN 350-2 1994). The treatability of some important woods is given in Table 3.2.

The transport of wood artifacts in closed containers raises the question of what kind of dimensional movement to expect as a result of temperature variations. Kamba and Nishiura (1993) found that in the range of 10–40°C

Table 3.2. Treatability of selected wood species. (European Norm EN 350-2 1994)

Species	Treatability
Maple	Good
Birch	Good
Yellow birch	Good
Beech	Good
Hornbeam	Good
Linden	Good
Horse chestnut	Good
Oak, sapwood	Good
Red oak, sapwood	Good
Poplar, sapwood	Good
Pine, sapwood	Good
Pitch pine, sapwood	Good
Yellow cedar, sapwood	Good
Ash	Moderate
Hickory, heartwood	Moderate
American white oak	Moderate
Spruce, sapwood, moist	Moderate
Larch, sapwood	Moderate
Fir, sapwood	Moderate
Soft pine, heartwood	Moderate
Walnut, heartwood	Poor
Poplar, heartwood	Poor
Elm	Poor
Spruce, air-dry	Poor
Pine, heartwood	Poor
Southern pine, heartwood	Poor
Western red cedar	Poor
Oak, heartwood	Very poor
Robinia	Very poor
Red beech, with tyloses	Very poor
Larch, heartwood	Very poor
Douglas-fir, heartwood	Very poor
Pitch pine, heartwood	Very poor

Japanese cypress was less dimensionally stable when silica gel was placed in the container, probably because of the higher sorption capacity of the drying agent compared with the wood. Thus, it would be better to arrange for sufficient insulation in place of the drying agent, in order to reduce temperature variations as much as possible.

When insect infestations are controlled by freezing treatments, the accompanying dimensional and material changes are of concern. Schirp and Kübler (1968) experimented with tangential and radial specimens of various species at moisture contents ranging from oven-dry to water-saturated which they cooled from +20 to -40°C and then warmed up again, both in continuous and stepwise increments. Their results indicate that the observed dimensional changes due to cooling are due to four factors with mutually overlapping domains. Whereas thermal contraction is the deciding factor for oven-dry and for air-dry wood, at higher moisture content levels "coldness shrinkage" due to moisture leaving the cell walls and freezing in the cell lumens becomes the most important factor. In water-saturated wood formation of ice crystals within the cell walls and the volumetric expansion of the free water in the cell lumens as it turns to ice become increasingly important, and frost cracks can occur.

Liquids other than water will often lead to an altered shrinking and swelling behavior of wood (Kollmann and Côté 1968). Even dilute alkali will cause increased swelling of wood, whereas dilute acids may not have much effect. Concentrated acids such as sulfuric acid will not only cause increased swelling but eventually destroy wood by hydrolysis. For the conservation of wood artifacts, the swelling of wood in aqueous solutions of salt and sugar, and in organic solvents is of interest. In most aqueous solutions the swelling will be similar to that in water, but some saturated salt solutions can cause increased swelling (Kollmann and Côté 1968). Relative swelling values of wood in organic solvents, compared with water at a value of 100, are listed in Table 3.3, based on data by Mantanis et al. (1994). This shows that solvents such as methanol, ethanol and acetone swell wood not very much less than water, which may make them undesirable as solvents for consolidation, especially in cases of polychromed or otherwise coated wood objects. With regard to swelling behavior, weakly polar or non-polar solvents such as toluene or octane would then be preferable. The relative swelling of wood in organic solvents is temperature dependent, which suggests a chemical mechanism (Mantanis et al. 1995). Removal of extractives from wood may result in somewhat increased swelling in the solvents.

3.1.2

Historical Wood

Aging, biological pests, reattachment of coatings, chemical treatments to straighten warped panel paintings, impregnation with preservatives or consolidants can all influence wood-moisture relations of dry wood in varied

Table 3.3. Swelling of wood in organic solvents. (Mantanis et al. 1994)

Solvent	Swelling factor (water = 100)
Octane	8
Tetrachloromethane	13
Toluene	17
Chloroform	30
Ethyl acetate	37
1-Propanol (<i>n</i> -propanol)	60
Acetone	69
Ethanol	76
1,4-Dioxane	83
Methanol	90
Acetic acid	102
Ethylene glycol	109
Dimethylformamide	138
1-Butylamine (<i>n</i> -butylamine)	191

ways. Buck (1952) found that in various wood species aging led to only a minor decrease in hygroscopicity. Shrinking and swelling behavior, however, did not show any signs of changes compared with recent wood. Kohara (1984) found that hinoki wood (*Chamaecyparis obtusa*) from a 1300-year-old temple had much lower equilibrium moisture content values than recent wood, and that tangential shrinkage of hinoki decreases with age. According to Erhardt et al. (1996), the age of wood and moderate variations of temperature and relative humidity have only minor effects on physical and mechanical properties when comparing new pine and pine dating to the seventeenth century.

Brown rot results in a decrease of the equilibrium moisture content reached during adsorption, which is proportional to mass loss, whereas the desorption curve remains unchanged by brown rot (Noack 1990). White rot, on the other hand, does not affect the hygroscopicity because it tends to decompose all constituents of wood equally. Capillary absorption of liquid water is greater in wood with fungal decay.

Dimensional movements of paintings on oak panels were determined in a controlled climate room and in exhibition spaces using inductive transducers (Klein and Bröker 1990). A panel painting from the seventeenth century changed its transverse dimensions up to 0.1 % compared with a painted new oak panel which changed 0.15–0.17% in response to a change in relative humidity of 10%. Paintings on wood panels tend to react rather slowly to changes in the relative humidity of the surroundings, and will never actually reach equilibrium (Legrum 1993). Very high levels of relative humidity can result in elevated moisture contents of the wood panels, and lead to stretching of the paint layer (Schwarz and Gadesmann 1994). Subsequent drying of the panels can cause waviness of the paint surface if the paint layers have been

permanently stretched. The effect of chemical treatments to recover warping of panel paintings, to impart wood preservatives, and to consolidate deteriorated wood on the hygroscopicity of wood will be discussed in Chapters 7 and 11.

Whereas comprehensive overviews of changes in the physical and mechanical properties of dry historic wood, either sound or biologically degraded, are not available, such data have been collected by Schniewind (1989a, 1990) for archaeological wood. The constituents of wood are fundamental factors in the sorption behavior of archaeological wood. The sorption isotherms of hemicellulose, cellulose and lignin differ (Niemz 1993), and in some species extractives have a significant effect on the hygroscopicity of wood (Skaar 1989a). At a given temperature and relative humidity, hemicellulose will reach the highest equilibrium moisture content, followed by cellulose and lastly by lignin. Thus, one would expect that archaeological waterlogged wood with preferential carbohydrate degradation, leaving a high lignin content, would be less hygroscopic than recent wood. According to Noack (1965), more often the opposite is found, which can be explained on the basis of increased accessibility of hydroxyl groups and a breakdown of the crystal structure of the remaining cellulose. Waterlogged oak wood from the *Bremen Cog* was found to be more hygroscopic than recent wood (Fig. 3.3). The difference is greater at relative humidity values above 80%. The fiber saturation point of the waterlogged wood was found to be about 50%, so that compared with recent wood, it will begin to shrink at higher moisture content levels. Schniewind (1990) compiled data on equilibrium moisture content at relative humidities of 98–100% for wet archaeological wood ranging in age from 570 to 4700 years

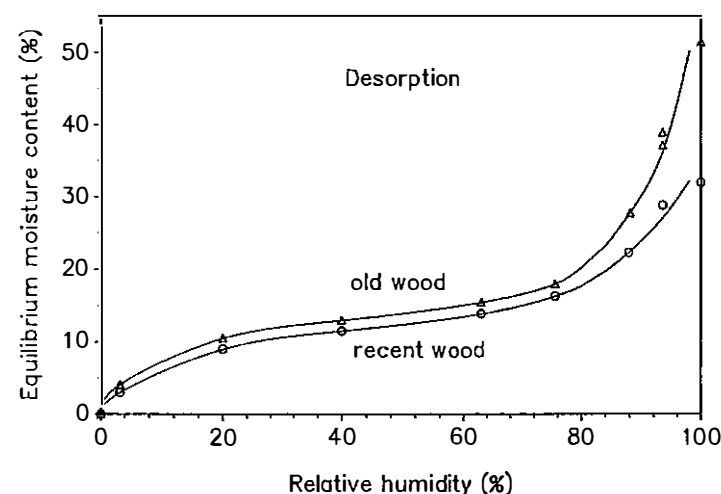


Fig. 3.3. Desorption isotherms for waterlogged oak. (Schniewind 1990)

compared with recent wood. The data show that hygroscopicity in old, waterlogged wood increases to varying degrees. The reasons are to be found in the extent as well the mechanism of the decomposition. Age alone did not appear to be a factor in the increase of hygroscopicity, at least in the case of oak.

Shrinking and swelling behavior of waterlogged archaeological wood is of major importance to its drying and stabilization. In contrast to recent wood, in which drying stresses and changes in shape can be largely sustained by the inherent strength of the material, waterlogged wood is often subject to extreme levels of shrinkage and drastic changes in shape upon drying, owing to two fundamental factors (Schniewind 1990). For one, the decomposition of the carbohydrates in waterlogged wood also decreases the crystallinity of the remaining cellulose, which results not only in increased hygroscopicity but also in increased shrinkage, especially in the longitudinal direction. Secondly, extreme shrinkage of waterlogged wood is caused by the great losses in strength due to cell wall decomposition. As drying proceeds, the weakened cell walls are unable to withstand the stresses imposed by the surface tension of the receding columns of liquid water, leading to collapse of the wood structure (Sakai 1991). Comparing the shrinkage in the three principal directions of waterlogged archaeological and fossil wood of various ages with that of recent wood showed that the former always shrinks more than the latter (Schniewind 1990). The most noticeable increases are in longitudinal shrinkage, which can reach values as high as 10%. The decomposition of cellulose microfibrils is thought to be responsible; a clear increase in longitudinal shrinkage can thus be considered an indicator for structural deterioration. As an example, archaeological remains of a boxwood table showed significantly higher longitudinal shrinkage (Payton 1984).

Generally, the shrinkage of old, waterlogged wood increases as the residual density decreases, but decreased density is not the only criterion for increased shrinkage. However, a linear relationship has been observed between maximum moisture content and longitudinal, tangential, and volumetric shrinkage (De Jong 1979; Hoffmann et al. 1986). Taking the ratio of shrinkage or swelling of old to recent wood for each of the three anatomical directions, and plotting this against residual density, the ratio is found to increase as the residual density decreases (Schniewind 1990). This is particularly pronounced in the longitudinal direction (Fig. 3.4).

Dry, collapsed, waterlogged wood will regain its shape in contact with water to only a very limited extent; the collapse is usually irreversible. In most cases, zones of collapsed cells will exist side by side with zones of cells that shrank normally. The existing swelling potential of the latter zones can then be used, for example, in recovering the shape of turned wood objects, whereby in addition to water, stronger swelling agents such as a 1% solution of sodium hydroxide may be required (Hoffmann 1988, 1993). Objects with mostly collapsed zones cannot be recovered even with sodium hydroxide

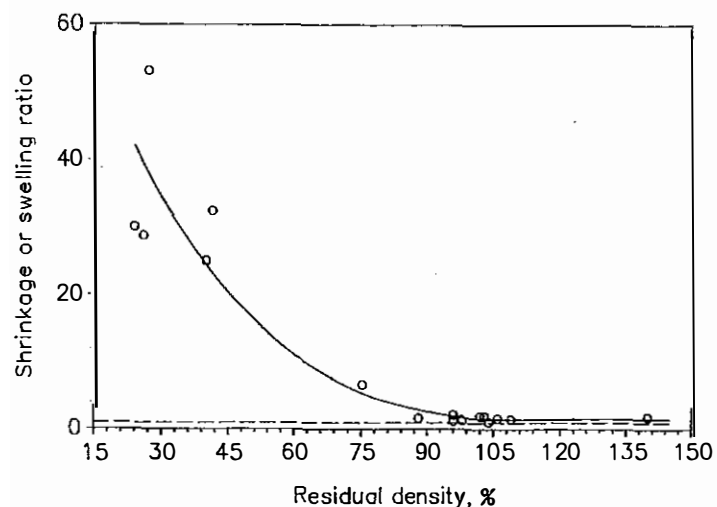


Fig. 3.4. Longitudinal shrinkage ratio for old and recent woods as a function of their respective density ratios. (Schniewind 1990)

solutions, but they can be softened to permit recovery of shape by physical means.

3.2 Density of Wood

3.2.1 Recent Wood

Density is defined as the ratio of mass and volume of a substance. Wood as a porous solid may contain gaseous (air, water vapor), liquid (water, preservatives) or solid (salts, consolidants) matter which can change both mass and volume. Moisture is the most important, and it is therefore necessary to specify the basis for making the measurements. Most commonly, density measurements of wood are made based on oven-dry mass and: (1) oven-dry volume, (2) green (fully swollen) volume, or (3) volume "at test", which is often chosen as volume at 12% moisture content (Kellogg 1989). Density based on oven-dry mass and green volume has been termed conventional density. Alternatively, true density may be determined as the ratio of mass and volume, both "at test," in what may appear to be the most straightforward method. This requires, however, that the moisture content at which this measurement is made be specified, since the result depends on the quantity of moisture present. As moisture is adsorbed by dry wood, both mass and volume will increase. The effect of these changes on density based on mass and volume "at test" is shown graphically in Fig. 3.5. Table 3.4 lists density

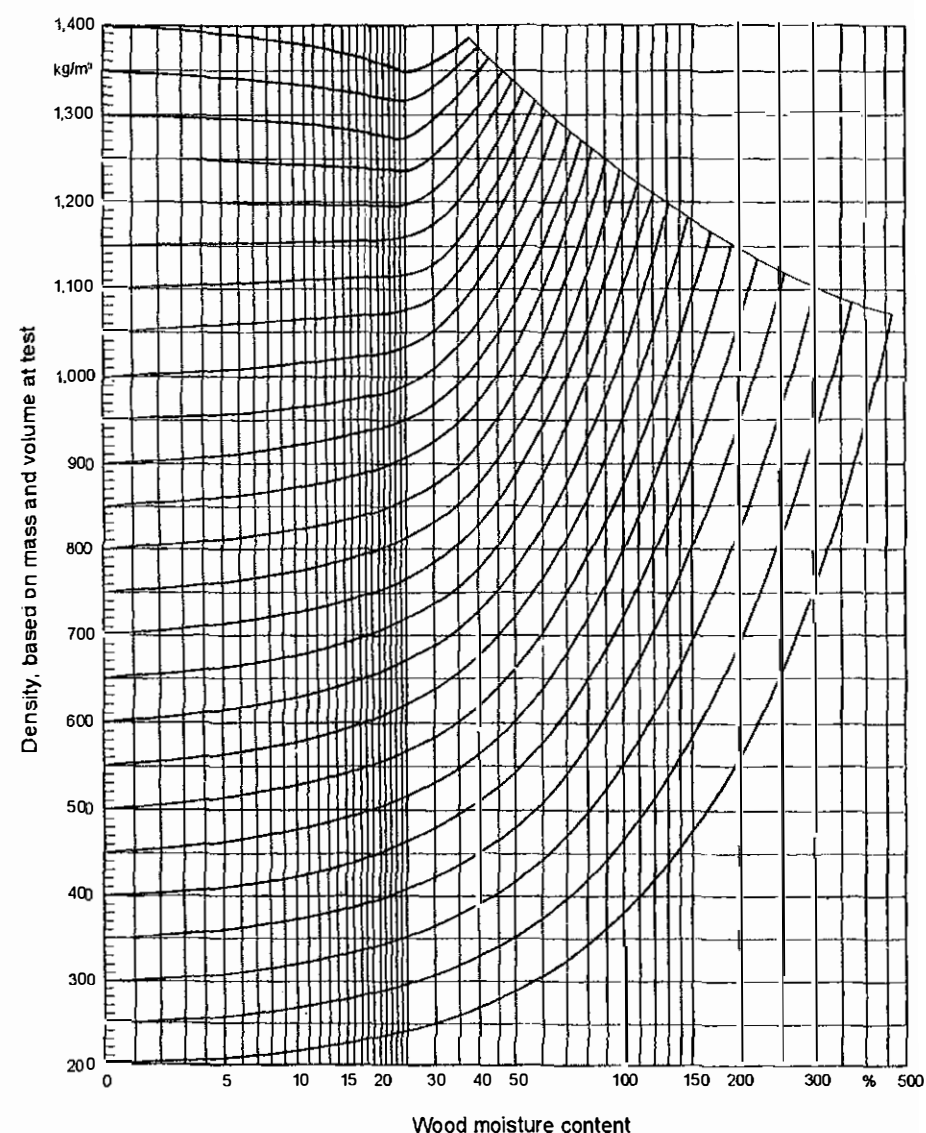


Fig. 3.5. Density based on mass and volume "at test" as a function of moisture content. (Kollmann and Côté 1968)

values based on oven-dry mass and volume and conventional density for selected Central European species. As may be seen, the latter are always lower than the former. Conventional density is particularly suitable for characterizing deteriorated waterlogged wood because of its tendency to shrink excessively during drying.

The density of wood is affected by such structural factors as percentage of latewood and location within the tree trunk. The density of dry wood cell wall substance is a relatively constant 1500 kg/m^3 regardless of wood species.

Table 3.4. Density based on oven-dry mass and volume, and conventional density for some Central European species. (Dietz 1975)

Species	Oven-dry mass and volume (kg/m ³)	Conventional density (kg/m ³)
Poplar	396	347
Fir	450	403
Spruce	458	403
Pine	475	418
Linden	496	429
Alder	506	447
Larch	515	458
Cherry	559	491
Birch	598	513
Maple	614	532
Ash	653	568
Oak	653	577
Beech	688	578
Hornbeam	721	598
Robinia	728	644

Table 3.5. Natural decay resistance of the heartwood of selected US native and imported woods. (Forest Products Laboratory 1987)

Resistant or very resistant	Moderately resistant	Slightly or nonresistant
Cedars	Douglas-fir	Ash
Black cherry	Western larch	Aspen
Junipers	Chestnut oak	Beech
Black locust	Eastern white pine	Birch
White oak	Longleaf pine	Hemlock
Redwood	Slash pine	Maple
Black walnut	Tamarack	Red oak
Brasilian rosewood	Apitong	Pines (except those at left)
Greenheart	European walnut	Spruce
Jarrah	African mahogany	Fir
Lignumvitae	Bagtikan	Balsa
American Mahogany	Red lauan	Ceiba
Meranti	Tanguile	Limba
Teak	Sapele	White lauan

The density of gross wood is therefore a measure of the porosity of wood. For example, a sample of wood with a measured density of 500kg/m³ based on oven-dry mass and volume consists of approximately one third cell wall substance and two thirds pore space. Conversely, density is also a measure of the amount of wood substance contained in a unit of volume. It is therefore to be expected that wood density will be an important factor affecting most wood properties. As already pointed out, woods of high density generally

shrink and swell more. The strength and stiffness of wood also depends greatly on density. Although the resistance of wood to biological deterioration depends on many factors, woods of lower density tend to have lower natural resistance. Natural durability of wood species is increasingly taken into consideration in wood construction. Table 3.5 shows a list of selected US native and imported species classified according to the decay resistance of the heartwood only, since the sapwood of all species has little or no natural resistance.

Methods of determining wood density are discussed in Chapter 6.

3.2.2

Historical Wood

Based on the effect of wood density, moisture content, and the presence of certain constituents on the natural durability of wood, generally only highly resistant species will survive long periods and unfavorable environments. The decrease in density of historic woods compared with recent wood is a measure of the degree of deterioration. Dry wood which has undergone deterioration by insect or fungal pests will have a reduced density compared with recent, sound wood. Wood which has been attacked by insects becomes more permeable to impregnation the greater the damage. For liquids of low viscosity the frass will act like a wick, but the frass may act as a barrier to more viscous polymer solutions. Wood heavily damaged by insects may retain low viscosity liquids only poorly, so that at small increases in temperature a significant amount may run out again.

Similarly, decayed wood can generally be impregnated more easily than recent, sound wood because of the increased permeability of the former, but the effect may not be evenly distributed because of zones of impermeable wood resulting from structural factors such as aspirated pits. Bacterial damage is often localized or irregular, causing localized excessive absorption of surface coatings, such as varnish, and a spotty appearance.

Whereas the density based on oven-dry mass and volume or other bases requiring drying for volume measurement can be determined for insect damaged or decayed wood with sufficient accuracy if care is taken, these measures are not suitable indicators for other properties of deteriorated, water-logged wood because of its extreme shrinkage. If conventional density is taken instead, volume measurements can be avoided altogether by using the maximum moisture content. Investigations on foundation piles (Böttcher 1989) showed a strong correlation between conventional density and the maximum moisture content, which can be expressed by the following empirical equation:

$$R = 1000 \times (u_{max}/100 + 0.667)^{-1},$$

where R is the conventional density, in kg/m³, and u_{max} is the maximum moisture content, in percent. This equation is based on the assumption that all pore

Table 3.6. Conventional density of buried fossil and archaeological oak wood. (Schniewind 1990)

Age (years)	Conventional density (kg/m ³)	Residual density (percentage of recent wood density)
50	767	95
300	410	75
330, sapwood	122	21
330, heartwood	462	80
440	265	49
440	397	74
570, sapwood	150	32
570, heartwood	504	94
810	490	89
810	530	96
1000, sapwood	130	20
1000, heartwood	620	91
1500	530	96
1600	200	36

spaces in the wood are completely filled with water, that the cell wall substance shrinks in proportion to the water that is removed, and that the dry cell wall substance reaches a density of 1500 kg/m³ (Schniewind 1989a). The maximum moisture content can easily be determined.

Whereas the maximum moisture content of recent Central European woods ranges from 92% for hornbeam and 111% for oak to 205% for poplar (Trendelenburg 1955), it can be as high as 800% for deteriorated waterlogged wood (Noack 1969). Conventional density is a better indicator of decomposition processes and strength reductions compared with recent wood than density measures which require volume determinations of dried wood. Data on the density of old, buried wood of various species collected by Schniewind (1990) show that age alone is not a reliable indicator of mass loss (Table 3.6). Environmental conditions before and during exposure in the soil or water are decisive factors in the decomposition. Although old softwoods tend to have higher residual density values than old hardwoods, it is not justified to conclude that softwoods have a higher resistance to deterioration (Schniewind 1990). The extent of decomposition of waterlogged wood is of particular importance for its treatability. Waterlogged oak, for instance, which has deteriorated only in the surface zones cannot readily be stabilized with suitable substances to avoid changes in shape, because the interior is too impermeable. With buried wood, treatability can often be improved by prior cleansing operations.

3.3 Strength and Stiffness Properties

3.3.1 Recent Wood

The mechanical properties of wood can be characterized by measures of strength, i.e., the maximum stress – force per unit area – that can be sustained, and by measures of stiffness, i.e., parameters that express the resistance to deformation. The most important strength properties are those in compression, tension, bending, and shear (Schniewind 1989b). The stiffness of wood is characterized by nine independent elastic constants, of which the modulus of elasticity, usually determined in bending, is the most important. Another important property is shock resistance in impact bending, or toughness, which measures the energy required to cause failure.

Wood is highly anisotropic, i.e., its strength depends on direction within the wood structure. Tensile strength is as much as 20 times greater parallel to rather than perpendicular to the fiber direction; for compression the difference is not quite as great at a factor of about 10. Stiffness properties depend on fiber direction as well. There are also differences between the radial and tangential directions but they are considerably less, at a factor of generally less than 2. When measured in the fiber direction, tensile strength is greater than compression strength by a factor of about 2. In bending, both compressive and tensile stresses are present, and therefore the bending strength is intermediate to the strengths in compression and in tension. Shear strength depends on whether the failure plane is parallel to the fiber direction or perpendicular to it, but in this case the strength in shear perpendicular to the fiber direction is much greater than parallel to it.

Perhaps the most important factor determining wood strength is species. The bending strength of the strongest species may differ from the least strong by a factor of more than 10.

Much of this difference is due to differences in density, and density is an important factor for within-species variations. Within-species differences may be due to such structural factors as the proportion of latewood. Other structural factors affecting strength are cross grain, when the fiber direction is inclined at an angle to the direction of the applied loads, and such attributes as knots, checks and splits, and pitch and bark pockets. The chemical composition can be a factor in that a high lignin content tends to favor compression strength and a high cellulose content tends to favor tensile strength.

When wood is dried below the fiber saturation point, its strength properties and its stiffness will increase. The one exception is toughness, which either increases little or may even decrease. The increased stiffness upon drying in essence makes wood more brittle and less able to absorb energy on impact. The general rate of increase continues to about 8% moisture content and

Table 3.7. Strength and stiffness of selected species at a nominal moisture content of 12%. (From German Institute for Standardization DIN 68364 1979)

Species	Density, mass and volume air-dry (kg/m ³)	Strength (MPa)			Modulus of elasticity (GPa)		
		Compr. parallel	Static bending	Tension parallel	Long.	Tangent.	Radial
Western red cedar	370	35	54	60	8	–	–
Spruce	470	40	68	80	10	0.45	0.8
Fir	470	40	68	80	10	0.45	–
Pine	520	45	80	100	11	0.5	1
Douglas-fir	540	50	80	100	12	0.7	0.9
Larch	590	48	93	105	12	–	–
African mahogany	500	43	75	62	9.5	0.42	1.04
American mahogany	540	45	80	100	9.5	0.57	0.99
Maple	610	49	95	82	9.4	0.89	1.55
Birch	650	60	120	137	14	0.63	1.13
Oak	670	52	95	110	13	1	–
Beech	690	60	120	135	14	1.16	2.28
Ash	690	50	105	130	13	0.82	1.5
Robinia	730	60	130	148	13.5	–	–
Hornbeam	770	60	130	135	14.5	–	–
Afzelia	790	70	115	120	13.5	–	–
Hickory	800	65	130	150	15	–	–

either becomes less thereafter or there may even be a maximum for some properties such as tensile strength with some decreases in strength below 6 or 7% moisture content. Temperature effects on wood are of two kinds. One is a transient and immediate effect which results in decreasing mechanical properties as temperature increases, and also increases in strength at reduced temperatures. In general, mechanical properties will decrease about 0.5–1% for each increase in temperature of 1 °C. The second kind of temperature effect is time-dependent, and results in thermal degradation. Permanent reductions in strength can occur even at temperatures as low as 60 °C for lengthy exposures. Table 3.7 lists some strength and elastic properties of selected species which have been conditioned in a standard humidity room designed to produce a nominal moisture content of 12%.

3.3.2

Historical Wood

The mechanical properties of dry wood which has been aged but is otherwise sound, when compared with recent wood, are either the same or only slightly changed. Roof timbers of southern pine in an academic building built in 1904

and razed in 1989 did not show any evidence of strength reduction over the 85-year service life (Fridley et al. 1996). Rug and Seemann (1989) found that strength properties of old pine, spruce, and oak wood from the eighteenth to the twentieth centuries correspond to those of recent wood, and that quantitative predictions of strength can be made based on a strong correlation with density and modulus of elasticity. Compression test results of old roof timbers had greater variability but were of the same general magnitude as for recent wood (Deppe and Rühl 1993). However, the mechanical properties of wood attacked by insects will be reduced. Compression and bending strength of spruce attacked by wood wasps, for instance, are reduced in proportion to the density of bore holes in the cross section of the test specimen. Reductions in compression strength of up to 10% and in bending strength of up to 30% have been observed (Niemz 1993). When freezing is used as a treatment for an active insect infestation, reduced temperatures will be accompanied by transient increases in strength (Florian 1986).

Blue stain and other fungal stains only ordinarily cause slight changes in mechanical properties (Forest Products Laboratory 1987). Decay fungi, namely brown rot, white rot, and soft rot under favorable conditions can cause significant strength reductions and eventually lead to complete destruction of the wood. The effects of decay on strength can be very significant even at very low levels of mass loss. Toughness, the resistance to impact loading, is the property most sensitive to decay, and losses in toughness of 80% or more have been observed in wood with a mass loss due to brown rot of only 5–10% (Wilcox 1978, 1989). Brown-rot damage is characterized by cubicular failures. White rot leads to brash failures like the failures of a fresh carrot snapped in two, and soft rot failures are similar and may take on a shell-like appearance.

Marine piling of pitch pine, 100 years old, was found to be severely deteriorated to a depth of 2 mm and discolored to a depth of 10 mm, but the wood below was comparable in strength to recent wood (Bröker 1985a). By and large, the same results were obtained on deck planks of teak, Douglas-fir, and pitch pine of a shipwrecked barque. Only the toughness of the planks was somewhat lower, which was attributed to the infiltration of sodium chloride (Bröker 1985b). Similarly, 70-year-old foundation piles of Douglas-fir which had been attacked by bacteria showed significant deterioration in the surface layers but the interior had strength properties comparable to recent wood (Schniewind et al. 1982).

Examination of Table 3.8 shows that in many cases the residual strength is lower than the residual density, so that strength losses are not proportional to mass losses and reduction in density. It might be expected that decomposition of the carbohydrates would affect bending strength more than compression strength, but this is not born out by the data in Table 3.8. Toughness is generally a good indicator of the early stages of decay or thermal degradation because it is more sensitive than any of the other mechanical properties. Schniewind (1990) found that residual toughness of buried wood of varying

Table 3.8. Compression and bending strength of fossil and archaeological wood. All material was buried under wet conditions; the specimens marked *air-dry* were dried before testing

Species	Age (years)	Residual density (%)	Moisture content	Compression parallel to grain		Static bending	
				Strength (MPa)	Residual (%)	Strength (MPa)	Residual (%)
Cunninghamia	2,100	113	Air-dry	34.9	97	–	–
Douglas-fir	70	92	Wet	18.2	77	39.6	76
Fir, white	900	98	Air-dry	37.1	79	65.2	80
Fir	17	97	Air-dry	41.0	85	75.0	106
Juniper	2,000	113	Air-dry	42.7	107	–	–
Pine	900	100	Wet	17.0	70	33.7	60
Spruce	17	98	Air-dry	42.0	93	76.0	99
Yew	2,400	72	Air-dry	33.5	50	–	–
Acacia	30,000	–	Air-dry	67.2	71	54.9	29
Ash, Japanese	16,000	42	Air-dry	11.8	24	11.8	9
Ash, Japanese	16,000	58	Air-dry	13.7	28	31.4	23
Beech	570	27	Wet	0.7	2	–	–
Birch	3,000	31	Air-dry	2.7	5	3.2	2
Bischofia	6,570	90	Air-dry	34.0	75	66.1	72
Elm	900	64	Wet	9.9	39	19.5	39
Linden	3,000	44	Air-dry	–	–	2.5	2
Live oak	50	95	Wet	30.9	83	54.3	66
Live oak	240	75	Wet	13.9	37	33.9	41
Oak	330	71	Wet	16.8	57	34.3	58
Oak	570	94	Wet	24.5	66	32.6	49
Oak	700	88	Air-dry	–	–	33.6	47
Oak	800	106	Air-dry	–	–	74.9	105
Oak	800	109	Air-dry	45.7	73	80.3	113
Oak	810	89	Wet	13.2	43	–	–
Oak	810	96	Wet	16.9	55	–	–
Oak	900	102	Wet	11.0	35	26.3	40
Oak	900	111	Air-dry	65.7	112	–	–
Oak	1,000	75	Air-dry	–	–	15.6	22
Oak	1,100	102	Air-dry	–	–	58.2	82
Oak	1,100	140	Air-dry	37.9	60	89.0	125
Oak	1,600	36	Wet	0.9	3	1.3	2
Oak	1,600	73	Wet	3.8	12	4.3	7
Oak	1,600	96	Air-dry	–	–	47.2	66
Oak	3,000	49	Air-dry	9.6	16	2.4	3
Oak	4,700	96	Air-dry	38.5	65	71.0	81
Oak	4,700	103	Air-dry	33.3	56	34.4	47
Oak	8,500	97	Air-dry	44.9	79	–	–

ages included very low as well as very high values, including a number of cases where the toughness was higher for old than for recent wood. High values of toughness have been attributed to decreased stiffness (Hoffmann et al. 1986) and increased plasticity (Jagels et al. 1988) of waterlogged wood. A comparison of residual bending strength and residual toughness of fossil and archaeo-

logical wood yielded almost identical average values. This indicates that degradation by decay or thermal exposure takes place by mechanisms which differ from those involved in the degradation of buried wood.

References

- Böttcher P (1989) Untersuchungen zur Dauerhaftigkeit von Gründungspfählen. Holz Roh Werkst 47:179–184
- Bröker F-W (1985a) Technologische Untersuchungen an langjährig verbauten Dalben und Uferbefestigungen. Holz Roh Werkst 43:476
- Bröker F-W (1985b) Technologische Untersuchungen am Holz einer gesunkenen Bark. Holz Roh Werkst 43:476
- Buck RD (1952) A note on the effect of age on the hygroscopic behaviour of wood. Stud Conserv 1:39–44
- De Jong J (1979) Conservation of water-logged wood. Netherlands National Commission for UNESCO, Amsterdam
- Deppe H-J, Rühl H (1993) Zur Beurteilung alter Bauhölzer. Holz Roh Werkst 51:379–383
- Dietz P (1975) Dichte und Rindengehalt von Industrieholz. Holz Roh Werkst 33:1135–141
- DIN 68 364 (1979) Kennwerte von Holzarten. Festigkeit, Elastizität, Resistenz
- EN 350–2 (1994) Natürliche Dauerhaftigkeit von Vollholz
- Erhardt D, Mecklenburg MF, Tumosa CS, Olstad TM (1996) New versus old wood: differences and similarities in physical, mechanical, and chemical properties. ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, 1–6 Sept 1996, vol II, pp 903–910
- Florian M-L (1986) The freezing process – effects on insects and artifact materials. Leather Conserv News 3:1–13,17
- Forest Products Laboratory (1987) Wood handbook, agriculture handbook no 72. US Dept of Agriculture, Washington, DC
- Fridley KJ, Mitchell JB, Hunt MO, Senft JF (1996) Effect of 85 years of service on mechanical properties of timber roof members, part I. Experimental observations. For Prod J 46(5):72–78
- Hoffmann P (1988) Zur Rückformung mittelalterlicher Drechslerware. Teil II. Hölzer mit Schwindungsschäden. Arbeitsbl Restaur, Gruppe 8, pp 171–185
- Hoffmann P (1993) Restoring deformed fine medieval turned woodware. ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 22–27 Aug 1993, preprints 257–261
- Hoffmann P, Peek R-D, Pulz J, Schwab E (1986) Das Holz der Archäologen: Untersuchungen an 1600 Jahre alten wassergesättigtem Eichenholz der "Mainzer Römerschiffe". Holz Roh Werkst 44:241–247
- Jagels R, Seifert B, Shottafer JE, Wolfhagen JL, Carlisle JD (1988) Analysis of wet-site archaeological wood samples. For Prod J 38(5):33–38
- Kamba N, Nishiura T (1993) Measurement of the dimensional change of wood in a closed case. ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 22–27 Aug 1993, vol I, pp 406–409
- Kellogg RM (1989) Density and porosity. In: Schniewind AP (ed) Concise encyclopedia of wood & wood-based materials. Pergamon Press, Oxford/MIT Press, Cambridge, Massachusetts, pp 79–82
- Klein P, Bröker F-W (1990) Investigations on swelling and shrinkage of panels with wooden support. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden, 26–31 Aug 1990, vol I, pp 41–43
- Knigge W, Schulz H (1966) Grundriß der Forstbenutzung. Parey, Hamburg
- Kohara J (1984) Wood-based culture and the Japanese. Asahi Shimbunsha, Tokyo
- Kollmann FFP, Côté WA Jr (1968) Principles of wood science and technology I: solid wood. Springer, Berlin Heidelberg New York
- Legrum J (1993) Temperatur- und Feuchteverhalten von Holztafelbildern. Institut für Steinkonservierung in Hessen, Rheinland-Pfalz und Saarland, Heft 2

- Mantanis GI, Young RA, Rowell RM (1994) Swelling of wood, part II. Swelling in organic liquids. *Holzforschung* 48:480–490
- Mantanis GI, Young RA, Rowell RM (1995) Swelling of wood, part III. Effect of temperature and extractives on rate and maximum swelling. *Holzforschung* 49:239–248
- Niemz P (1993) Physik des Holzes und der Holzwerkstoffe. DRW-Verlag Weinbrenner, Leinfelden-Echterdingen
- Noack D (1965) Der gegenwärtige Stand der Dimensionsstabilisierung von Holz und Schlußfolgerungen für die Konservierung der Bremer Kogge. *Brem Jahrb* 50:20–52
- Noack D (1969) Zur Verfahrenstechnik der Konservierung des Holzes der Bremer Kogge. Die Bremer Hanse-Kogge, Monographien der Wittheit zu Bremen, vol 8. Röver, Bremen
- Noack D (1990) Holzphysik. Vorlesungsmanuskript, Universität Hamburg
- Payton R (1984) The conservation of an eighth century BC table from Gordion. In: Bromelle NS, Pye EM, Smith P, Thomson G (eds) *Adhesives and Consolidants*. International Institute for Conservation of Historic and Artistic Works, London
- Rug W, Seemann A (1989) Ermittlung von Festigkeitskennwerten an alten Holzkonstruktionen. *Holztechnologie* 30:69–73
- Sakai H (1991) Syutsudo-mokuzai to mizu no sougosayo kanso to kyushitu (Interaction between waterlogged wood and water: drying and water absorption). *Gango-ji bunkazai kenkyu* 37:2–8, AATA 30–1292
- Schirp M, Kübler H (1968) Untersuchungen über die kältebedingten Längenänderungen kleiner Holzproben. *Holz Roh Werkst* 26:335–341
- Schniewind AP (1989a) Archaeological wood. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. Pergamon Press, Oxford/MIT Press, Cambridge, Massachusetts, pp 14–18
- Schniewind AP (1989b) Strength. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. Pergamon Press, Oxford/MIT Press, Cambridge, Massachusetts, pp 245–250
- Schniewind AP (1990) Physical and mechanical properties of archaeological wood. In: Rowell RM, Barbour J (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington, DC. *Adv Chem Ser* 225:87–109
- Schniewind AP, Gammon B, Bendtsen BA (1982) Strength of untreated Douglas-fir foundation piles after some 70 years' service. *For Prod J* 32(11/12):39–46
- Schwarz A, Gadesmann D (1994) Holzfeuchtemessungen an Tafelgemälden – Untersuchungsergebnisse aus der Celler Schloßkapelle, Teil 2. *Restaurio* 100:256–261
- Skaar C (1989a) Hygroscopicity and water sorption. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. Pergamon Press, Oxford/MIT Press, Cambridge, Massachusetts, pp 143–147
- Skaar C (1989b) Shrinking and swelling. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. Pergamon Press, Oxford/MIT Press, Cambridge, Massachusetts, pp 243–245
- Sutter H-P (1986) *Holzschädlinge an Kulturgütern erkennen und bekämpfen*. Haupt, Bern
- Trendelenburg R (1955) *Holz als Rohstoff*. Hanser, München
- Wilcox WW (1978) Review of literature on the effects of early stages of decay on wood strength. *Wood Fiber* 9(4):252–257
- Wilcox WW (1989) Decay during use. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. Pergamon Press, Oxford/MIT Press, Cambridge, Massachusetts, pp 71–75

4 Corrosion Behavior of Wood

4.1

Effect of Chemical Media

4.1.1

Water

At normal temperature and pressure, water has no chemical effects on wood. However, long periods of submersion in water as during log rafting or placement in log storage ponds lead to loss of water soluble extractives. In some cases this may increase resistance to attack by insects and staining fungi.

At elevated temperatures, starting at about 50°C, and elevated pressures, water has a hydrolytic effect on the components of wood, which is catalyzed by any acids that may be present. Prolonged exposure to water under these conditions can therefore lead to damage proceeding inward from the surface zones of the wood.

4.1.2

Acids and Bases

The effect of acids and bases on wood depends on their type, their concentration, the pH-value, the length of exposure and temperature. In general, some species of wood are quite resistant to dilute mineral and organic acids, oxidizing acids damage wood more than non-oxidizing acids, alkaline solutions degrade wood more than acidic solutions, and softwoods are more resistant to both acids and bases than hardwoods. Attack by acids or bases will first lead to color changes in the wood. Extended exposure to acids leads to hydrolysis of the polysaccharides, starting on the wood surface. Similar processes take place in the anaerobic environment of foundation piles (Meseck and Knüpfer 1988; Böttcher 1989), where acid soils may be the trigger for long-term hydrolysis. Increasing acid concentration and temperature will result in definite reductions in mechanical strength.

Bases, depending on concentration and temperature, will first cause wood swelling, followed later by decomposition of hemicelluloses and lignin. Also,

Table 4.1. Corrosion resistance of some species to acids and bases.^a (After Müller 1993)

solution	Concentration (%)	Wood species					
		Spruce	Pine	Larch	Fir	Oak	Beech
Sulfuric acid, H ₂ SO ₄	2	1	1	1	1	1	1
	5	1	1	1	1	1	1
	10	2	2	2	2	2	2
Nitric acid, HNO ₃	2	1	1	1	1	2	2
	5	1	2	1	2	3	2
	10	1	1	1	2	3	2
Hydrochloric acid, HCl	2	1	1	1	1	1	1
	5	2	2	1	2	2	2
	10	2	2	2	2	3	4
Acetic acid, CH ₃ COOH	2	1	1	1	1	1	1
	5	1	1	1	1	1	1
	10	1	1	1	1	2	1
Sodium hydroxide, NaOH	2	1	1	1	1	2	2
	5	2	2	2	2	4	3
	10	3	3	3	2	4	4
Ammonium hydroxide, NH ₄ OH	2	1	1	1	1	2	2
	5	1	1	1	1	4	3
	10	2	2	2	2	4	4

^a1, Completely stable, mass loss <0.1 g/m²·h; 2, sufficiently stable, mass loss 0.1–1.0 g/m²·h; 3, fairly stable, mass loss 1.0–3.0 g/m²·h; 4, barely stable, mass loss 3.0–10.0 g/m²·h.

salts will be deposited, especially in the earlywood. Longer periods of exposure (>60 days), and higher concentrations and temperatures will result in noticeable reductions in mechanical strength and resistance to biological attack. The degraded wood becomes brittle, i.e., it loses its ability to warn of impending failure and breaks suddenly with a loud noise.

According to Table 4.1, hardwoods such as oak and beech are, on average, less resistant to acids and bases than softwoods such as spruce, pine, larch and fir. The greater resistance of softwoods is based on their higher lignin content and lower hemicellulose content compared with the hardwoods, and in the case of spruce, pine, Douglas-fir and larch to their higher resin content.

Concentrated acids (hydrochloric acid, sulfuric acid) will decompose wood cellulose to glucose even at normal temperatures. Wood can be macerated (broken down into individual fibers or fiber bundles) with 60% nitric acid and potassium chlorate, or with chromic acid.

4.1.3 Salts

Many inorganic salts in aqueous solution will dissociate and make the solution more or less strongly acidic or alkaline. The effect on wood depends on the salt

concentration and the degree of hydrolysis. Relative humidity and the corresponding wood moisture content play an important role in the deposition of salt within the wood structure and the latter's subsequent destruction (Erler 1984, 1990). Well-known examples are industrial wood buildings contaminated with chemicals, where the surface corrosion layer deepens with increasing time of exposure, and the reduction of mechanical strength is practically limited to the affected surface zone (Wegener and Fengel 1986).

Sodium chloride (table salt), which in the past has been impregnated into wood members in historical structures as a preservative against insects and decay fungi but also as a fire retardant, causes destruction of the wood (Wegener and Kühn 1991). Causative factors are mechanical splitting due to crystallization of the salt within the wood structure and hydrolysis reactions by acid groups of wood components. Spruce wood treated with table salt will reach a moisture content of 28.5% at a relative humidity as low as 85%, in contrast to normal wood where that moisture content corresponds to the fiber saturation point. Roof timbers which had been treated with historic fire retardants such as Glauber's salt (NaSO₄·10H₂O) or Epsom salt (MgSO₄·7H₂O), as well as with strongly alkaline substances such as mixtures of soda and potash, often will have developed a fibrous (macerated) surface (Becker 1986).

Ettel et al. (1992) recommend the following measures to avoid or minimize the corrosion of structural timbers by aggressive media: (1) regular inspection for early detection of damage, (2) removal of salt accretions or regular cleaning, (3) coating of members exposed to chemicals with tar-modified epoxy resins or hot linseed oil, and (4) increased member sizes when corrosion is to be expected.

4.1.4 Gases

Wood's capability for gas absorption depends on species (wood density), the anatomical direction, the dimensions of the piece and its age, whether it is sapwood or heartwood, and the density of the gas. Sorption of gases decreases at elevated temperatures. Reaction of gases with wood or any surface coatings is strongly influenced by the presence of water. The higher the relative humidity of the air or the moisture content of the material, the greater the opportunity for corrosive effects.

The application of sulfur dioxide (used in the past to fumigate libraries by burning sulfur; cf. Chap. 8) leads to the formation of sulfurous and sulfuric acids, which can lead to irreversible damage of wood as well as more sensitive materials such as painted paper and parchment. Wood will suffer losses in strength, characterized by brash failures when stressed. Ammonia is absorbed readily and swells wood under formation of ammonium hydroxide. This should be considered when ammonia is used to "smoke" wood such as oak or mahogany to obtain dark colorations.

Table 4.2. Discoloration of wood by ferrous metals. (After Grosser and Teetz 1985; Sell 1989)

Discoloration	Wood species
Light gray	Spruce, pine, beech, elm, hornbeam, alder, linden, birch, chestnut, limba
Blue-gray	Larch, Douglas-fir, makoré
Blue-gray to black	Oak, walnut

Corrosive effects of fumigants such as hydrogen cyanide, bromomethane, sulfuryl fluoride, formaldehyde, and carbon dioxide on wood, paints, and other materials relevant to cultural property will be discussed in Chapter 8.

4.1.5 Metals

The interaction between wood and metals depends principally on wood moisture content, species, environmental conditions, and the type of metal. Wood at a moisture content of <10% will be changed little by contact with metals. In the range of 20–30% moisture content, certain metals can have more pronounced effects on wood. Table 4.2 shows that some woods are stained bluish gray to black by metals containing iron. Sufficiently long exposure to iron will reduce the tensile strength but not the compression strength of oak.

Under anaerobic conditions, the corrosion products of iron appear to have localized biocidal effects. Waterlogged oak wood which has been subject to biological deterioration has been found to be less deteriorated in those places where iron bolt connections had formerly been located. The effects of incorporated corrosion products of iron and copper on the extent of wood degradation depend on the length of submergence, the wood species, and the type of metal corrosion product incorporated in the wood structure (MacLeod and Richards 1997). The longer the wood is exposed to aerobic marine conditions, the greater the extent of wood degradation.

4.1.6 Corrosive Effects of Wood on Materials

Aqueous extracts of many wood species are weakly acidic, and can cause metal corrosion. Ferrous metals are affected most by oak, sapele, and utile (Table 4.3). The presence of tannins in oak and its emission of formic and acetic acid can lead to corrosion of lead and calcareous objects by formation of lead white and carbonates, respectively (Berndt 1990). In some cases, wood containing preservatives or fire retardants causes increased metal corrosion (Editor 1985). Wood treated with chemical stains may give off ammonia, which attacks other materials (Schnabel 1989). Organic amines in tropical woods can also be the cause of corrosion. Formaldehyde emissions from par-

Table 4.3. Corrosive effects of some woods on ferrous metals. (After Grosser and Teetz 1985; Sell 1989)

Corrosive effect	Wood species
Weak	Larch, alder
Pronounced	Douglas-fir, oak, linden, sapele, utile

Table 4.4. Damage to wood finishes by extractives. (After Böttcher 1994)

Species	Finish ^a				
	PUR	AC	CN	Oil	UP
Spruce (<i>Picea abies</i>)				I	I
Pine (<i>Pinus silvestris</i>)					I
Larch (<i>Larix decidua</i>)		I			I
Oak, European (<i>Quercus petraea</i>)				D	
Mansonia (<i>Mansonia altissima</i>)				I	I
Iroko (<i>Chlorophora excelsa</i>)				I	I
Limba, heartwood (<i>Terminalia superba</i>)					I
Ebony (<i>Diospyros</i> sp.)			B	I	I
East Indian rosewood (<i>Dalbergia latifolia</i>)				I	I
Teak (<i>Tectona grandis</i>)	F	F	F	I	I

^aPUR, polyurethane varnish; AC, acid catalyzed finish; CN, cellulose nitrate lacquer; Oil, drying oil varnish; UP, unsaturated polyester varnish; I, inhibition of drying or setting; D, discoloration of the finish; F, fogging; B, bleeding of extractives.

ticle board have been found to produce blooms of sodium formate on glass beads with a high content of Na₂O (Schmidt 1992).

A number of wood species (Table 4.4) contain phenolic extractives, which can influence the drying or setting and the appearance of surface coatings. In order to avoid problems, such woods need to be first treated with suitable sealers.

4.2 Weathering

Wood surfaces are slowly altered by exposure to direct sunlight (Derbyshire and Miller 1981). Prolonged exposure leads to darkening of the wood surface because of chemical degradation reactions caused by the UV content, especially in light-colored woods. Southern yellow pine will darken upon exposure to UV radiation of 350nm (Chang 1985), whereby lignin is attacked preferentially. The degree of degradation is proportional to the energy of the light and the length of exposure. At wave lengths above 400nm chemical changes do not take place.

Wood exposed to outdoor weathering will take on a characteristic gray color due to preferential degradation and subsequent leaching of lignin. In

addition to discolorations, the surface texture will change because of mechanical erosion of wood substance through wind and rain. According to Sell and Feist (1986), the rate of erosion depends on wood density and therefore on the relative cell wall thickness. The erosion rate is approximately linearly related to density in the range of 300–1000 kg/m³, the rate decreasing with increasing density. Thin layers of wood such as veneer are more severely affected by weathering than solid wood.

In softwoods, unlike in hardwoods, prolonged weathering can create deeply textured surfaces because low density earlywood erodes at a higher rate than high density latewood. In weathered beech the phenomenon of protruding broad rays may be observed, which arises from the differential shrinkage of the rays and the other tissues (Kučera and Sell 1987) and becomes especially pronounced when the moisture content fluctuates widely. Outdoor exposure of beech therefore requires special care to protect the wood from light and moisture, and thick coatings with heavy, opaque pigmentation are therefore suggested.

Depressions and fissures in weathered wood surfaces are ideal loci for colonization by bacteria and fungi which can lead to biological surface degradation (biological corrosion). Since the affected zones will lose their mechanical strength, the depth of degradation must be considered when dealing with load-bearing members of historical structures during restoration or repairs. Allowable loads must then be calculated based on the remaining cross section of sound wood. Even for intact wood members which have been subjected to long-term dead loads, reduction factors are recommended when calculating safe loads (Mönck 1987).

Natural weathering primarily causes degradation of lignin and hemicelluloses, which can be confirmed by IR spectroscopy (Anderson et al. 1991). The erosion due to weathering can be retarded by treatment with an aqueous solution of chromium trioxide which forms light-resistant lignin complexes (Evans et al. 1992).

UV radiation can also have beneficial effects. Surface layers of crushed and damaged fibers on machined wood can be removed readily with UV lasers, which leads to improved application of coatings and adhesives (Seltman 1995). Waterborne wood preservatives based on chromium and copper become fixed, i.e., are made insoluble, by exposure to UV radiation (Anonymous 1989).

References

- Anderson EL, Pawlak Z, Owen NL, Feist WC (1991) Infrared studies of wood weathering, part 1: softwoods, part 2: hardwoods. *Appl Spectroscopy* 45:641–652 (AATA 29-677)
- Anonymous (1989) Aus der Forschung. UV-Strahlen verbessern Holzschutz. *Holz-Zentralblatt* 115:1347
- Becker H (1986) Umwelteinflüsse auf Holz. *Prakt Schädlingsbekämpfer* 5:63–64,66
- Berndt H (1990) Measuring the rate of atmospheric corrosion in microclimates. *J Am Inst Conserv* 29(2):207–220

- Böttcher P (1989) Untersuchungen zur Dauerhaftigkeit von Gründungspfählen. *Holz Roh Werkst* 47:179–184
- Böttcher P (1994) Holz – ein natürlicher Werkstoff. Holz in der restauratorisch-denkmalflegerischen Praxis. 2. Fortbildungsveranstaltung für Restauratoren, Hannover, 11.03.1994. Materialien zur Fort- u. Weiterbildung. Niedersächsisches Landesverwaltungsamt, Institut für Denkmalpflege
- Chang ST (1985) Effect of light wavelength on the degradation of wood. *For Prod Ind* 4:118–123
- Derbyshire H, Miller ER (1981) The photodegradation of wood during solar irradiation. *Holz Roh Werkst* 39:341–350
- Editor (1985) Corrosion of metals by wood. *BRE Digest*, Heft 301
- Erler K (1984) Wirkungen aggressiver Lösungen auf Kiefernholz. *Holztechnologie* 25:249–252
- Erler K (1990) Korrosion und Anpassungsfaktoren für chemisch-aggressive Medien bei Holzkonstruktionen. *Holztechnologie* 30:228–233
- Ettel WP, Diecke W, Wolf H-D (1992) Bautenschutzaschenbuch. Verlag für Bauwesen, Berlin, pp 183–192
- Evans PD, Michell AJ, Schmalzl KJ (1992) Studies of the degradation and protection of wood surfaces. *Wood Sci Technol* 26:151–163
- Grosser D, Teetz W (1985) Einheimische Nutzhölzer (Loseblattsammlung). Centrale Marketinggesellschaft der deutschen Agrarwirtschaft mbH Bonn und Arbeitsgemeinschaft Holz e.V., Düsseldorf
- Kučera LJ, Sell J (1987) Die Verwitterung von Buchenholz im Holzstrahlbereich. *Holz Roh Werkst* 45:89–93
- MacLeod ID, Richards VI (1997) The impact of metal corrosion products on the degradation of waterlogged wood recovered from historic shipwreck sites. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp 331–353
- Meseck H, Knipfer J (1988) The bearing behavior of historical wooden pile foundations. Symposium on geotechnical aspects of restoration and maintenance of infrastructures and historical monuments, Bangkok, 29 November–2 December 1988, pp 115–124 (AATA 28-673)
- Mönck W (1987) Schäden an Holzkonstruktionen. Bauwesen, Berlin
- Müller K (1993) Holzschutzpraxis. Bauverlag, Wiesbaden
- Schmidt S (1992) Na-Formiatbildung auf Glasoberflächen – Untersuchungen an historischen Objekten. *Berl Beitr Archäometrie* 11:137–183
- Schnabel H (1989) Exhalate – eine potentielle Gefahrenquelle für Sammlungen. *Neue Museumskd* 32:60–62
- Sell J (1989) Eigenschaften und Kenngrößen von Holzarten, 3rd edn. Baufachverlag, Zürich
- Sell J, Feist WC (1986) Role of density in the erosion of wood during weathering. *For Prod Ind* 36:57–60
- Seltman J (1995) Freilegen der Holzstruktur durch UV-Bestrahlung. *Holz Roh Werkst* 53:225–228
- Wegener G, Fengel D (1986) Untersuchungen zur Beständigkeit von Holzbauteilen in aggressiven Atmosphären. *Holz Roh Werkst* 44:201–206
- Wegener G, Kühn C (1991) Auswirkungen der Kochsalzeinlagerung in 180 Jahre alten Fichtenbalken. *Holz Roh Werkst* 49:160

5 Biological Deterioration of Wood

5.1

Insects

5.1.1

Classification

Insects are the most important and most frequently found animal pests attacking wood. Wood is used by insects for food, shelter, and breeding. The most common wood-destroying insects belong to the orders Coleoptera (beetles) and Isoptera (termites). These are the primary pests for wood and are also referred to as wood-eating (xylophagous) insects. In addition to the wood-eating insects, there are also secondary pests, such as insects which breed in wood (e.g. ambrosia beetles), colonizing insects (e.g., ants) and those attacking stored materials (e.g. hide or leather beetles). Insects can also be divided into dry-wood pests and damp(green)-wood pests (ecosystematic classification, Table 5.1). Dry-wood pests live in air-dry wood (i.e., m.c.<20%) free of decay. Damp-wood pests can be further divided into insects attacking fresh or green wood and those living in decayed wood. The former attack living trees or freshly felled logs, while the latter are specialized to live in wood with fungal decay.

5.1.2

Morphology

All insects have a similar structure (Fig. 5.1). The body consists of three parts, namely head (caput), chest (thorax), and posterior (abdomen). The head contains eyes, biting jaws (mandibles), the main part of the brain, and a pair of antennae which bear various sensory organs. A pair of jointed legs is attached to each of three rigidly connected segments of the thorax. In many insects the second and third segments each have a pair of wings formed by cuticular projections supported by sclerotized veins. The thorax thus serves for locomotion. The abdomen consists of 6–11 articulated segments, and contains especially the parts of the digestive and reproductive systems. Many insects have reproductive members at the tip of the abdomen which define

Table 5.1. Ecosystematic classification of selected wood insects

Wood condition	Insect Type	Species	Egg deposition		Pupation	
			In buildings	Not in buildings	In buildings	Not in buildings
			a	b	a	b
Damp (green)	Damp (green)-wood insects	Scolytidae				
		Siricidae	X	(X)	X	X
		<i>Ernobius mollis</i>	X		X	(X)
Decayed	Decayed-wood insects	<i>Coelostethus pertinax</i>	X		X	
		<i>Xestobium rufovillosum</i>	X		X	
Sound, dry	Dry-wood insects	<i>Hylotrupes bajulus</i>	X	(X)	X	(X)
		<i>Anobium punctatum</i>	X		X	
		<i>Ptilinus pectinicornis</i>	X		X	
		<i>Lyctus brunneus</i>	X	(X)	X	(X)

a, On wood with bark; b, on processed wood; X, main occurrence; (X), occasional occurrence.

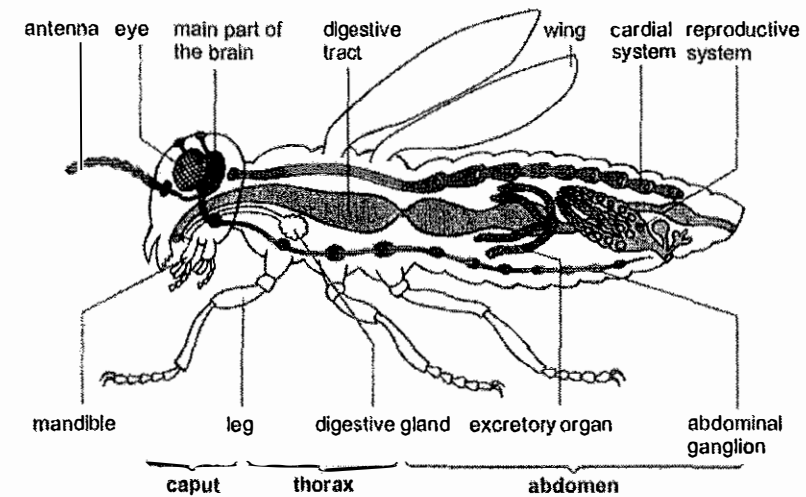


Fig. 5.1. Morphology of an insect. (After Meincke et al. 1980)

the gender. The body surface is impregnated with chitin as a stabilizing agent.

Insects breathe through tracheae which extend through the entire body and are present even in the antennae, legs, and wings. The tracheae originate in small openings (stigmas) in the chitinous exoskeleton. The nervous system of insects consists of the main part of the brain and the ventral, ladder-shaped abdominal ganglion.

5.1.3 Development and Reproduction

Insects experiencing complete transformation (holometabolism) during their life span, undergo metamorphosis which embraces four developmental stages (Fig. 5.2): egg, larva, pupa, and adult (the complete insect – imago). The development from egg to adult represents one generation, and the time required the generation period.

The sensory organs and the emission of pheromones play a decisive role in the search for mating partners. Inseminated females lay their eggs directly on wood surfaces or, depending on species, into bark, splits, checks or old insect galleries of wood by means of a laying tube (ovipositor). Egg placement differs among species and maybe in clusters (Cerambycidae), in rows (Anobiidae), or singly (Siricidae). In the choice of location for the eggs, wood-destroying insects are capable of astounding sensory discrimination. Material

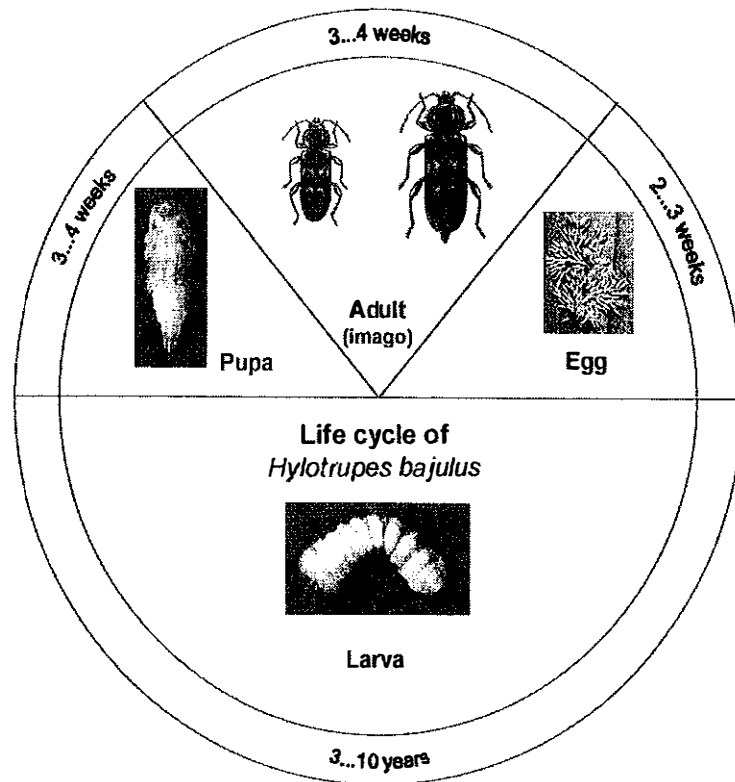


Fig.5.2. Overview of the life cycle of insects

condition such as a rough surface, as well as certain wood constituents can play a role in the laying and placement of eggs.

The larvae of many wood-destroying insects differ greatly from the adults. Among those insects undergoing complete metamorphosis, the larvae emerge from the eggs and quickly bore into the wood where the eggs have been laid. The whitish larvae of the most important wood-destroying insects are worm- or grub-shaped (Fig. 5.3), and the head with its dark biting jaws stands out clearly from the ring-shaped segments of thorax and abdomen. The growth of the larvae to the stage just prior to pupation is made possible by repeated sloughing (shedding) of the skin. The principal damage to wood is caused by the feeding activity of the larvae. For this reason insect attack in buildings is often said to be caused by "wood worms" without consideration of the developmental cycle. Shortly before pupation, the larva creates a pupal chamber, an enlarged section of gallery.

The pupal stage is characterized by a stage of rest and metamorphosis which must be completed for the successful transition from larva to adult insect. Adults emerge from the pupae and reach their final size within a few minutes or hours after emergence. This transition leaves behind exit holes which are characteristic of different insect species.

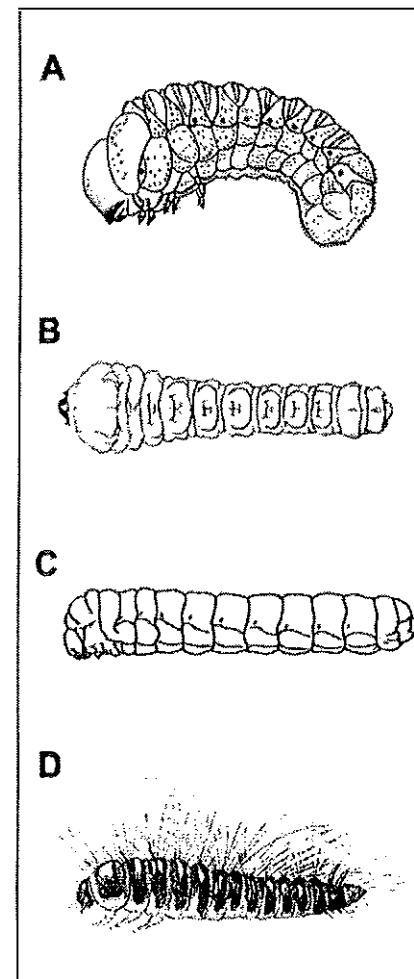


Fig. 5.3. Typical forms of insect larvae. A *Anobium punctatum*. B *Hylotrupes bajulus*. C Siricidae. D *Dermestes lardarius*. (A, C With permission from Dominik and Starzyk 1983; B with permission from Schmidt 1962; D after Zacher 1950)

For most wood-destroying insects, the larval stage occupies the major part of the generation period, whereas the egg and pupa stages last only a few weeks and the adult insect usually dies a short time after reproduction.

5.1.4 Physiology

The physiological development of the larvae of wood-destroying insects is essentially controlled by three factors, namely nutrients, wood moisture content and temperature. With respect to nutrients, the larval rate of development is controlled by the usually very low protein content of wood. The utilization of the abundantly available wood carbohydrates differs among insect

species. Some can metabolize only readily soluble sugars, while others depend on wood starches. Certain species are able to digest cellulose using their own enzymes. Many species have protozoans, bacteria, yeasts (fungi), or other microorganisms in their digestive systems which can also effect digestion of cellulose.

Some insects attack only hardwoods, others only softwoods, while a third group can attack both. Some species confine themselves to the bark, while others enter shallowly into wood only for the pupal stage. There are also differences in attack according to sapwood and heartwood, as well as earlywood and latewood. Some insects such as Scolytidae and Platypodidae (ambrosia beetles) depend on the presence of ambrosia fungi. Insects can also bring fungal spores, such as those of blue-stain fungi, into wood.

Insect species differ in their preference for wood depending on its moisture content (cf. Table 5.1). Species which attack freshly felled, green wood (m.c.>50%) are found exclusively in the forest or in log storage piles. The growth rate of larvae in air-dry wood depends on a moisture content level of not less than about 7%. Some types of insects start their development in wood stored under damp conditions and can conclude it after several years in air-dry material (e.g., wood wasp, bark borer).

Temperature greatly influences the life processes of insects. When the ambient temperature falls below certain levels or rises above others, larval activities such as feeding or movement will cease. Increasing temperatures generally are accompanied by greater activity up to an optimum level, the limits of which can differ considerably among species. Swarming of adult insects is determined to a certain degree by ambient temperatures. Some insects swarm in spring, others in summer, and even the temperatures during a given day may influence swarming behavior.

5.1.5

Wood-Destroying Insects

5.1.5.1

Coleoptera (Beetles)

Overview

Beetle morphology is characterized by front wings (elytra) which are highly chitinized and shaped into wing covers. The first of the three thorax segments usually takes the shape of a neck shield (pronotum) that extends over the head, and the biting jaws (mandibles) are equipped for chewing.

The most common wood-destroying beetles are found in the families Anobiidae (furniture beetles), Lyctidae (powder post beetles) and Cerambycidae (longhorn beetles). They have differing demands for nutrients (Table 5.2). The larvae of *Anobium punctatum* (common furniture beetle) are largely independent of nutrient composition, because their digestive system

Table 5.2. Nutrient requirements of the larvae of wood-destroying beetles. (Chemical compounds in order of importance)

Species	Chemical compounds
<i>Anobium punctatum</i>	Cellulose, protein (small quantities)
<i>Hylotrupes bajulus</i>	Protein, cellulose, hemicelluloses, vitamin B
<i>Lyctus brunneus</i>	Starch, protein, sugar, trace elements

Table 5.3. Wood-destroying beetles and their food sources

Species	Softwood	Hardwood	Other Characteristics
<i>Anobium punctatum</i>	X	X	
<i>Coelostethus pertinax</i>	X		Decayed wood
<i>Ptilinus pectinicornis</i>		X	Heartwood with small pores
<i>Xestobium rufovillosum</i>		X	Decayed oak wood
<i>Hylotrupes bajulus</i>	X		Sapwood
<i>Lyctus brunneus</i>		X	Sapwood

contains yeast cells and the symbiosis with the yeast makes it possible to digest the cellulose in wood. The presence of protein will promote growth of larvae, but it is not essential for survival. It is therefore incorrect to assume that heat treatment causing coagulation of proteins in wood will be sufficiently prophylactic against *Anobium punctatum* attack. In other beetles, such as *Xestobium rufovillosum* (death watch beetle), *Coelostethus pertinax* and *Priobium carpini* the yeast symbiosis is weaker, and wood which has already been attacked by wood-decay fungi is therefore preferred. The larvae of *Hylotrupes bajulus* (house longhorn beetle), unlike those of *Anobium punctatum*, do not have any symbionts and require protein for optimum development. For these larvae protein which has been altered by heat treatment or aging is nearly or totally indigestible. For this reason wood which is over 70 years old or which has been heat treated is only rarely attacked by *Hylotrupes bajulus*, or if attack does occur, the larvae are seriously retarded.

Lyctus brunneus (brown powder post beetle) requires wood which contains starch and protein, which is one reason why it does not attack pine, a species with very low starch content. Table 5.3 lists which woods are generally or preferentially attacked by certain insect pests, and this information can be of diagnostic value. *Coelostethus pertinax* and *Hylotrupes bajulus* are softwood pests, whereas *Anobium punctatum* attacks both softwoods and hardwoods. However, anobiid larvae develop more rapidly in hardwoods, especially in linden and hazelnut wood, than in softwoods (Unger 1995). *Ptilinus pectinicornis*, *Xestobium rufovillosum* and *Lyctus brunneus* are found in hardwoods.

Another important factor is the structure of the wood surface. Rough, cracked surfaces with fungal damage invite the females of wood-destroying insects to lay their eggs more readily than smooth, intact surfaces. Only the females of the Lyctidae will bore into wood surfaces to lay eggs.

Relative humidity and temperature are extremely important factors in the development of wood-destroying insects. Table 5.4 lists moisture requirements of the larvae of some wood-destroying beetles. For *Anobium punctatum* a wood moisture content of 28–30% is optimum, but when the moisture content reaches 47–50% the larvae will cease growth. At relative humidity values consistently below 60%, wood moisture content will equilibrate to about 11% or less, and growth of anobiid larvae will slow greatly. The larvae of *Hylotrupes bajulus* require a wood moisture content above the fiber saturation point in the range of 30–40% for optimal development, and can tolerate higher values up to 65%. A wood moisture content as low as 14–16% is sufficient for optimal development of *Lyctus brunneus* larvae, which makes dry hardwoods, including tropical woods, with high starch contents (limba, abachi) especially susceptible to attack. The larvae of the beetles discussed here belong to the dry-wood pests, which means that they can survive drying out of the wood for a considerable length of time. The ability to survive starvation is particularly strong in the larvae of *Hylotrupes bajulus*.

The influence of temperature on the development of larvae is very pronounced (Table 5.5). Anobiid larvae grow optimally between 21 and 24 °C, but do not tolerate temperatures above 29 °C very well. They are more heat

Table 5.4. Moisture requirements of the larvae of some wood-destroying beetles

Species	Wood moisture content [%]			Relative humidity [%]		
	Min.	Optimum	Max.	Min.	Optimum	Max.
<i>Anobium punctatum</i>	10–12	28–30	47–50	~60	~90	>95
<i>Hylotrupes bajulus</i>	9–10	30–40	65–80	~50	~90	>95
<i>Lyctus brunneus</i>	7–8	14–16	23	~30	>80	~90

Table 5.5. Effect of temperature on development and killing of the larvae of some wood-destroying beetles

Species	Temperature [°C]			
	Min.	Optimum	Max.	Lethal
<i>Anobium punctatum</i>	12	21–24	29	47–50
<i>Hylotrupes bajulus</i>	16–19	28–30	35	55–57
<i>Lyctus brunneus</i>	18	26–27	30	49–65

sensitive than *Hylotrupes bajulus* larvae and are killed more readily by heat treatment. Below 12 °C the activity of *Anobium punctatum* larvae decreases greatly. *Hylotrupes bajulus* has a strong preference for warm conditions and thus seeks out the timbers of roofs exposed to sunshine. Optimum larval development takes place at 28–30°C, and even at 35°C larvae have gained mass in laboratory experiments. At low temperatures, such as –10 °C, the larvae of *Hylotrupes bajulus* hibernate and will not feed until the temperature rises again. *Lyctus brunneus* larvae reach their greatest activity at 26–27°C, but will grow in the range 18–30°C according to laboratory experiments. Because of these differing temperature requirements, various kinds of beetles are found in different locations. Damage caused by *Hylotrupes bajulus* is often greatest in roof framing, whereas *Anobium punctatum* prefers cooler surroundings and is often found in basements or on the ground floor of buildings.

Exact identification of individual insect species requires examination of adults or larvae (Florian 1997). However, these are often not available, requiring recourse to using external and internal characteristics of damaged wood (Fig. 5.4). Shape, size, and condition of exit holes on the wood surface and the location and course of galleries often make it possible to limit the number of species which may have been responsible. Furthermore, chew marks on the gallery walls and the color, shape, and size of fecal pellets can be indicative of the kind of beetle involved. The choice of certain wood species (Table 5.3) already indicates which are likely pests.

Species

Anobiidae (Furniture beetles)

The adult beetles of the Anobiidae family are only a few millimeters in size and brown in color. A typical characteristic is a neck shield which covers the head like a hood. When disturbed, the beetles of many species play dead by lying motionless, often for long periods, with retracted legs. The circular exit holes have a diameter of 1–4 mm. The anobiid larvae measure only a few millimeters in length, are white to yellowish, are grub-shaped and have three pairs of legs (cf. Fig. 5.3A). On their back, the front half of the abdominal rings is studded with many small spines (Langendorf 1988). Formerly, the name “death watch beetle” was applied to the Anobiidae in general, but according to more recent findings this is not correct, since *Anobium punctatum*, for instance, does not make tapping noises when searching for a mate. Only *Xestobium rufovillosum* makes such noises, and is thus considered the true “death watch beetle”. Individual anobiid species exhibit significant differences in habit (Fig. 5.5), by which they can be identified (Unger and Unger 1986). Not all Anobiidae are wood-destroying insects; the member species *Stegobium paniceum* (drugstore beetle) and *Lasioderma serricorne* (cigarette beetle), for instance, are pests of stored materials.

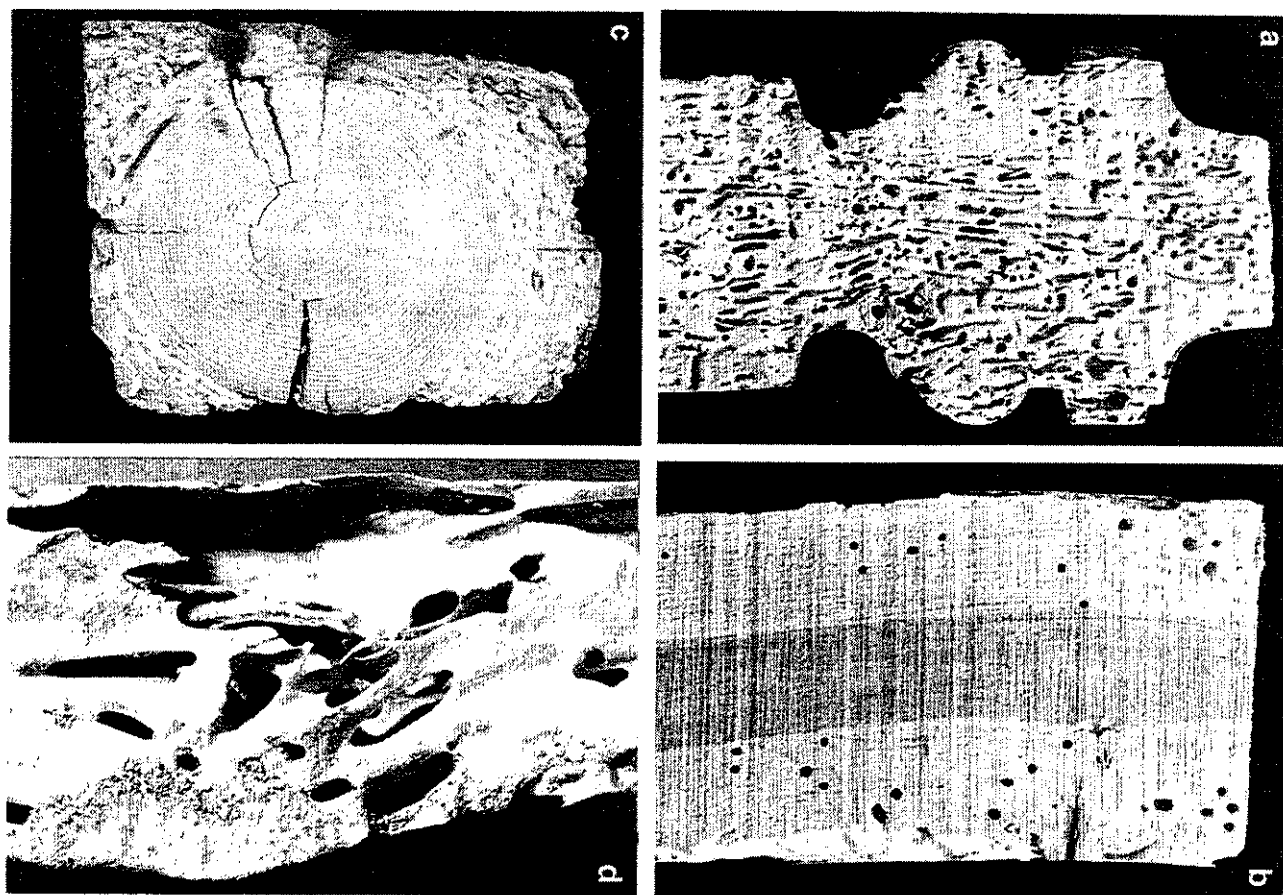


Fig. 5.4. Damage characteristics of wood-destroying insects. a *Anobium punctatum*, b *Lyctus brunneus*, c *Hyloterpes bojardi*, d Isoptera. (a, b and d Courtesy of R. Pausewein)

The Anobiidae family

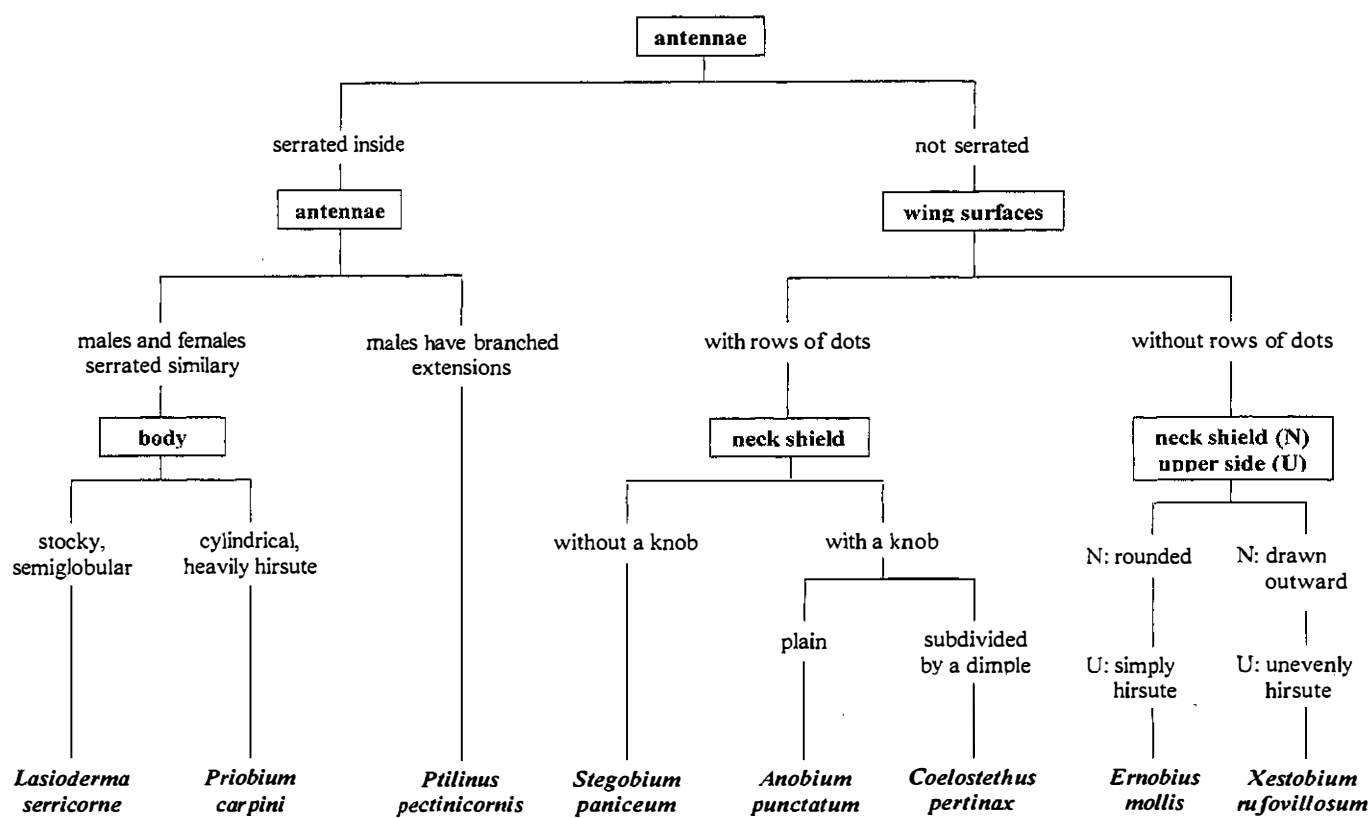


Fig. 5.5. Identification key for the most important species of the Anobiidae family

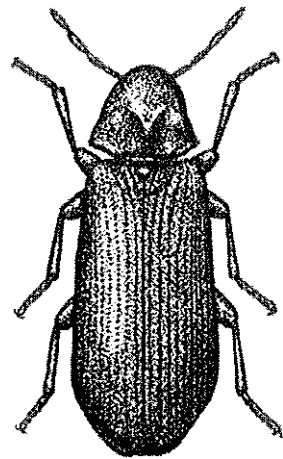


Fig. 5.6. Common furniture beetle, *Anobium punctatum*.
(With permission from Schmidt 1962)

Anobium punctatum (Degeer) (Common Furniture Beetle; Fig. 5.6)

Synonym. *Anobium striatum* Ol.

Distribution. Distributed widely in Europe, especially in England and Ireland, but has also been introduced into North America, South Africa, South Australia, and New Zealand. It can coexist remarkably well with the human inhabitants of buildings.

Damage Characteristics. Exit holes are circular and 1–2 mm in diameter. In hardwoods, galleries are irregular and 1–2 mm in diameter, and are partially filled with crumbly frass and cigar-shaped fecal pellets. The pellets are drawn to a fine point either on the thinner end or on both ends (Sutter 1986). In hardwoods with colored heartwood the galleries extend primarily through the sapwood. In softwoods the weaker earlywood is consumed preferentially (Fig. 5.4a), leaving lamellae of latewood untouched. Feeding proceeds almost to the wood surface, so that in cases of heavy infestation only a thin surface layer of wood remains.

Distinguishing Characteristics. Eggs are white, glassy, lemon-shaped, and about 0.3 mm long. Larvae are the color of ivory, grub-shaped, with thickened thorax (Fig. 5.3A), tapered abdomen, three pairs of five-jointed legs, and are up to 6 mm long. The larvae can digest wood cellulose with the assistance of symbiont yeast in the digestive system (Vité 1952). Therefore they can feed on very old wood, although at a reduced growth rate. According to Serdjukova and Toskina (1995), hemicelluloses appear to constitute an important part of the larva's food. Adults are dark brown with rounded to cylindrical bodies. As seen from the side, a knobbed neck shield extends over the head like a hood. The antennae are finely jointed (11 segments) without bends, with the three distal segments somewhat elongated. The wing surfaces bear closely spaced rows of dots (stria). Females are somewhat larger than males, and can be distinguished by the ventral side of the last abdominal segment. In males this

segment has a clearly visible depression, and the anal segment is semicircular. Body length is 3–5 mm. Dead beetles lying on the ground look like mouse droppings. During swarming, the beetles may be found on window sills. In the so-called tail position the female emits a sex hormone – stegobinon – which may be used in insect traps as an attractant to indicate the presence of males (cf. Sect. 5.1.8).

Development. The beetles, which are excellent flyers, swarm from April to August, peaking in May or June. Adults do not feed, and live for 1–3 weeks. Females will lay 20–40 eggs into fine cracks in wood, onto roughly sawn wood surfaces, or into old galleries. After 2–4 weeks the larvae emerge and will immediately bore into the wood. After 2 years (in oak sapwood) or 4–8 years (in softwoods) the larvae pupate in the spring inside a pupal chamber close to the wood surface. Following 4–6 weeks of pupal rest, the adult insect emerges, bores through the remaining thin layer of wood and reaches the outside (Cymorek 1984). Optimal conditions for larval development are a temperature of 21–24°C and a wood moisture content of 28–30%. Occasional moistening of the wood, as may occur with poor subfloor ventilation, promotes larval development, whereas persistent dryness makes it nearly impossible.

Occurrence. The common furniture beetle attacks nearly all of the important hardwoods and softwoods of Europe. However, some non-European species such as eucalyptus (*Eucalyptus* spp.; Creffield 1996), and ilomba (*Pycnanthus angolensis*), abachi (*Triplochiton scleroxylon*) and limba (*Terminalia superba*; Cymorek 1984) are not attacked by *Anobium punctatum*. Frequently attacked objects are furniture, sculptures, picture frames, panel paintings, altars, organ housings, church pews, flooring, stairs and banisters, as well as structural timbers.

Special Characteristics. *Anobium punctatum* (1) prefers seasoned, even very old wood since direct utilization of cellulose is possible (Toskina 1987), (2) tends to be location-bound, i.e., the eggs are laid again and again into wood already attacked, so that the inside of some objects consists almost entirely of frass, (3) can cause a more serious loss of strength in structural timbers than an attack by powder post beetles, (4) can be readily distinguished from *Stegobium paniceum*, which is a pest of stored materials found in museums, because it has a round neck shield (cf. Fig. 5.5), and (5) causes great difficulty in the determination of an active attack and subsequent remedial treatments because of its hidden life cycle.

Ernobius mollis (L.) (Bark Borer; Fig. 5.7)

Synonym. *Anobium mollis* L.

Distribution. Europe, North America, South Africa, Australia, New Zealand.

Damage Characteristics. Exit holes are circular and about 2 mm in diameter. Galleries are passages about 1 mm deep between the bark and the outermost sapwood zone. The fecal pellets are lens-shaped with either wood-colored or

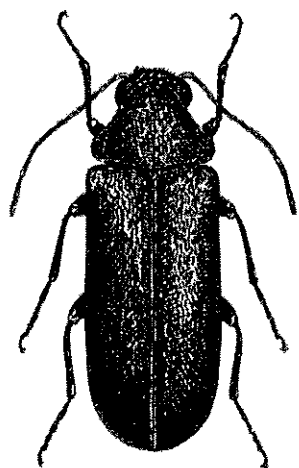


Fig. 5.7. Bark borer, *Ernobius mollis*. (After Lepesme 1944)

brown particles depending on whether the larvae had been feeding in wood or in bark. The damage is superficial and the strength of the wood remains virtually unchanged (Vité 1952; Mori 1975; Unger and Unger 1986).

Distinguishing Characteristics. Eggs have not been investigated in detail. Larvae are 8 mm long, yellowish, with slightly reddish hairs (seta). In contrast to the larvae of *Anobium punctatum*, the 9th ring of the abdomen has small spines. A darkly colored portion of the forehead (fronts) is almost twice as broad as it is long. Adults are rust red with fine, flatly placed gray hairs, and their wing surfaces are without rows of dots. The neck shield is not knobbed, and its back corners are rounded (Fig. 5.5). The small shields are covered with whitish, felt-like hairs. The chitin skeleton is not as hard as in other Anobiidae. The body is 4–5 mm long.

Development. Swarming usually takes place from April to June in the Northern Hemisphere. The female lays eggs only on softwood bark which is left on construction timber. The larvae will bore in and live on the innermost bark and the outermost sapwood zones. Their rate of development depends on the starch content of the wood (Richardson 1993). Larval development usually takes 1 year.

Occurrence. The bark borer lives in stored wood or wood in buildings which contains bark. Living trees or green timber are not attacked. It is often found in sawmills in lumber with bark edges. By using such material in building construction, noticeable damage can occur when the adult beetles emerge by way of exit holes bored through wainscoting or interior plywood paneling.

Special Characteristics. The bark borer can live in company with *Callidium violaceum*. If the bark is removed further attacks will not take place, and infestations will not spread in buildings.

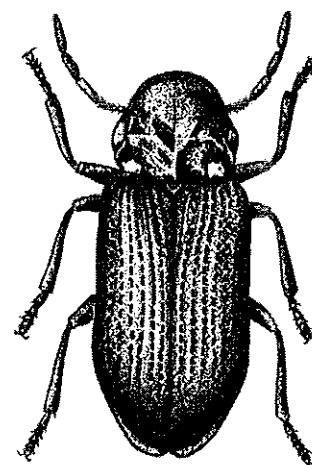


Fig. 5.8. *Coelostethus pertinax*. (With permission from Dominik and Starzyk 1983)

Coelostethus pertinax (L.) (Fig. 5.8)

Synonyms. *Anobium pertinax* (L.), *Dendrobium pertinax* L.

Distribution. Europe, especially Scandinavia, scattered in West and East Siberia, paleoarctic.

Damage Characteristics. Circular exit holes about 2–3 mm in diameter, often in pine sapwood with fungal decay. Galleries of about 4 mm diameter are wider than those of *Anobium punctatum* and are mainly in the earlywood; the hard latewood remains in the shape of lamellae. The frass is darker than that of *Anobium punctatum* because of the decay, and the fecal pellets are trough-shaped.

Distinguishing Characteristics. Eggs have not been investigated in detail. Larvae are somewhat larger and at the head end somewhat thicker than those of *Anobium punctatum*, and the body is more hairy. Adults at 4.5–6 mm in length are longer than *Anobium punctatum*. The wing surfaces have rows of dots, and the neck shield bears a dimpled knob which looks like a Y (cf. Fig. 5.5). The adult is black-brown and as a special characteristic has yellowish-gray, round hair spots at the back corners of the neck shield.

Development. The beetles swarm during the evening hours of April and May. Six to eight eggs are laid singly onto the wood. The development of the larvae takes 2 or more years. The adults emerge in late autumn after a few weeks of pupal rest, hibernate in the pupal chambers made up of decayed wood particles and bore to the outside only in the following spring (König 1957).

Occurrence. Prefers softwood already damaged by decay fungi, and is found in damp or poorly ventilated ground floors of buildings, in half-timbered structures, and in historic, sacred and secular buildings.

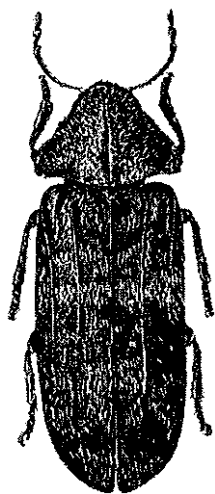


Fig.5.9. Death watch beetle, *Xestobium rufovillosum*, (After Lepesme 1944)

Special Characteristics. Following remedial treatments of the decay and subsequent maintenance of dry conditions in the wood members, the attack by *Coelostethus pertinax* will soon cease.

***Xestobium rufovillosum* (Degeer) (Death Watch Beetle; Fig. 5.9)**

Distribution. Asia Minor, Europe, widespread in southern England, the Netherlands, and Belgium, and rare in mountainous regions.

Damage Characteristics. Exit holes are circular and 2–4 mm in diameter, and fecal pellets are large, brown, and lens-shaped. In oak usually the earlywood is destroyed while the latewood remains. A special characteristic is a brown discoloration of the wood, which originates from simultaneous attack by decay fungi.

Distinguishing Characteristics. Eggs are white, lemon-shaped and, at 0.4 mm, remarkably small. Larvae are up to 11 mm long with golden-yellow hairs. Adults, with their body length of 4.5–9 mm are the largest of the anobiid species. On the surface they are dark brown with irregularly distributed blotches of yellowish-gray hair. The wing surfaces are without rows of dots, and the back corners of the neck shield are significantly drawn outward (cf. Fig. 5.5).

Development. The adult beetles swarm in May, June, and July at ambient temperatures greater than 17°C (Belmain et al. 1999). Females lay 50–100 eggs. Development of the larvae takes 2–10 years. Young larvae appear to be more dependent on decayed wood than are older ones. Their optimum development occurs at 22–25°C and 80% relative humidity. Pupal rest begins in late summer. Adults emerge a few weeks later, hibernate inside the wood and

bore to the outside in the following spring. They spread by flight, the main activity taking place in the afternoon or evening hours.

Occurrence. *Xestobium rufovillosum* is an important pest mainly in damp, decaying structural timber in half-timbered buildings, castles, and churches, and of lesser importance in carved items and sculptures. It is found in oak and other hardwoods, less often in softwoods.

Special Characteristics. This pest often is found together with the widespread decay fungus *Donkioporia expansa*. If the wood is allowed to dry out, the insect infestation will diminish. Males and females communicate by noticeably loud tapping noises produced by hitting the forehead on the gallery floor. These noises explain the name “death watch beetle”. They occur in series of 8–11 taps over a period of 2 s, which is utilized in monitoring these insects (cf. Sect. 5.1.8). Trapping and monitoring experiments in England have shown that the beetles are attracted to natural light, especially on white-colored traps, and to UV light (Belmain et al. 1999).

***Ptilinus pectinicornis* (L.) (Fig. 5.10)**

Distribution. Europe except Sweden and Finland, Asia Minor, Mexico and South America.

Damage Characteristics. Galleries are circular in cross section and extend in the fiber direction, especially in beech. The frass is very fine, and is compacted into solid wicks about 2 mm wide. Both the wicks and the gallery walls bear fine stripes extending lengthwise. The fecal pellets taper to a point at one end and are blunt at the other, without any extended point. Exit holes are 1–1.5 mm in diameter. The interior of wood objects can become completely destroyed by this pest.

Distinguishing Characteristics. Eggs are extremely thin, about 0.075 mm wide and 1.5 mm long. Larvae change their shape from the thread-like egg larvae to their Anobiidae grub-shape in four stages. They are a golden yellow, covered with fine bristles, and about 7 mm long. Adults are medium to black-

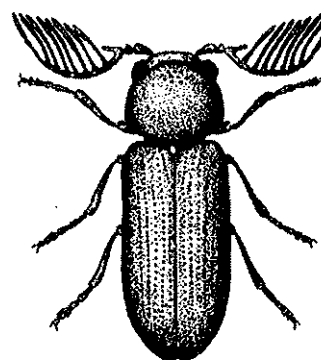


Fig. 5.10. *Ptilinus pectinicornis*. (With permission from Dominik and Starzyk 1983)

brown, with hairs shiny like silk, a cylindrical body 3–5.5mm long, a spherical neck shield, and no rows of dots on the wings. Females have serrated antennae, and those of the males have branched extensions (cf. Fig. 5.5).

Development. Swarming takes place from May to July in the Northern Hemisphere. Females will bore into wood perpendicular to the fiber direction in order to lay eggs. They will use existing exit holes for this, including those of *Anobium punctatum*. The eggs are laid into the lumina of vessel elements. The females then die and their body remains as a plug. Development takes 1, 2, or more years.

Occurrence. *Ptilinus pectinicornis* is an important pest in dry hardwoods with small pores (beech, maple, poplar, willow), including heartwood, whereas softwoods are largely immune. It attacks furniture, carved items, panel paintings, and wooden book covers, and is also found in lumber yards.

Special Characteristic. Can occur in a community with *Anobium punctatum*.

Other Wood-Destroying Species of the Anobiidae Family (Cymorek 1984; Unger 1990)

Oligomerus ptilinoides (Wollaston); *Nicobium castaneum* (Olivier);
Nicobium hirtum Illiger

Distribution. Southern and southeastern Europe in Atlantic and Mediterranean regions, increasingly being introduced into central Europe. *Nicobium hirtum* has been found in temples in Japan.

Damage Characteristics. Galleries extend primarily in the fiber direction, and the exit holes are 1.3–3 mm in diameter. The fecal pellets are the color of wood or a mixture of brown and glassy, and are shaped like shelled peanuts. Typical for the two *Nicobium* species are pupa cocoons made of fecal pellets which are placed close to the exit hole.

Distinguishing Characteristics. The beetles have cylindrical bodies 3 to 6 mm long, with fine hairs. *Nicobium hirtum* has dark spots on the wing surface, which often merge into serrated bands.

Occurrence. The beetles are found in hardwoods and softwoods. Attacks have been documented in wood shelving and wall paneling in libraries and archives, in furniture, and in panel paintings.

Lyctidae (Powder Post Beetles)

The lyctid beetles, which are brown and just a few millimeters long, form a family composed of about sixty species but with worldwide distribution. The Lyctidae are closely related to the Bostrychidae family, the auger beetles. Both are hardwood pests which have been introduced more and more into Europe and North America by way of increased utilization of tropical woods, causing

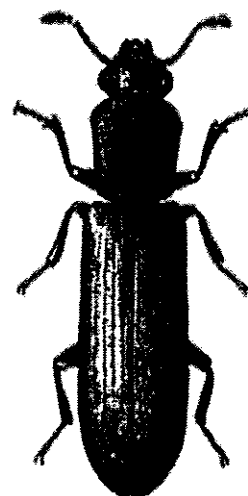


Fig. 5.11. Brown powder post beetle, *Lyctus brunneus*. (With permission from Dominik and Starzyk 1983)

damage in housing, carpentry and cabinet shops, and in museums. Only the larvae will live inside the wood, and they destroy only sapwood, leaving the heartwood untouched. As dry-wood pests with very low moisture requirements and a very short generation period of 3–12 months they cause great damage.

Lyctus brunneus (Steph.) (Brown Powder Post Beetle; Fig. 5.11)

Distribution. This is a cosmopolitan species and occurs especially in the tropics but has been introduced and spread in Europe, North America, Australia, and Japan.

Damage Characteristics. Exit holes are circular and 1–1.5 mm in diameter. The galleries are 1–2 mm wide, extending primarily in the fiber direction, but exclusively in the sapwood of hardwoods (Fig. 5.4b). The galleries are similar to those of *Anobium punctatum*, but the frass differs in that it is an extremely fine and light colored powder which does not form typical fecal pellets. Damage is usually great because the sapwood is completely pulverized, leaving only a thin surface layer, hence the name powder post beetle. In its initial stages an infestation is often not discovered.

Distinguishing Characteristics. Eggs are elongated and stemmed. Larvae are whitish, grub-shaped, and up to 6 mm long. Unlike *Anobium punctatum*, they have a brownish, large breathing hole in the 8th abdominal segment, and their legs have three joints. Adults are active at night. They are reddish brown to black brown, with stick-like, slender bodies 2.5–8 mm long. The neck shield is trapezoidal, and the wing surfaces without rows of dots. The 11-jointed antennae end in two-jointed clubs.

Development. Swarming takes place in spring and summer. Females will lay about 70–75 eggs into old exit holes or open vessels (pores) either singly or in clusters of up to four. New infestation will take place only in hardwoods with sufficiently large vessel diameters. However, females can also make so-called bore marks perpendicular to the fiber direction. Under optimum conditions the larval development period is very short at 4 months. Larvae live on sugar and starch, but also need small amounts of protein. Sapwood with a starch content of less than 1.5% is reportedly largely immune to the powder post beetle. The larvae contain symbiotic microorganisms in their digestive system which are thought to provide vitamins. Grown larvae pupate close to the wood surface in oval pupal chambers. Adults leave by way of small exit holes and are very active in flight. Being a typical dry-wood insect, the powder post beetle requires a low wood moisture content with an optimum of 14–16%; temperature optimum is 26–27°C (cf. Table 5.4).

Occurrence. The beetles attack the sapwood of temperate hardwoods such as oak, ash, elm; tropical woods such as abachi and limba; and bamboo. Beech and softwoods reportedly are immune. Powder post beetles are often found in parquet flooring, veneer, furniture, and wall paneling, but also in pallets and shipping crates. They get introduced into buildings and museums by way of ethnographic objects and carpentry work.

Other Species of Lyctidae

Other species of Lyctidae found in museums and collections include: *Minthea rugicollis* (Walker), *Lyctus africanus* Lesne, *Lyctus linearis* (Goeze), and *Lyctus planicollis* Leconte (Weidner 1993). *Lyctus cavicollis* Leconte is native to North America but has been introduced into Germany by way of imported hardwood lumber beginning two decades ago, and has become naturalized (Geis 1996).

Bostrychidae (Auger Beetles)

Synonyms. Bostrychid powder post beetles, shothole borers (South Africa).

Distribution. In the tropical regions of Africa, South Asia, and the Americas they are frequent and dangerous pests in lumber and structural timbers. Some species are often introduced into temperate zones in shipping crates, lumber, and ethnographic objects.

Damage Characteristics. Entrance bore holes of the beetles are circular. The larval galleries are also circular, and extend ring-shaped under the bark and in the sapwood of hardwoods. The galleries are closely packed with fine, light-colored frass so that attacks in their early stages are often overlooked. Exit holes are 2.5–12 mm in diameter, depending on species.

Distinguishing Characteristics. Eggs have not yet been investigated. Larvae are whitish, grub-like, with four-jointed legs. Adults are dark brown to black,

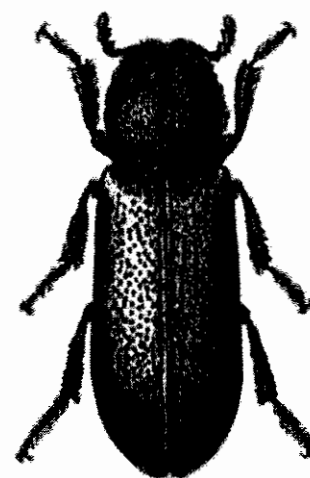


Fig. 5.12. *Bostrychus capucinus*. (With permission from Dominik and Starzyk 1983)

small to medium in size with a body length of 3–30 mm depending on species. The neck shield covers the head like a hood, and the distal three joints of the antennae are thickened.

Development. In contrast to other wood-destroying insects, it is both the larvae and the adults of the Bostrychidae family which destroy wood. Males and females will bore into wood where breeding takes place in a circular breeding gallery which is free of frass. Larvae bore circular galleries in the sapwood. Both larvae and adults harbor symbiotic microorganisms. Larvae require mostly starch for development. Pupation takes place in destroyed material close to the wood surface. Depending on the species, auger beetles will attack damp as well as dry wood, and thus belong to the green-wood and the dry-wood insects.

Occurrence. Especially in dense hardwoods; heartwood of hardwoods and softwoods are avoided. They are pests in cooperage, parquet flooring, veneer, utensils and souvenirs.

Special Characteristics. Often occurs in community with Lyctidae. In the tropics auger beetles along with termites belong to the most feared wood-destroying pests.

European Species. *Bostrychus capucinus* (L.) (Fig. 5.12).

Tropical Species. *Apate monachus* (Fabr.), *Heterobostrychus brunneus* (Murr.), *Dinoderus minutus* (Fabr.).

Cerambycidae (Longhorn Beetles)

The Cerambycidae differ from other wood-destroying beetles by their body size of 10–30 mm and their prominent, long and curved antennae. Most of the species are green-wood insects, whose damage is often found and occasion-

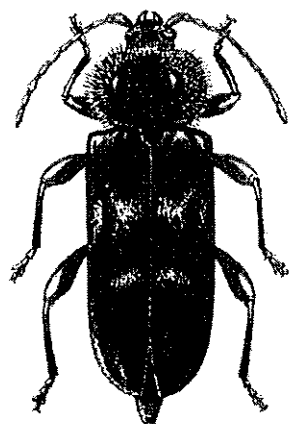


Fig. 5.13. House longhorn beetle, *Hylotrupes bajulus*. (With permission from Schmidt 1962)

ally misinterpreted in dried wood. Dry wood in use is attacked mainly by the house longhorn beetle (Kollmann 1955).

Hylotrupes bajulus (L.) (House Longhorn Beetle; Fig. 5.13)

Synonyms. Old house borer (USA), European house borer.

Distribution. Temperate zones of Europe (but not in Ireland and to only a limited extent in Norway, Finland, and England), Asia Minor, Africa and the Americas.

Damage Characteristics. Exit holes are irregular and oval (5–10 × 3–5mm). The oval galleries extend close to the wood surface, leaving only a paper-thin layer of wood. In areas rich in nutrients, galleries are locally wider. Larvae feed primarily in the sapwood of softwoods (cf. Fig. 5.4c), especially in the earlywood. The frass is uniformly yellowish, and the fecal pellets are typically cylindrical. Gallery walls are often finely grooved. During the summer months, rasping feeding noises of the larvae can be heard.

Distinguishing Characteristics. Eggs are shiny white and 2 mm long. Larvae are ivory colored, and on their heads are strong, dark biting jaws and three pairs of pointed eyes. The body is 15–30mm long and consists of clearly visible, ring-shaped segments with checkered creeping welts, and little hair covering (cf. Fig. 5.3B). The first three segments of the thorax each have a pair of leg stumps. Adults are dark to black-brown, inconspicuous, with whitish-gray hairs and a flat body. Wing surfaces are shiny with dull hairs and light, V-shaped cross ties which are made up of very small hairs. Antennae are 11-jointed and curved, and the neck shield has two shiny black spots. Females have an ovipositor (cf. Fig. 5.13) which they can extend up to 25mm. Body length of females is 10–25mm and of males, 8–16 mm.

Development (cf. Fig. 5.2). Swarming takes place from June to August during hot midday hours. Females use the egg duct to lay 200–400 eggs, divided into several clusters, into checks and splits in the wood. Egg larvae emerge after 10–20 days and immediately bore into the wood. Under favorable conditions, i.e., a wood moisture content in the vicinity of the fiber saturation point and ambient temperature of 24–30 °C, development takes 3 years; otherwise up to 10 years may be required. During this time, the destruction of wood inside a structural member can be very extensive. The rate of development of the larvae depends greatly on the protein content of the wood (Becker 1963), but holocellulose is also utilized. A certain amount of vitamin B is also necessary for larval viability. Larvae are able to survive poor conditions through periods of fasting lasting several months. These characteristics – modest food requirements and the ability to live and to propagate in dry wood – are responsible for the success of this species and its harmfulness. *Hylotrupes bajulus* is a typical representative of dry-wood insects.

After an extended period of significant temperature decrease, pupation takes place in pupal chambers which are closed off with rough shavings. Before that the larvae bore exit holes which are superficially closed. The beetles leave the wood and disperse through these when the temperature reaches ≥25 °C.

Occurrence. Major pest in load-bearing structural members of high-rise buildings, interior trim, painted softwood siding, half-timbered buildings, fence posts, utility poles, but rarely in furniture. Hardwoods and softwood heartwood are unsuitable food sources.

Special Characteristics. The danger of infestation is greater in newer, up to about 50-year-old buildings than in older structures. However, this is not a general rule since active infestations by *Hylotrupes bajulus* have been confirmed in very old secular and religious structures (Cymorek 1984; Grosser 1985). Newer structural timbers with a very low proportion of heartwood are more at risk than older ones with higher proportions of heartwood. The larvae also attack various plastics such as high and low density poly(vinyl chloride) (PVC), polyethylene, as well as rigid foams of polyurethane and polystyrene (cf. Chap. 11).

Males of the house longhorn beetle emerge slightly before the females and attract the latter with certain pheromones (Noldt et al. 1995). Host selection by insects suggests that males rather than females are most likely to select new breeding sites (Plarre and Hertel 2000).

5.1.5.2

Isoptera (Termites)

Overview

The termites form an order of insects which is closely related to that of the cockroaches (Blattidae). They undergo an incomplete transformation

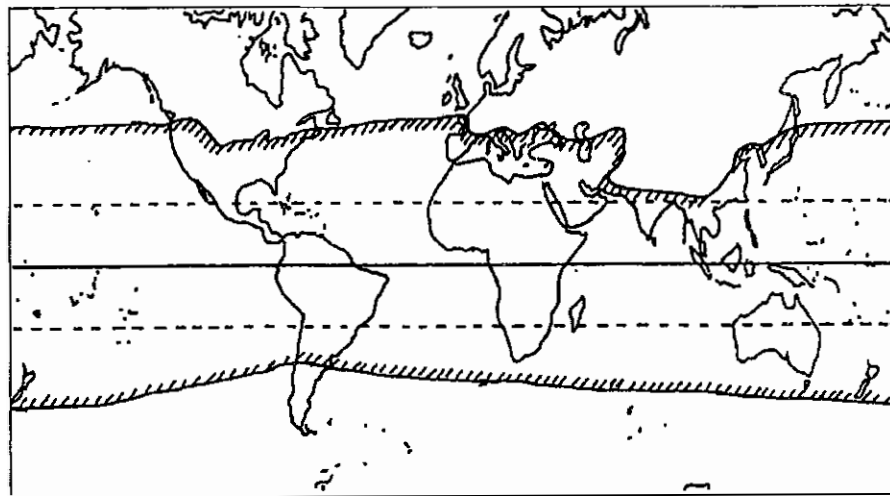


Fig. 5.14. Map of termite distribution. (After Richardson 1993)

(hemimetabolism). Although they are often referred to as white ants because of their color, they are not ants but there are certain parallels in their habit. Termites are social insects forming colonies, and often exhibit marked polymorphism (caste formation).

Termites live mainly in tropical and subtropical regions. They require warmth and moisture and therefore prefer a temperature of 26–32°C and a relative humidity of 70–90%. Accordingly, their natural distribution is mainly confined to regions south of the 10°C yearly isotherm (Fig. 5.14). Outside of the tropics, the number of species decreases sharply, and in Europe and North America they can be found mainly in the warmer regions.

More than 2000 species of termites are known, and of these about 30 species are of economic significance with regard to damage to wood structures. The number of individuals in a termite colony can range from 1000–2 million, depending on species. The average body length of these small to medium-sized insects is 10 mm. Since their surface is only weakly chitinized, termites avoid light and, except for the winged reproductives, will remain hidden.

The main food source of termites is plants, and many species specialize in wood. In the more primitive termites (Rhinotermitidae) wood digestion is supported by protozoan intestinal symbionts (polymastiginas) which are mostly lost during skin sloughing and are replaced by feeding on feces (trophallaxis). In the higher termites (Termitidae) these symbionts are absent, and nutrition is obtained through association with cultivated fungi.

The nature and composition of termite colonies are complex. They are arranged and controlled primarily by the reproductives in an oral and anal feeding system by way of nutrient exchange (trophallaxis) and hormonal influences. A colony consists of three great castes and developmental stages, namely fertile reproductives and infertile soldiers and workers (Fig. 5.15).

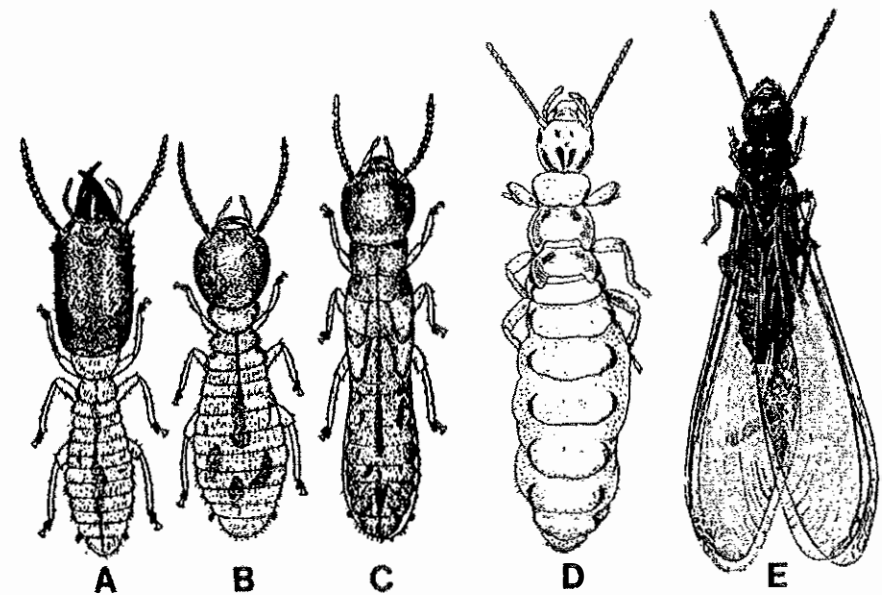


Fig. 5.15. Castes and development stages of termites of the genus *Reticulitermes*. A Soldier; B worker; C nymph; D secondary reproductive; E primary reproductive. (A, B, C With permission from Schmidt 1962; D, E after Cymorek 1984)

The task of the reproductives is to found new colonies. Male and female reproductives have two equally sized pairs of wings (hence the name Isoptera), complex eyes, and are heavily pigmented. They will swarm, mate, and then discard their wings. The king and queen remain together continuously after establishment of the nest. In some species the abdomen of the queen is immensely swollen (physogastry) because of the great development of the ovaries. A queen may produce thousands of eggs each day, and the manner of feeding after they hatch influences their ultimate differentiation into caste forms. If necessary, secondary reproductives come into being, but they will have stubby wings or none at all. Both primary and secondary reproductives (winged or wingless adults) may occur in each colony.

Workers and soldiers have neither wings nor eyes, and their male or female sexual organs are atrophied. The unpigmented workers (thus "white ants") ensure the feeding of all individuals in the colony, and take care of the brood and of nest building. Some species lack workers, which are then replaced by old larvae (pseudergates) which will never reach the adult stage. Soldiers protect the colony against enemy intrusion. Their large, usually sclerotized heads are equipped with defensive organs – pincer-like mandibles (mandible soldiers) or a tubular extension (gland soldiers) – so that enemies may be bitten or paralyzed with secretions. In addition to these castes there are numerous developmental stages such as eggs, larvae without wings, nymphs with wing pads, and pre-soldiers.

Termites destroy both softwoods and hardwoods, but they prefer the lower-density earlywood so that lamellae of latewood zones remain. Not every species of wood will be attacked equally, some species having a natural resistance to termites. Besides wood, termites can also attack plastics and other organic construction materials, so that in their own regions they are one of the most dangerous pests of wood and other materials. Attacks by termites are often discovered too late, because they will leave the outer wood surface intact while destroying the interior completely. They will attack all types of wooden objects including complete wooden buildings.

Acquisition of art and ethnographic objects from countries with termite populations can lead to the introduction of the pests into temperate zones of Europe and North America. If they remain undiscovered, they may survive under favorable conditions. Therefore it is advisable to subject new acquisitions to quarantine before incorporating them into the collection in order to avoid subsequent damage.

Species

Systematically, termites are divided into six families: Mastotermitidae, Termitidae, Hodotermitidae, Termitidae, Kalotermitidae, and Rhinotermitidae. Identification is difficult owing to the large number of species. In order to apply suitable protective and control methods, knowledge of occurrence and habit are very important (Richardson 1993; Creffield 1996). Termites are classified into tree-dwelling, damp-wood, dry-wood, and subterranean termites based on their habit. In the conservation of buildings and monuments and in museums the dry-wood termites and the subterranean termites are of principal significance.

Dry-wood termites

The family Kalotermitidae belongs to the dry-wood termites. Important genera are *Cryptotermes* which is found in most tropical countries, and *Kaloterme*s which is distributed through southern Europe and New Zealand. Winged reproductives of the dry-wood termites attack wood that does not have any direct connection with the earth and establish their relatively small colonies there. They are able to attack wood of low moisture content and are therefore also called "powder post termites." Dry-wood termites bore channels with clean and smooth walls into wood in many directions. Wooden objects can be severely damaged before the attack is noticed, because they will leave a thin surface layer of wood intact. The channels are connected by narrow tunnels which contain fecal pellets of a shape resembling poppy seeds. The discovery of masses of fecal pellets in the wood is an important diagnostic feature of dry-wood termite attack (Pinniger 1990).

*Kaloterme*s *flavicollis* (Fabricius)

Distribution. Mediterranean regions (Spain, southern France, Italy, the Balkans), coastal regions of Asia Minor and North Africa, and New Zealand.

This species has become known in Venice through damage to palaces, libraries, churches, wooden bridges, and mooring poles.

Damage Characteristics. In attacked objects only thin surface layers remain intact. Hexagonal, wood-colored or glassy-brown fecal particles are characteristic for the species. Galleries are seldom constructed, but the species often lives in closed feeding chambers.

Distinguishing Characteristics. Workers (pseudergates) have a body length of 4–7 mm. Soldiers have a neck shield about as wide as the head capsule, and the body is 7–9 mm long. Reproductives are about 11 mm long; the abdomen of the queen is not enlarged.

Development. In captivity eggs are not laid until 3 months after mating. The larvae do not develop completely into workers and are termed pseudergates. There are only few soldiers. Pseudergates can be formed into primary and secondary reproductives. Swarming takes place from July to October in the Northern Hemisphere. This species forms small colonies of 1000–1500 individuals.

Occurrence. The termites live in dry wood, but also in damp wood already damaged by decay.

Cryptotermes brevis (Walker)

This species is the most destructive of the dry-wood termites on earth. It occupies a special niche through its extreme tolerance of dry conditions. It has been found in Australia in Queensland, including Brisbane, and in Sydney. In Europe it has been introduced through infested ship fittings and has spread in the Canary Islands and in Spain. *Cryptotermes* species occur in warm climates ranging from the Caribbean to Florida, throughout the southern regions of the United States, Arizona and the West Coast, especially in southern California.

Subterranean Termites

Most of the wood-destroying termites are subterranean termites belonging to the families Mastotermitidae, Termitidae and Rhinotermitidae. Important genera are *Mastotermes* (northern Australia), *Nasutitermes* (Central and South America, Australia, Southeast Asia), *Heterotermes* (northeast Africa, Near East, Central America), *Reticulitermes* (Europe, North America, Central America), and *Coptotermes* (tropical countries).

According to Cassens et al. (1995), subterranean termites are distributed throughout the USA, whereas dry-wood termites only occur in the south and southwest. They establish nests in the earth or in dead wood, but can also build mounds. Workers traverse as much as 100 m between the nest and the attacked wood members in buildings.

Some species of subterranean termites which do not have symbiont flagellates (especially members of the Termitidae) attack mainly wood damaged

by decay fungi, where cellulose in digestible form is available, or they establish fungal gardens in their nests. Other species where symbiont flagellates are present in the intestines (especially members of the Rhinotermitidae) prefer very moist wood, which is why they are also referred to as moist-wood termites.

The formation of galleries, including the construction of shelter tubes as a connection between the earth and wood which is not directly in contact with it, is characteristic for the species. The galleries are constructed of earth, wood particles, and fecal matter and they maintain a constant level of moisture. Termites move very quickly inside the galleries. The infested wood is also covered with galleries, and owing to their content of earth they are distinctly different from the clean channels made by dry-wood termites. Another characteristic is that subterranean termites prefer earlywood, so that latewood lamellae covered with earth particles remain. The feeding spaces of subterranean termites never contain fecal pellets, in contrast to the dry-wood termites. As is also apparent from their name, the source of moisture of subterranean termites is principally the earth (or a similarly moist material) from which they can spread, often unnoticed. In historical buildings and monuments and in museum objects, massive and rapid attacks by subterranean termites can lead to complete destruction of the wood (cf. Fig. 5.4d).

Rhinotermitidae

Reticulitermes lucifugus (Rossi)

Distribution. Europe along the 46th latitude from the Atlantic coast to the Ukraine, mainly in the Mediterranean region.

Damage Characteristics. The wood interior is hollowed out, whereby earlywood is destroyed more severely than the latewood. Only a thin layer remains intact on the surface, so that an attack is discovered rather late. The wood is attacked from the earth or by way of shelter tubes.

Distinguishing Characteristics. Workers are largely unpigmented, without eyes, and have a body length of about 4.5 mm. Soldiers have a characteristically pigmented head with pincer-like jaws, have no eyes, and a body length of 5–6 mm. Secondary reproductives lack fully developed wings, have pigmented skin, and are about 9 mm long. Primary reproductives have wings and are pigmented. Egg-laying queens have a somewhat enlarged abdomen and a body length of about 9 mm.

Development. This species forms large colonies. After the courtship flight and the discarding of the wings, males and females will mate, and eggs are laid from May to September. Workers develop through two larval stages, and soldiers develop from the workers. Winged reproductives go through nine different stages in 10–11 months before becoming adults. Swarming takes place

on warm, sunny days from April to June (Cymorek 1984). Termite breeding is carried out mainly by secondary reproductives.

Occurrence. *Reticulitermes lucifugus* invades buildings and damages structural wood members, works of art, and books. Various plastics are also attacked. Infestation of libraries and archives is relatively frequent. Outside, these termites often can be found in pine stumps.

Reticulitermes santonensis De Feytaud

This species was formerly considered a variety of *R. lucifugus* but today is recognized as a separate species. It is found in the area around Paris and is used in Europe as a test termite to determine the biological efficacy of wood preservatives.

Reticulitermes flavipes (Kollar)

This species is native to the USA and has been introduced into Europe repeatedly. In Hamburg, Germany, for instance, infestations have existed for years. Reproduction appears to take place only through secondary reproductives.

Coptotermes formosanus Shiraki, and *C. acinaciformis* (Frogatt)

Coptotermes species are not easily distinguished because they have very similar habits. In Japan, China, and Australia they are economically the most important group of termites. They can attack living trees as well as seasoned timber. Their nests are completely hidden, either in old trees or round, cone-shaped mounds which can reach a height of up to 3 m. Soldiers are relatively numerous in the colonies and will appear immediately when galleries are ruptured. They are about 6 mm long and easily recognized by their round, yellowish head with dark mandibles. In case of danger they spray a milky liquid from their front glands. A typical characteristic of an attack by *Coptotermes* in wood is a network of fecal matter in the interior galleries in the material (Creffield 1996). *Coptotermes formosanus* has been introduced into the US Gulf coast region (Su et al. 2000), Hawaii, Midway Island, the Marshall Islands and South Africa, probably via ships of the United States Navy (Krishna and Weesner 1970; Mori 1975).

5.1.5.3

Siricidae (Wood Wasps)

The wood wasps are large, slender, conspicuously colored green-wood insects with two integumentary wings, narrow waists between body sections, and an egg-laying ovipositor in the females. They belong to the Hymenoptera.

Species

Urocerus gigas (L.) (Giant Wood Wasp; Fig. 5.16)

Synonym. *Sirex gigas* L.

Sirex juvencus (L.)

Synonym. *Paururus juvencus* L.

Sirex noctilio (Fabricius)

Distribution. These three species of wasp are native to Europe, and have been introduced into Australia and New Zealand. Australian Container Standards provide for quarantine of wood imports (Richardson 1993).

Damage Characteristics. Circular, smooth-edged exit holes of about 4–10 mm diameter. Galleries in wood are 6–9 mm wide, are often curved, and are about 200, sometimes 400 mm long. The frass is light in color, medium fine, and compacted in the galleries so that an infestation is often not recognized.

Distinguishing Characteristics. Eggs have not been described. Larvae are whitish with soft skin. Bodies are cylindrical with three pairs of stumpy feet and a dark colored, spine-like sting at the end of the abdomen (cf. Fig. 5.3C). Old larvae are up to 30 mm long.

Urocerus gigas adults are marked black and yellow. The female is 24–45 mm long and has a brilliantly yellow abdomen; the males are 20–32 mm long and have a reddish-yellow abdomen with dark, ring-like stripes.

Sirex juvencus female imagoes are black-blue with a metallic sheen, and are 14–35 mm long. Males have a reddish-yellow abdomen and are 8–25 mm long.

Sirex noctilio female imagoes are blue-black and males have a reddish-yellow abdomen. Legs and antennae are black. The imagoes are 15–20 mm long.

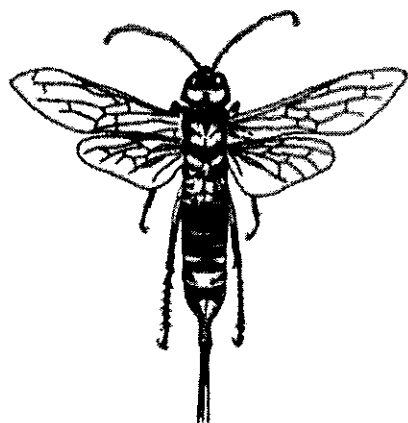


Fig. 5.16. Giant wood wasp, *Urocerus gigas*. (With permission from Dominik and Starzyk 1983)

Development. Wood wasps swarm in the summer months. Females will lay about 350 eggs in stored, green wood with bark. Wood wasps often live communally with fungi. Their development takes 2–3 years.

Occurrence. *Urocerus gigas* is found in pine, spruce, fir, and larch. *Sirex juvencus* occurs mainly in pine, but also in spruce and fir. *Sirex noctilio* is found in spruce and various species of pine (Mori 1975).

The insects occur principally in lumber yards. Larvae are introduced into buildings in infested lumber used in remodeling or new construction, and adult wasps will subsequently emerge. Materials that might be in the way, such as books, paper, leather, wall coverings and fabric, are then bored through, so that the wasps' occurrence can have unpleasant consequences. Since the wasps will not lay eggs in seasoned wood in buildings (green-wood insects!) a danger of repeat infestation does not exist.

5.1.6

Other Insect Pests of Wood

Overview

The species of insects to be discussed here cause considerably less damage than the wood-destroying insects, because the former use wood only temporarily for food, breeding, or shelter. For certain species such as the ambrosia beetles which breed inside wood, a prior incidence of decay in the green wood is an important prerequisite for development. Once the wood dries, the infestation will disappear. Ants may use wood to build their nests, but they will not use it for food. Certain pests of stored materials will seek out wood as shelter, or as a place for pupation. In most cases this will be in wood which has prior damage by decay fungi or insects. Some essential differences between insect pests of wood and stored materials are listed in Table 5.6. These secondary pests in wood are not truly wood-destroying insects.

Table 5.6. Differences in the behavior of larvae and adults of wood pests and stored-materials pests in buildings

Wood pests	Stored-materials pests
Larvae are wood-destroying and feed on wood	Larvae occasionally enter wood with prior damage for pupation
Larvae do not migrate inside the wood and can therefore be controlled with localized measures	Larvae and adults in wood with prior damage can migrate and escape control measures
Larvae often live several years in the wood	The larval stage is very short. Under favorable conditions several generations a year are possible
The generation period is long	The generation period is short which favors massive infestations
Adults leave the wood during the summer months	Adults are present throughout the year
Adults usually do not feed on wood	Larvae and adults often occur jointly as pests

Species

Oedemeridae

Nacerdes melanura (L.) (Wharf-Borer Beetle; Fig. 5.17)

Synonym. *Nacerda melanura* (L.)

Damage Characteristics. Exit holes are round to oval, with a diameter of about 5mm. Galleries are up to 300mm long and will follow the earlywood layers. The galleries are filled with long, crude, gnawed strands of wood which are interwoven into a ball, and with irregular, rounded, disc or cone-shaped fecal pellets.

Distinguishing Characteristics. Eggs are white, smooth, slightly curved, and 2mm long. Larvae are white, have three short pairs of legs, a round abdominal end, and are 12–30mm long. Beetles are reddish yellow to reddish brown, with black tips on the wing surface, and a largely black underside. Bodies of males are 6.4–13mm long, and those of females 7.4–13mm.

Development. Beetles live about 2–10 days. Mating takes place early April to June, and the female will lay 1–99 eggs in clusters. Larvae emerge after 6–14 days and bore themselves up to 10mm into wood damaged by microbiological decay. The pupal stage lasts 9–11 days.

Occurrence. The larvae usually live in softwoods or hardwoods which are periodically wetted by ocean or river water (marine installations, wooden boats). Ship's timbers made of oak, poplar and pine in the harbor in Hamburg (Germany), and of the *Mary Rose* in Portsmouth, England, with a moisture content of 130–670% exhibited damage by this insect during storage in a holding tank (Pitman et al. 1993; Noldt and Tiedemann 1998).

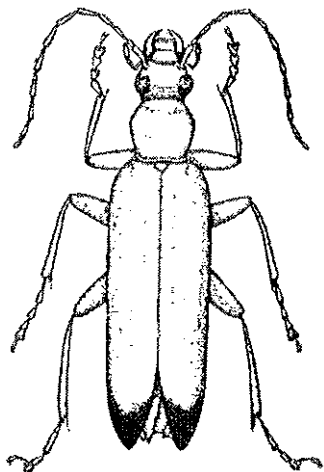


Fig. 5.17. Wharf-borer beetle, *Nacerdes melanura*. (With permission from Schmidt 1962)

Scolytidae, Platypodidae, and Lymexylonidae

These are green-wood insects which have only minor importance for the conservation of historic buildings and of recovered waterlogged wood. Propagation is not possible in dried wood.

Formicidae (Ants)

Ants are social insects and, like the wood wasps, belong to the Hymenoptera. An ant colony consists of three castes: winged males, winged females (queens), and wingless females (workers).

Camponotus herculeanus (L.) (Red Carpenter Ant; Fig. 5.18)

Damage Characteristics. An often irregular system of galleries and chambers in the low density, chewed out earlywood, leaving latewood lamellae intact. In contrast to the galleries of subterranean termites which are covered with earth and fecal particles, the galleries of the ants are smooth and clean (Cassens et al. 1995).

Development. After the mating flight the males die off, while the females (queens) discard their wings and begin to establish a colony. The asexual workers feed the other castes of the colony and move along so-called ant roads. Outside they can be found on trees with aphids whose feces they use for food. They do not use wood as food (wood inhabiting insects).

Occurrence. Ants live mainly outside, including on living trees (ant trees). They can invade buildings through cracks, inhabit beams, flooring, and wall paneling, and build their nests there. In recent years damage to buildings has increased in Scandinavia.

Another species of ant which builds its nests in damp structural timber is *Lasius fuliginosus*.

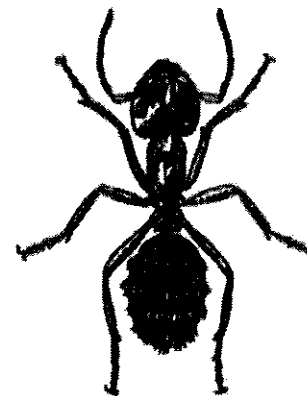


Fig. 5.18. Red carpenter ant, *Camponotus herculeanus*. (With permission from Dominik and Starzyk 1983)

Dermestidae (Hide Beetles)

Dermestes lardarius L. (Larder Beetle; Fig. 5.19)

Synonyms. Bacon beetle, ham beetle.

Damage Characteristics. Entrance and exit holes are almost circular with a diameter of 3–5 mm. The enlarged pupal chambers have a length of about 6–16 mm. Galleries in wood with prior decay damage have a certain similarity to those made by ants in dead wood. The bored galleries are extensive; some lamella-shaped zones remain intact.

Distinguishing Characteristics. Eggs are white and elongated (2×0.6 mm). Larvae have brownish backs with long, reddish-brown hairs, bodies of elongated cylindrical shape 11–13 mm long, and two spines at the end of the abdomen (cf. Fig. 5.3D). They excrete feces in long strings which can be found in infested wood. Larvae develop quickly and slough their skin four to six times. These skins are indicative of an infestation by *Dermestes lardarius*. The basic color of adults is brownish-black to black, with a thick coat of yellowish hairs on the front half of the wing surface, which also bears six black dots. Their body length is 8 mm.

Development. Mating takes place in the spring. Females will lay about 150 eggs. Both larvae and adults feed on material of animal origin, such as skins, fleece, furs, wool, and other animal products. For pupation, chambers are constructed in wood, cork, cardboard, textiles, and books. The generation period is 35–60 days at room temperature, so that several generations can be formed per year.

Occurrence. Found in fleece, skins, furs, smoked meats, animal products, textiles, and plant materials containing fats. Larvae will attack decayed wood, but not sound wood, for pupation, and structural timbers with prior decay damage can thereby be completely destroyed.

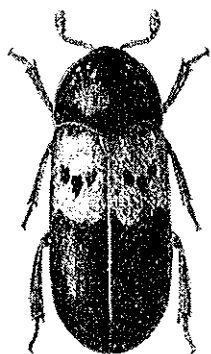


Fig. 5.19. Larder beetle, *Dermestes lardarius*. (After Lepesme 1944)

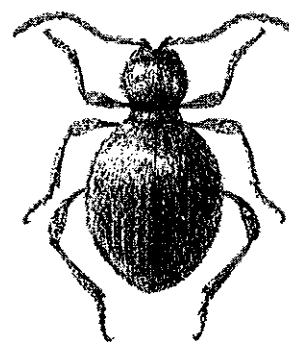


Fig. 5.20. Golden spider beetle, *Niptus hololeucus*. (After Lepesme 1944)

Ptinidae

Niptus hololeucus (Fald.) (Golden Spider Beetle; Fig. 5.20)

Synonym. Yellow spider beetle.

Damage Characteristics. Prior to pupation, larvae will chew superficially into the surface of earlywood zones of wood damaged by decay or wood-destroying insects, but will penetrate no more than a few millimeters. The pupal cocoons can be found on infested objects. The principal pests are the adults which will eat holes into textiles, carpets, and upholstery.

Distinguishing Characteristics. Eggs are white, later yellowish, and measure 0.6×0.5 mm. Larvae are whitish to yellowish with curved bodies and 5–7 mm long. Adults have a spherical appearance, resemble spiders, and are about 2.5–4.5 mm long. Their body is deeply constricted behind the neck shield, has golden-yellow hair with a brassy sheen, and long antennae.

Development. Females lay about 100 eggs. The larvae feed on plant (grains and grain products) and animal products. For pupation they spin cocoons of 1.8–3.2 mm length from food particles and secretions and fasten these on objects. Generation period is about 4–6 months, but as a rule only one generation a year is formed. Adults can live for several months.

Occurrence. Found mainly in old buildings such as farms, rectories, or manor houses. Larvae live mostly in crawl spaces and hollow walls which contain accumulations or fill of plant materials such as straw. The voracious adults are very mobile (but cannot fly) and spread quickly through the entire building.

5.1.7

Enemies of Wood-Destroying Insects

Overview

The organisms discussed here can much reduce the propagation and spread of infestation by wood-destroying insects and thus can reestablish a biologi-

cal equilibrium. They offer a starting point for the directed biological control of insect pests of wood (cf. Chap. 10). The most important representatives of enemies belong to the Ichneumonidae, Braconidae, Bethylidae, Cleridae and Acari (Weidner 1993).

Species

Ichneumonidae

Rhyssa persuasoria (L.)

Distinguishing Characteristics. Adults are black with white spots on the head. Body length is 22–34mm without ovipositor, which is about a quarter longer than the body. Females cannot sting humans with the ovipositor. In contrast to the Siricidae, the Ichneumonidae have a distinct waist between thorax and abdomen.

Development and Occurrence. Females will use their long ovipositor to lay eggs on or into the body of Cerambycidae and Siricidae larvae (König 1957). The parasitic larvae will then develop and pupate inside their hosts, which subsequently die. The wasp emerging from the cocoon will then bore a round exit hole in the wood and will mate again.

Monolexis fuscicornis (Foerster)

This is a parasitoid of powder post beetles (Graf 1992).

Braconidae (Fig. 5.21)

Spathius exarator (L.)

Damage Characteristic. Round exit holes maximally 1 mm in diameter.

Distinguishing Characteristics. Body length is 2–7mm without ovipositor which is as long as the body.

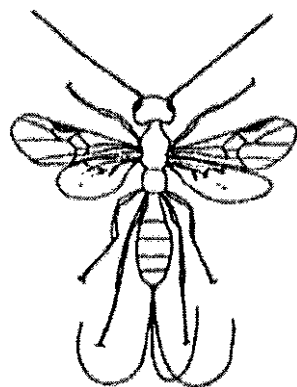


Fig.5.21. Braconidae. (After Richardson 1993)

Development and Occurrence. Females lay their eggs onto anobiid larvae, especially those of *Anobium punctatum*. The developing parasitic larvae can destroy up to 95% of the wood-destroying larvae. In buildings and housing with extensive anobiid infestation, massive populations of these wasps can occur (Weidner 1993).

Bethylidae

Scleroderma domesticum (Latr.)

This wasp is a parasitoid of *Anobium punctatum* and *Hylotrupes bajulus*.

Cleridae

Opilo domesticus (Sturm) (Fig. 5.22)

Distinguishing Characteristics. The wing surfaces of the adults are brown or yellow with a lighter spot at the shoulder, the middle and the end. The shoulder spots do not form cross ties. Body length is 7–12mm.

Development and Occurrence. The larvae hunt the anobiid and *Hylotrupes* larvae in their galleries and destroy them, while the adults hunt the anobiid adults and eat them.

Korynetes caeruleus (Degeer)

Synonym. *Corynetes coeruleus* (Degeer).

Distinguishing Characteristics. Adults are shiny blue, with barely spotted head and neck shield, reddish brown antennae, and a body length of 3.5–6.5 mm.

Development and Occurrence. Larvae and adults wander about the galleries in the wood and feed on the larvae and adults of wood-destroying insects, especially the Anobiidae. Monitoring of historical landmark buildings in England for *Xestobium rufovillosum* yielded evidence of coexistence with



Fig. 5.22. *Opilo domesticus*. (After Lepesme 1944)

Corynetes coeruleus (Belmain et al. 1999). In order to make room they throw large quantities of the frass and fecal pellets of the anobiid larvae out of old exit holes (Vité 1952).

Acari (Mites)

Pyemotes tritici Lag. & Mont. (Grain Itch Mite)

Synonym. *Pediculoides ventricosus* Newp.; *Pyemotes ventricosus* Newp.

Distinguishing Characteristics. At a length of only 0.2–0.3 mm they are small, spindle-shaped, colorless to slightly yellowish. The abdomen of the pregnant female will swell into a spherical shape.

Development and Occurrence. The males live on the abdomen of the pregnant female. The mites live off the larvae and the adults of wood-destroying insects, especially of *Anobium punctatum*. The mites and their feces can cause allergic reactions in humans (Vité 1952).

5.1.8

Monitoring of Insect Infestations

If treatments for control of pests in objects, buildings, or monuments is contemplated, it must first be ascertained absolutely if an active infestation is actually present inside the wood. The hidden habit of the insect pests often makes it very difficult to determine the insect species and its activity with certainty. Indications of the presence of insect pests can be found in the surroundings, on the surface, and inside of suspect objects (Table 5.7). During

Table 5.7. Methods of diagnosing active infestations by wood-destroying insects

Search strategy	Indicators or methods
In the surroundings	Living or dead adults on the panes, frames, or sills of windows Appearance of enemies of the pests, also on windows or elsewhere Placing pheromone (sex hormone) traps
On the damaged object	Exit holes with bright rims Fresh powder falling out Appearance of enemies of the pest
Inside the damaged object	Cutting into the damaged wood (invasive) to find larvae Registering feeding noises of pest larvae by: direct listening listening with a stethoscope recording acoustic emissions Locating larvae by periodic X-rays by means of: traditional X-ray technology computer tomography (X-ray CT scans) Carbon dioxide respiration measurements

swarming of the insects (April to August), living or dead adults may be found on windows or window sills. These may include not only wood-destroying insects but also their enemies (cf. Sect. 5.1.7). The appearance of enemies on the object or its surroundings is an indication of an active infestation. The presence of sexually mature adults, the extent of the infestation and its location can be determined or estimated for certain anobiid species with the aid of pheromone traps (sex attractant traps; Binker 1996; Pinniger and Child 1996). *Anobium punctatum* males can be trapped in pheromone traps containing the attractant stegobinon. The traps are only suitable for monitoring, and not for treatment. Because of the volatility of the pheromone, its effectiveness is limited to a period of 0.5–2 months. Males of the house longhorn beetle *Hylotrupes bajulus* attract females with a sex hormone, and a method for their control is being developed (Noldt et al. 1995). Beetles of *Xestobium rufovillosum* were attracted to natural light, especially on white colored traps, and to UV light (Belmain et al. 1999).

On the surface of damaged objects, exit holes with bright rims and fresh, light yellow piles of frass indicate the presence of the larvae of wood-destroying insects. However, their enemies can also rid the galleries of frass by ejecting it from exit holes (cf. Sect. 5.1.7), but in this case the piles are formed irregularly. Old exit holes have gray rims due to dust deposition and the effect of UV radiation. Fecal pellets contained in the frass can point to particular species of insect pest (cf. Sect. 5.1.5).

Whether the inside of the damaged object contains live larvae of insect pests or termites can be determined by destructive as well as nondestructive methods. It may be permissible to use a chisel or even an ax to expose the interior of less important structural members in historic buildings or monuments in order to search for live larvae or termites. For art objects and other cultural property invasive methods will generally not be acceptable, and non-invasive methods will have priority. The feeding noises of some wood-destroying larvae such as *Hylotrupes bajulus* may already be audible to the unaided ear in quiet surroundings. For other species such as anobiid and lyctid larvae the aid of a stethoscope or a combination of microphone, amplifier and earphones may be necessary. Active insect pests can also produce vibrations in the ultrasound range which can be recorded and interpreted by acoustic emission technology (cf. Chap. 6). Coupling of transducers presents a problem for objects with uneven surfaces, and specialized instruments suitable for practical use in museums are still under development.

Locating active larvae in mobile objects is also possible with periodic X-rays using either conventional technology or X-ray computer tomography. Furthermore, since live larvae must breathe, the carbon dioxide liberated in the process can be measured to obtain evidence of active infestation. For this purpose the object must be placed into a gas-tight container (cf. Chap. 6).

5.1.9

Attacks on Surface Decorations, Glues, and Consolidants

Natural and synthetic polymers are used extensively in combination with wood in the form of surface decorations – polychromy, metallic or clear surface coatings – glues and consolidants. In the choice of these materials, their biostability plays an important role. When wood is attacked by insect pests – beetles and termites – the material will be destroyed mechanically through their boring activity. The biological stability of the polymers used in paint films, adhesives and consolidants with respect to insects depends not only on their chemical composition but also on their hardness and surface condition. Termites destroy many synthetics (Unger and Unger 1984), but wood-destroying beetles can also bore through plastic films and rigid foams (Unger and Unger 1995). Wood which has been damaged by insects and subsequently consolidated with natural or synthetic polymers often does not have sufficient biostability (Unger et al. 1996a, 1998). The egg larvae of wood-destroying beetles such as *Hylotrupes bajulus*, for instance, are able to bore their way through consolidated zones in order to reach interior zones which did not receive consolidant. If sufficient food source is available, the larvae can grow and cause further destruction of the object. The biostability of specific consolidants is discussed in Chapter 11.

Conservators of panel paintings, sculptures and furniture are interested in knowing whether egg larvae emerging from eggs laid on the surface of objects with surface coatings are able to bore through the paint or varnish layers and then destroy the wood underneath. Whereas pure film-forming binders and the various components of varnishes are, in most cases, not resistant, complete paints, gilding, silvering, and oil-based finishes with pigments do form effective barriers (Unger et al. 1996b, 1997). The resistance of the latter systems is presumably due to the thickness of the coatings and the pigments they contain.

5.2

Fungi

5.2.1

Taxonomy

The fungi (Mycota) do not form a phylogenetically uniform group. According to Schmidt (1994) a generally accepted system of classification does not exist. The systematic classification given here is based on typical developmental characteristics and the type of fruit body formation of the various fungi. Accordingly, Müller and Loeffler (1992) and Eaton and Hale (1993) distinguish between two divisions: the slime molds (Myxomycota) and the true fungi (Eumycota). The true fungi contain five subdivisions. Wood-damaging

Table 5.8. Classification of wood-damaging fungi according to their damage characteristics and taxonomy

Destroying fungi			Staining fungi		Surface molds
Brown rotters	White rotters	Soft rotters	Blue-stain fungi	Other staining fungi	
Basidiomycota	Basidiomycota	Ascomycota, Deuteromycota	Ascomycota, Deuteromycota	Ascomycota, Deuteromycota	Ascomycota, Deuteromycota

fungi are primarily found among the Basidiomycota, the Ascomycota, and the Deuteromycota or Fungi imperfecti. Each subdivision contains several classes. The following description is based on the systematic classification chosen by Eaton and Hale (1993).

In addition to the taxonomic classification, wood-damaging fungi can also be distinguished on the basis of their living conditions and therefore according to their presence in living trees, on stored wood, or on wood in buildings as tree stem, storage, or house decay fungi (Grosser 1985; Schmidt 1994).

The most useful classification of wood-destroying fungi is based on their effect on the wood, where generally a distinction is made between wood-destroying fungi, wood-staining fungi, and surface molds (Table 5.8). Accordingly, the wood-destroying white rotters and brown rotters belong to the Basidiomycota, whereas the soft rotters which are also wood-destroying fungi may belong to the Ascomycota or the Deuteromycota. Wood-staining and mold fungi are Ascomycota or Deuteromycota (Sutter 1986).

A new kind of classification especially of the house rot fungi is based on genetic studies to determine the special sequence of the deoxyribonucleic acid (DNA) for every fungus (Schmidt and Moreth 1998, 1999).

5.2.2

Morphology

The development of true fungi includes the morphologically distinct stages of spore, hypha, mycelium, and fruit body.

Spores are microscopically small, sexual or asexual reproductive cells. They are often produced in great quantities, are almost always present, exhibit different shapes and colors, and may be unicellular or multicellular. The generatively (sexually) formed spores of the Ascomycota and Basidiomycota are referred to as ascospores and basidiospores, respectively, and the vegetatively (asexually) formed spores of the Deuteromycota, as conidia. Under suitable conditions the spores absorb water, swell, and germinate, and the resulting germ tubes initiate colonization of the wood.

A hypha is a single, tube-shaped fungal cell, which has protoplasm and may be vacuolated. One or more relatively small, true cell nuclei with a nucleolus,

mitochondria, ribosomes, and an endoplasmic reticulum as organelles are typical hyphal features for reproduction and nourishment. Since hyphae lack plastids (organelles for photosynthesis) and assimilation colorants, fungi are incapable of photosynthesis. Fungi are carbon heterotrophic organisms dependent on a supply of organic substances which may be obtained from wood. Reserve substances may include lipids, volutin (polymetaphosphate) and glycogen. Starch and saccharides are not formed, and the cell wall of fungi consists mainly of chitin (Schmidt 1994).

Hyphae combine to form a mycelium, a stringy, leathery, fluffy, or compact mat, which is also referred to as a thallus because fungi do not have any true tissues. The function of the mycelium is to decompose the wood and thereby provide nourishment. If sufficient food is available, mycelium is capable of growing indefinitely. In this sense fungi can reproduce vegetatively. The mycelium of Basidiomycota, Ascomycota, and Deuteromycota is septate, and growth in length occurs at the tips of the hyphae (apical growth).

In wood the mycelium grows largely below the surface, so that decay, especially in the initial stages, is often not noticeable from the outside. In some species of fungi surface and aerial mycelium are also formed, the latter being a densely structured surface mycelium. Some fungal species form mycelial strands (rhizomorphs) which extend from the surface mycelium and are morphologically distinct units. The mycelial strands typical of certain species of fungi causing decay in buildings consist of generative basic hyphae, fiber hyphae to provide strength, and vascular hyphae for the transport of water and nutrients (Schmidt 1994).

The formation of fruit bodies begins with tissue-like structures (plectenchyma) of the mycelium, bearing spore deposits on their inner or outer surfaces. The most important part of the fruit bodies of the Hymenomycetes class of the Basidiomycota is the fruit layer (hymenium), which is the spore producing layer. The structure of the fruit layer of the Hymenomycetes, e.g., in the form of pores or lamellae, is an important characteristic for identification. Particular species are referred to as gill fungi or pore fungi, for instance, on the basis of these forms. Fruit bodies of wood decay Basidiomycota are divided into layer, bracket, or cap fungi according to their position with respect to the wood surface (Fig. 5.23). The fruit bodies of Ascomycota found on wood are usually only a few millimeters in size and are either spherical, pear-shaped or disc-shaped (Fig. 5.24).

5.2.3

Reproduction

Vegetative development of fungi occurs through the growth of mycelium by formation of masses of hyphae which can support the formation of reproductive structures. The formation of fruit bodies ensures survival and spread of the species. Reproduction of wood-destroying fungi is either asexual or sexual. Asexual reproductive structures are formed during the development

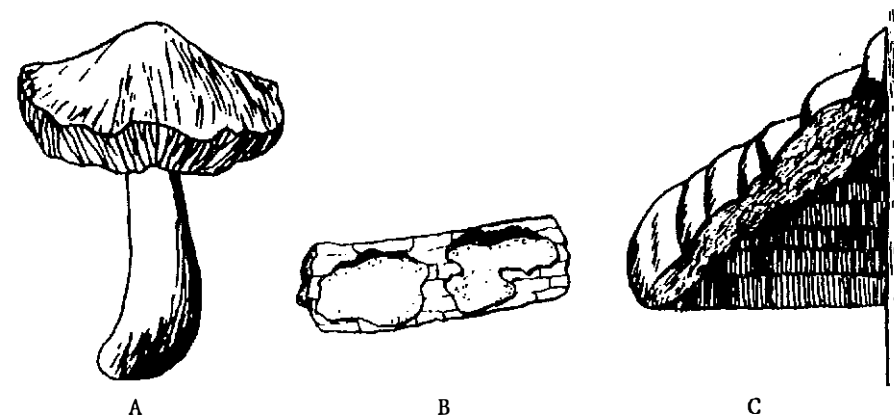


Fig. 5.23. Fruit body types of Basidiomycota found on wood. A Cap. B Layer. C Bracket. (With permission from Schmidt 1994)

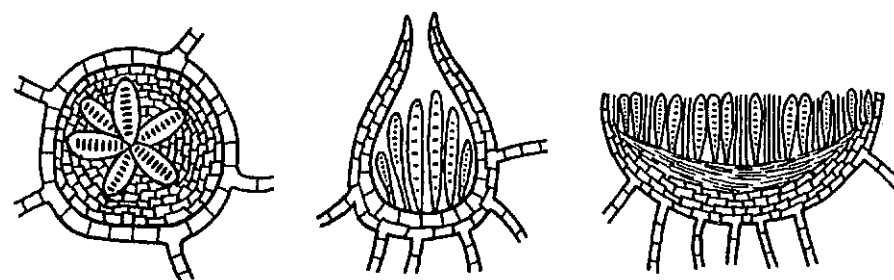


Fig. 5.24. Fruit body types of Ascomycota. (With permission from Schmidt 1994)

cycle of Deuteromycota following mitotic division of the nuclei resulting in formation of conidia (Fig. 5.25; Florian 1997).

In the Ascomycota and Basidiomycota, at the first stage of sexual reproduction, cell fusion (plasmogamy) of different mycelia takes place, followed by nuclear fusion (karyogamy) and meiosis resulting in spore formation in the Ascos and Basidios. In the Basidiomycota the hyphae often divide with the formation of clamp connections at the septa. In special cases there are double or multiple clamp connections, which are identifiable characteristics for various species. The ascospores of the Ascomycota are formed in groups of eight in the ascus, a sac-shaped cell. In the Basidiomycota, spores are formed on tubular basidia, which have four protrusions, each bearing one basidiospore. Ascospores and basidiospores are the perfect (sexual) form of fruiting (teleomorph). For some fungi an additional, imperfect fruiting form involving the production of asexual conidia (anamorph) is typical (Fig. 5.25).

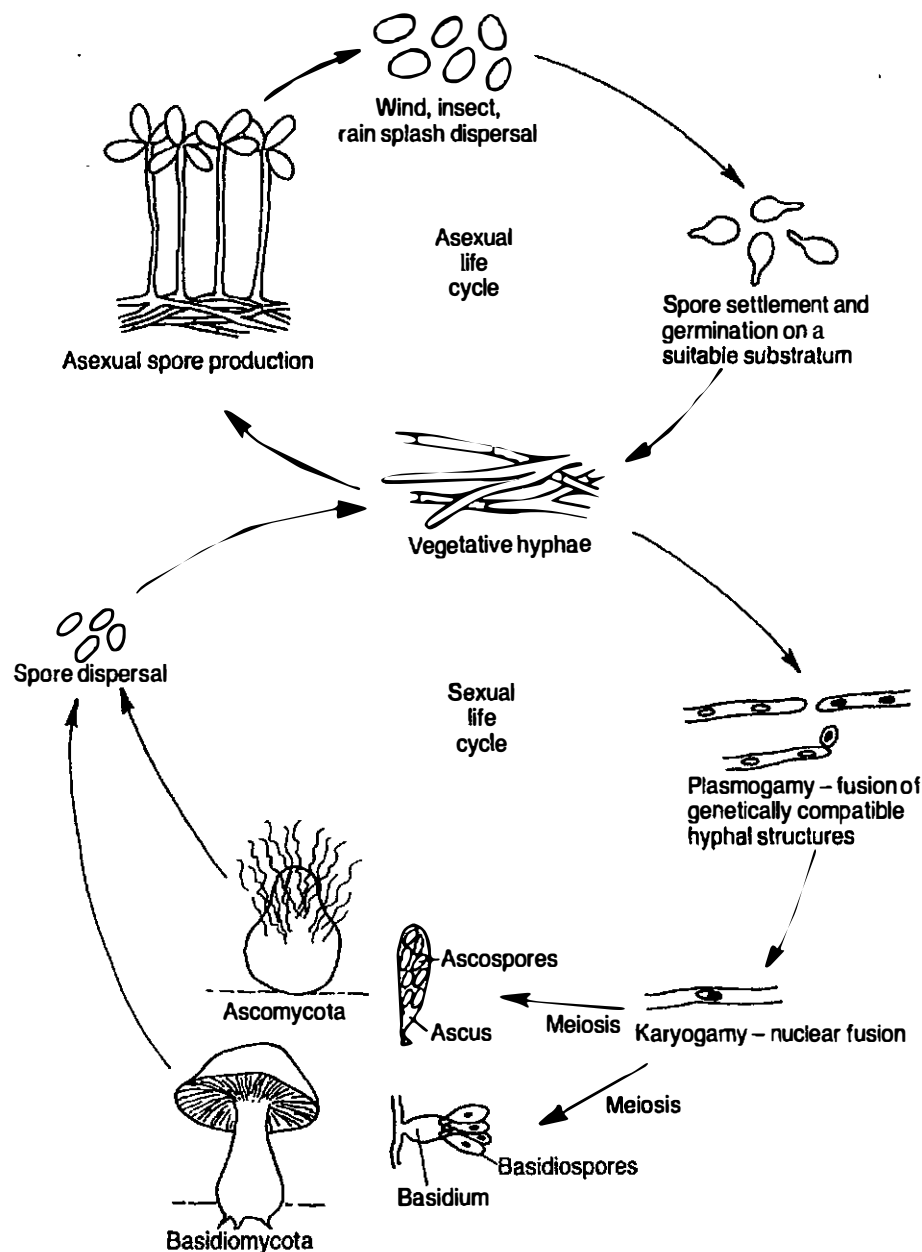


Fig.5.25. Overview of the life cycle of fungi. (After Eaton and Hale 1993)

5.2.4 Physiology

Most wood-destroying fungi live saprophytically on stored wood or wood in service. A few are pathogenic by attacking living tissue in the tree. Most of the saprophytic fungi can be cultured. In the natural cycle of wood material many species of fungi are ecologically important for the decomposition of wood. For wood in service, however, this process should be prevented by suitable methods of wood protection (Kempe 1999).

The physiology of fungi concerns especially the functions and performance of the mycelium, the growth of which depends mainly on the available food source and the ambient moisture and temperature conditions. Light, the pH value of the wood, the occurrence of divalent metal ions and oxygen also play a role in fungal physiology.

Nutrition

For many fungi wood is an ideal substrate for colonization, as it makes available organic and inorganic compounds of various forms (Eaton and Hale 1993). Organic compounds serve particularly as sources of energy and carbon, since wood-destroying fungi are heterotrophic organisms. The brown-rot and soft-rot fungi utilize mainly the cellulose and hemicelluloses in wood, whereas white-rot fungi can also decompose lignin. Staining and mold fungi do not cause much loss of wood substance, as they meet their carbon requirements from readily soluble sugars and starch in the cell lumina. Fungi can also utilize starch and the small amounts of fats and proteins in wood. Since wood has very little nitrogen content, fungal hyphae can take up nitrogen from sources in the surroundings. Fungi also need inorganic nutrients for growth, which must contain the most important elements such as phosphorus, calcium, potassium, sulfur, and magnesium, as well as the so-called micronutrients such as iron, copper, zinc, and boron.

Some species of fungi prefer either softwoods or hardwoods, or may even inhabit particular wood species. Other fungal species can attack softwoods and hardwoods equally. Some decay fungi which attack living trees destroy only the heartwood, while most decayers of wood in service attack sapwood and heartwood. Some wood species contain extractives in the heartwood which offer extensive protection against fungal attack, imparting a high level of natural durability to these woods.

Wood Moisture Content

Wood with a persistently high moisture content of 20% or more becomes a suitable habitat and food source for decay and stain fungi (Eaton and Hale 1993; Blanchette 1998). Starting from the ubiquitous spores, stain fungi such as blue stain can be active after a few days or weeks, and decay fungi after 2–3 months. Water serves as a solvent and transport medium for nutrients, and is a prerequisite for enzymatic processes.

Wood which is either completely saturated with water, or is kept dry continuously (i.e., at a moisture content of less than 20%), will not be attacked by fungi. Wood in structures kept under those conditions will usually be free of any significant strength reductions caused by fungi, even after centuries of use. Most fungi require wood moisture content levels between 35 and 60% (Grosser 1985; Unger 1995), but optimum levels of moisture content have been shown to vary for different species (Table 5.9). Compared with low density wood, wood of high density has less pore space and becomes saturated with water at lower moisture content values. The significance of moisture content values above the fiber saturation point (roughly >30%) therefore depends on the dry wood density of a particular species. *Coniophora puteana* and *Paxillus panuoides*, for instance, grow particularly well at a constant wood moisture content of 50–60%, although Liese (1954), gives an optimum moisture content of only 35%. These fungi have been referred to as “wet decay” fungi. The same optimum moisture contents have been cited for various species of *Gloeophyllum*, but they can survive for years in dry wood. *Lentinus lepideus* requires only 30–40% moisture content. *Serpula lacrymans* occupies a special position, because although it initially requires a wood moisture content of 30–40% (Cartwright and Findlay 1969), it can grow into air-dry wood with less than 20% moisture content due to its ability to transport water in the mycelium and in mycelial strands. In this manner it can create suitable moisture conditions at the growth zones. *Serpula lacrymans* therefore does not belong to the “wet decay” fungi, and in Europe is also referred to as “the true dry rot fungus.” Fungi are best referred to by their Latin names in order to avoid confusion. In the United States, the term “dry rot” is unfortunately used popularly for any kind of fungal decay. In a more restricted sense it is used for *Meruliporia incrassata* which is found in the Gulf States and along the Pacific Coast, and also in Canada (Scheffer 1973).

Table 5.9. Effect of wood moisture content on mycelial growth of wood-damaging fungi

Species	Wood moisture content [%]		
	Min.	Optimum	Max.
Brown-rot fungi	20	35–60 ^a	>70 ^a
<i>Coniophora puteana</i> ^b	20	50–60	
<i>Serpula lacrymans</i> ^b	20	30–40 ^c	40–60 ^d
<i>Antrodia vaillantii</i> ^b	20	35–45	
<i>Gloeophyllum sepiarium</i> ^b	20	38 ^e –60	
<i>Lentinus lepideus</i> ^b	20	30–40	
<i>Paxillus panuoides</i> ^b	20	35 ^e –70	
Molds	20	30–70 ^a	

^aViitanen and Ritschkoff (1991).

^bData of Bavendamm, from Grosser (1985) and Unger (1995).

^cCartwright and Findlay (1969).

^dIn the initial stages.

^eLiese (1954)

Blue-stain and soft-rot fungi colonize wood at higher moisture contents, often above 100%, as for example in freshly sawn softwood pallet timber and wood elements in water cooling towers. In wood window frames, rapid attack by a mixed microbial flora can be observed when moisture penetrates beneath coats of paint. High relative humidity favors fungal attack of wood, and high relative humidity is necessary for the formation of surface mycelium since the hyphae lack resistance to evaporation. Reducing air humidity in buildings by ventilation of rooms and especially of crawl spaces limits the infection by colonizing fungi. According to Viitanen and Ritschkoff (1991), the growth rate of mold fungi is very high at a relative humidity of more than 95% and temperatures between 20 and 40°C, but if the relative humidity decreases below 65% at 20°C almost no growth of mold fungi can be observed.

Temperature

The enzymatic reactions of fungi are strongly influenced by temperature (Table 5.10), and the temperature dependence of fungal activity follows reaction rate theory (Zabel and Morrell 1992; Schmidt 1994). For each species of fungus there are three cardinal growth temperatures: the minimum temperature at which growth begins, the optimum temperature for best mycelial growth, and the maximum temperature at which growth ceases. Most wood-destroying fungi grow best between 15 and 40°C (mesophilic growth). Their growth curves show well-defined temperature maxima which range from 20–35°C (Grosser 1985; Unger 1995). Mycelial growth begins for some fungi at 3°C, and at temperatures below 0°C the fungus becomes dormant. According to Bavendamm (Grosser 1985) many species of fungi found outdoors can survive temperatures of –40°C without damage. Only *Serpula lacrymans* seems to be more sensitive to cold than other house decay fungi.

Above 39°C most species show almost no growth, and enter heat dormancy. *Serpula lacrymans*, however, ceases growth at 28°C (cf. Table 5.10). With an optimum of 21°C, this fungus is evidently adapted to the temperatures found

Table 5.10. Effect of temperature on mycelial growth of wood-destroying fungi

Species	Temperature [°C] ^a		
	Min.	Optimum	Max.
<i>Coniophora puteana</i>	0–5	20–32	29–40
<i>Serpula lacrymans</i>	0–3	17–23	28
<i>Antrodia vaillantii</i>		26–27	
<i>Gloeophyllum sepiarium</i>	5	26–35	39–44
<i>Gloeophyllum trabeum</i>		26–35	40
<i>Lentinus lepideus</i>	8	27–33	38
<i>Paxillus panuoides</i>	5	23–30	29

^aData from Liese (1955), Grosser (1985), Eaton and Hale (1993), Schmidt (1994), Palfreyman et al. (1995) and Unger (1995).

in buildings. Wood-destroying fungi such as *Lentinus lepideus* and *Gloeophyllum* spp. which outdoors are often exposed to higher summer temperatures tolerate temperatures up to 38 or 44°C.

Light

Light appears to be of little importance to the vegetative development of fungi. As a rule the mycelium grows in the dark, usually as substrate mycelium inside wood. Surface and aerial mycelium may develop at low light intensity in buildings in such species as *Antrodia vaillantii* and *Serpula lacrymans*. In the Basidiomycota fruit bodies are formed on the surface under incident light. *Serpula lacrymans* preferably fruits in dark conditions (Schmidt 1994), but light is an important factor for the development of some species (Bjurman 1984). In total darkness, as in mines and basements, some fungi, such as *Gloeophyllum* spp. and *Lentinus lepideus* will bear very deformed, usually sterile fruit bodies.

pH Value

The susceptibility of wood to attack by fungi also depends on its hydrogen ion concentration (pH value). Most wood species are weakly acidic with a pH value of approximately 5. Since wood-destroying fungi require such conditions for spore germination, mycelial growth, and formation of fruit bodies, the resistance of wood to fungi is low in most cases. The particular physiological significance of pH derives from its influence on the enzyme activity of the fungi. Brown-rot and white-rot fungi reach optimum growth at pH values of 5–6, the total growth range being 2.5–9, while soft-rot fungi tolerate alkaline substrates at pH values up to 11. Wood-staining fungi are also strongly influenced by pH value, and cease to grow if the pH value exceeds 5 (Zabel and Morrell 1992). Fungi are capable of excreting acids to adjust the pH value of their surroundings to their own requirements, and this can be used for the chemical diagnosis of fungal attack (cf. Chap. 6). The dry-rot fungus *Serpula lacrymans*, for instance, employs oxalic acid to bring the cellulolytic enzymes into contact with the tracheid walls inside wood. When no more acid production is necessary, calcium (or another divalent metal ion) found in buildings combines with oxalic acid to form the water-insoluble salt calcium oxalate. In this manner the pH value of the surrounding environment is regulated for further mycelial growth (Palfreyman et al. 1996).

Oxygen Content of the Air

Wood-destroying fungi are aerobic organisms which require oxygen in the air for respiration. Growth is only possible if at least 10–20% of the pore volume of the wood contains air. The optimum oxygen content has been given as 1–2% (Zabel and Morrell 1992) but a temporary lack of oxygen can be toler-

ated (Scheffer 1973). The dependence of mycelial growth rate on oxygen content varies from species to species. Soft-rot fungi require very little oxygen, which explains their presence in marine timbers, at the base of wood poles, and in cooling tower parts. Long-term reduction of oxygen content in wood can provide protection against fungal attack, something that takes place in underwater storage of wood. Experiments have also been carried out with storage of spruce logs in piles fumigated with carbon dioxide or with nitrogen gas (Mahler 1992).

5.2.5

Types of Damage to Wood

The life processes of fungi change the wood they inhabit (cf. Table 5.8, Fig. 5.26). Wood-destroying fungi can bring about a significant loss of wood substance and a reduction of wood strength. Staining fungi and surface molds, on the other hand, represent mainly an aesthetic problem to the user, but can also have economic consequences.

Wood attacked by fungi turns either dark brown or whitish, and the terms brown rot and white rot introduced by Hartig (1874) are still used today (Merrill et al. 1975). In the 1950s, a kind of fungal decomposition was studied which resembles brown rot but has special characteristics (Findlay and Savory 1954; Savory 1954; Liese 1955; Duncan 1960). Since the damage often results in a softening of the wood, it was termed soft rot. Nilsson (1988) defined soft rot for those types of wood damage which is mainly caused by Ascomycota or Deuteromycota. An overview of present knowledge of soft rot has been given by Daniel and Nilsson (1998).

Staining fungi and surface molds attack wood during high air humidity, or at high wood moisture content.

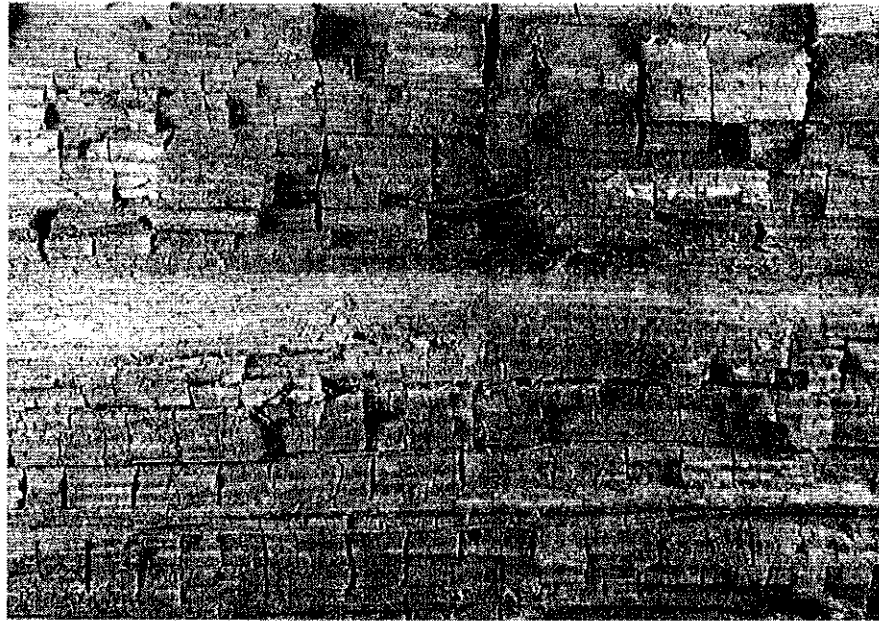
5.2.5.1

Wood Decomposition

Overview

Damage caused by wood-destroying fungi is based on their ability to decompose the structural elements of the lignified wood cell walls and to use them as their food source. As the hyphae penetrate into the wood, they excrete enzymes which convert the cellulose and hemicelluloses, and to some extent the lignin, present in the cell wall into various sugars and aromatic compounds of low relative molecular mass. The dissolved end products are then used for growth and as a source of energy.

The decomposition of cellulose and hemicelluloses are effected by various hydrolases – cellulases and hemicellulases (e.g., xylanases, mannanases, galactanases), respectively – while lignin is split up exclusively by oxidizing and ring-splitting enzymes, primarily by peroxidases and polyphenoloxidases

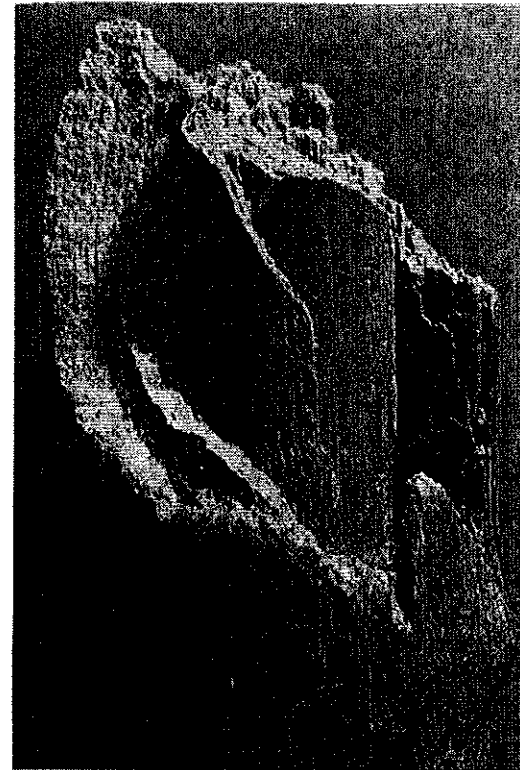


A

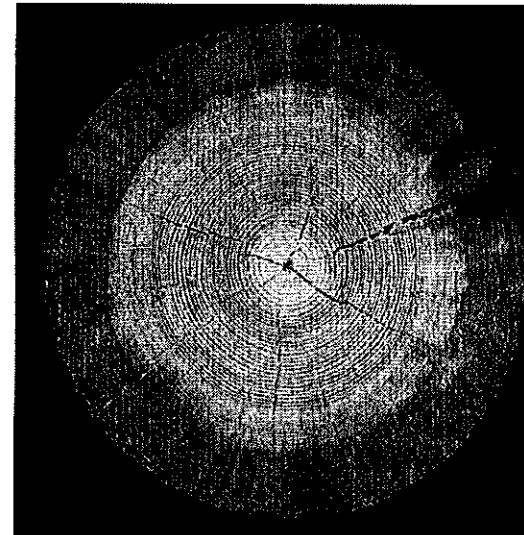


B

Fig. 5.26. Macroscopic view of fungal damage to wood. A Brown rot. B White rot. C Soft rot. D Blue stain. (A Courtesy of B. Weiß; B, C, D Courtesy of R. Pausewein)



C



D

Fig. 5.26. Continued

(e.g., laccase). Since the decomposition reactions can only take place in aqueous solutions, they are favored by high wood moisture content.

The enzyme systems present in particular species of fungi determine whether the damage occurs as brown rot, white rot, or soft rot. Extensive treatments of the metabolism of wood decay fungi can be found in Scheffer (1973), Fengel and Wegener (1989), Eriksson et al. (1990), Zabel and Morrell (1992), Eaton and Hale (1993), Schmidt (1994), and Bruce and Palfreyman (1998).

Brown Rot

The term brown rot comes from the dark brown to black-brown discoloration of wood caused by fungal attack. Brown rotters mainly decompose the polysaccharides of the wood – cellulose and hemicelluloses – exposing the lignin to oxidation by the air which leads to the characteristic brown discoloration. Most brown-rot fungi attack softwoods. Hyphae grow in the cell lumen and are in contact with the wood cell wall. Hyphae are thinner than the cell walls (Fig. 5.27A), and can be made visible under the microscope by staining. Within a short period of attack, decomposition of the framework substance causes a reduction in the mechanical strength and volumetric shrinkage of the wood. Characteristic cracks both parallel and perpendicular to the grain develop followed by decomposition into cubical pieces, so that brown rot is therefore also referred to as brown cubical rot (cf. Fig. 5.26A). At the latter stages of decomposition, the cubes can be crushed into a powder resembling humus, which consists mainly of largely unchanged lignin. At this stage cell structures are no longer recognizable under the microscope. Typical representatives of brown rot are species of *Gloeophyllum* among fungi attacking lumber in storage yards, and *Serpula lacrymans* among house decay fungi. Experiments have confirmed the production of large quantities of oxalic acid by *Serpula lacrymans* and *Coniophora puteana*, the most prominent brown-rot fungi of wood in buildings in Europe, which can lead to a reduction of the pH value from 5 to 3. Although white-rot fungi also produce oxalic acid, they have a special enzyme (oxalic acid-decarboxylase) which does not permit the accumulation of the acid. This explains the consistently higher pH values in cases of white rot compared with brown rot (Rypáček 1966), which can be used for the diagnosis of brown rot (cf. Sect. 5.2.8).

White Rot

White rot owes its name to a bleaching of wood (Eaton and Hale 1993; Schmidt 1994). White-rot fungi are able to decompose lignin as well as other cell wall components (polysaccharides), and these processes may take place simultaneously or sequentially (Liese 1970, 1975). Most of the white-rot fungi prefer hardwoods. They can be distinguished from other wood-destroying Basidiomycota because they are able to form phenol-oxidases (Bavendamm 1928). Since there are some differences in the enzyme action of certain white-rot fungi, the group is subdivided into simultaneous white rotters, where decomposition of cellu-

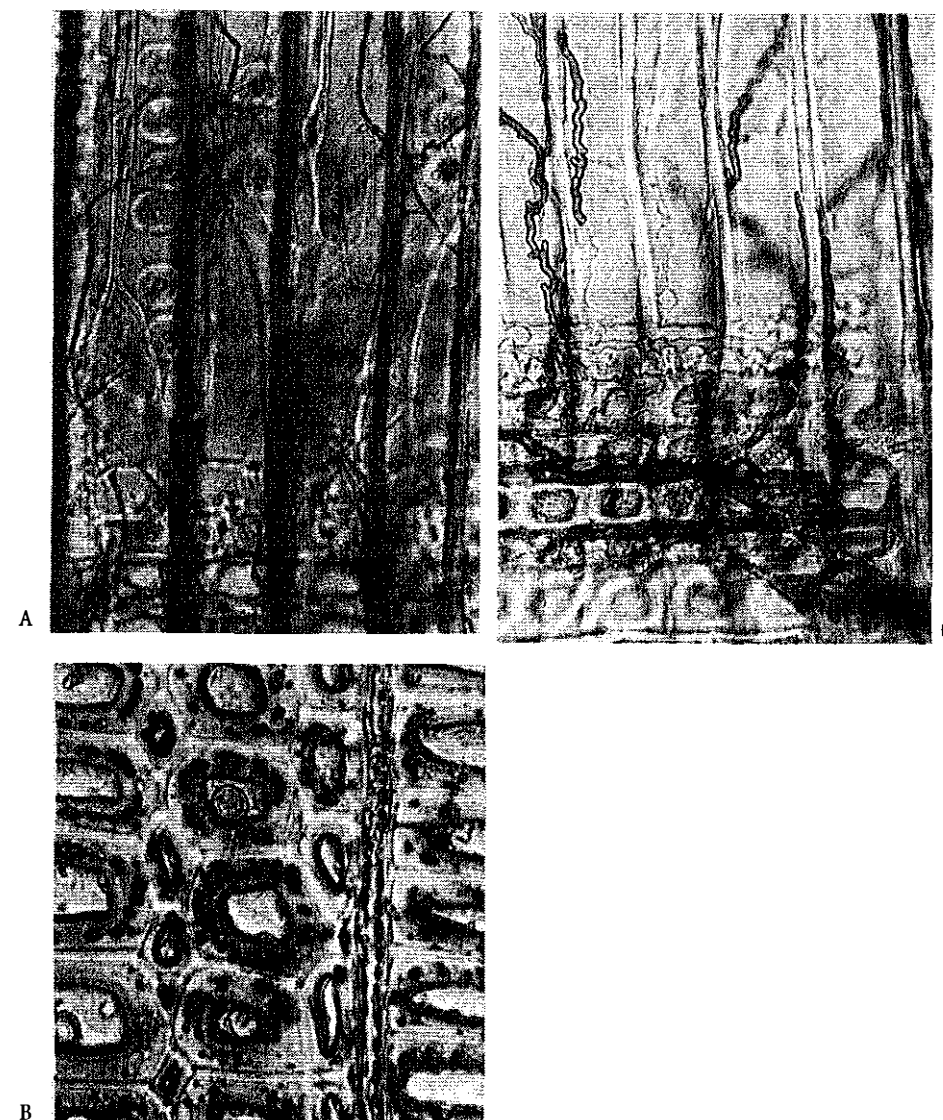


Fig. 5.27. Microscopic view of fungal damage to wood. A Brown rot. B Soft rot. C Blue stain. (A, C Courtesy of B. Weiß; B courtesy of T. Nilsson)

lose and lignin takes place at equal rates, and successive white rotters which, at first, decompose lignin at a higher rate than cellulose. In the older literature the term corrosion rot can be found for simultaneous rotters (Falck and Haag 1926). The lighter color of wood attacked by white-rot fungi (cf. Fig. 5.26B) can be explained on the basis of an increase in the proportion of cellulose. Wood and cell structure persist for a long time, since the decomposition of the cell

wall takes place as a uniform thinning starting at the lumen surface. An attack by white-rot fungi effects a decrease of strength properties and an increase of swelling (Fengel and Wegener 1989). At equal mass loss white rot does not cause as much reduction in strength as brown rot, because the cellulose framework is not attacked as much. White rot causes less loss of dimensional stability, and changes in shape, cracks, and decomposition into cubes do not occur. Increased void space increases the capacity for water absorption, and wood with white rot is spongy when it is wet, and light and soft with loose structure and unchanged volume when dry.

The oxidation of the lignin can initially cause brown, red, or violet discolorations which have led to such terms as "red rot", which is a heart rot in standing coniferous trees caused by *Heterobasidion annosum*, or "red striped rot", which is a decay in felled trees, caused by *Stereum sanguinolentum*. Chemically, red rot is a white rot, but initially the wood is dyed red by lignin decomposition products (Michael et al. 1985). As decomposition proceeds, the stained portions are destroyed and the remaining wood substances are brightened. Depending on the species of fungus, wood can also be discolored in streaks or may take on a marbled appearance (marble rot) by the formation of darker border or zone lines. The formation of dark lines of demarcation in wood with white rot has been attributed to border lines between different fungal species or between genetically incompatible mycelial strains of the same species which are growing in the wood together (Schmidt 1994).

Honeycomb rot, or pocket rot, is a particular type of white rot where decomposition of lignin and cellulose take place successively. Many small, evenly spaced, elongated holes are formed in the earlywood, which are lined with white cellulose remains (e.g., *Phellinus pini*). As the decay progresses, the holes in the earlywood are enlarged and eventually lead to ring shake, where wood separates parallel to the growth rings.

Soft Rot

Soft rot is classified as a separate type of wood decomposition, but the fungi are essentially equipped with enzyme systems similar to those of both brown-rot and white-rot fungi. They are able to degrade polysaccharides and lignin. Soft rot is found in softwoods and hardwoods, and results in various rates of reduction of strength properties. However, their enzyme activity is less, so that cellulose is decomposed at a slower rate than it is by brown-rot fungi. Lignin acts as an inhibitor, and is attacked only in the latter stage of the decomposition. Soft-rot fungi grow inside the wood cell wall. Wood is entered via the rays, and the hyphae grow inside the S2 layer of the secondary cell wall, creating longitudinally aligned cavities. These cavities, which are typical of soft rot termed Type 1, can be observed particularly well in cross sections of the attacked wood (cf. Fig. 5.27B). In soft rot Type 2, which is found especially in hardwoods, the hyphae destroy all cell wall layers, beginning from the lumen and progressing toward the primary wall and middle lamella (Zabel and

Morrell 1992; Schmidt 1994; Daniel and Nilsson 1998). The particular mode of decomposition by soft-rot fungi leads to considerable strength losses even at low mass loss, and in this respect hardwoods are at risk more than softwoods. Some soft-rot fungi even attack wood of high natural durability such as bongossi and teak.

Soft-rot fungi are found in continually damp or wet wood, e.g., in the soil-air transition zone in poles and pilings, in marine structures, railroad ties, cooling towers, open-air museums, and historical buildings with high levels of moisture. The moisture tolerance of soft-rot fungi ranges from dry dormancy to active decomposition at nearly complete water saturation (Schmidt 1994). *Chaetomium globosum* and *Paecilomyces* spp., for instance, did not show any inhibition of their decomposition activity in beech wood at 200% moisture content (Liese and Ammer 1964). Soft rot begins at the surface and proceeds toward the interior of the wood, which darkens in color. In advanced stages of decay the latewood, especially of softwoods, turns almost black, so that the growth ring structure becomes more prominent than in sound wood. Soft rot and sound wood can be found sharply demarcated from each other in the same piece of wood. Wet wood is soft on the outside, musty, greasy without fibrous structure, and of dark brown to black color. When dry, the wood surface shows fine, shallow, longitudinal and cross cracks (cf. Fig. 5.26C). Failures occur without warning and abruptly, e.g., sudden falling over of utility poles or wooden plant supports in agriculture.

In contrast to wood decay by Basidiomycota, where a single species of fungus can destroy wood completely, soft rot may be caused by a number of species taking part in the decomposition, often simultaneously. About 1600 species of Ascomycota and Deuteromycota have been isolated from wood with soft rot which had been installed in a soil-air or soil-water transition zone. Of these, about 120 species have been studied for their decomposition intensity and their effect on the microscopic structure of wood (Eaton and Hale 1993).

Soft-rot fungi are tolerant of the chromium-fluorine salts that are effective against brown-rot and white-rot fungi, but they are sensitive to copper compounds. Wood to be used in contact with soil should therefore be treated with preservatives containing copper compounds, unless creosote can be used (Schmidt 1994).

5.2.5.2

Fungal Stain and Surface Molds

Fungi which cause color changes and associated damage to wood during storage or in service are generally referred to as staining fungi (Eaton and Hale 1993). Numerous species of Ascomycota and Deuteromycota cause surface and internal stains by primarily colonizing the ray parenchyma cells, using freely available carbohydrates such as sugars and starch as nutrients. As a rule they are not able to decompose wood enzymatically and do not have a

significant effect on strength. Referring to blue stain as decay is therefore erroneous, because only a change of color takes place. Rustenburg and Klaver (1992) have assembled lists of many wood species, from various countries, which are very susceptible to infection by staining and mold fungi.

Discolorations of wood can have many causes. In addition to the blue-stain fungi, which produce blue discolorations via optical refraction of the dark brown color of their hyphae, are species of fungi whose colored hyphae also excrete extracellular pigments that sometimes lead to very intensive discolorations (e.g., the green coloration of wood by *Chlorociboria* spp.). Superficial discolorations can also be caused by pigmented spores of mold fungi.

Fungal Stain

The most important fungal discoloration of wood is blue stain, a blue to gray-black discoloration tending to radial stripes (cf. Fig. 5.26D), which can be caused by about 100 different species of fungi. Blue stain can be found in softwoods (sapwood of pine, spruce, fir, and larch), as well as in hardwood (beech) and tropical woods such as ramin (Schmidt 1994).

In contrast to the very fine hyaline hyphae of Basidiomycota, which must be stained to make them visible, the hyphae of blue-stain fungi are brown to black and relatively large in diameter. They enter the longitudinal tracheids by way of the rays (cf. Fig. 5.27C) and grow primarily through the bordered pits from cell to cell. Nutrients, such as soluble carbohydrates, proteins, and fats, are obtained mainly from the ray parenchyma cells and in certain softwoods also from the cells of the resin canals. The wood cell walls are practically unaffected by the fungal enzymes.

Blue-stain fungi are divided into different ecological groups on the basis of their habitat (Grosser 1985; Eaton and Hale 1993; Schmidt 1994). Blue stain in tree stems (primary blue stain) is initiated by spores of fungi such as species of *Ceratocystis* which are introduced into wounds in the bark by wind or by bark beetles. Blue stain in sawn timber (secondary blue stain) caused by attack of fungi occurs after sawing in storage yards when the timber is insufficiently dry or poorly piled. However, a generally valid distinction between blue stains in tree stems and in sawn timber cannot be made. In the literature a distinction is made between sap stain and blue stain. Sap stain is the stain in trees, felled logs and even sawn boards. Blue stain is therefore stain in dead wood in service which has been re-wetted.

Blue stain in painted wood (tertiary blue stain) is often caused by *Aureobasidium pullulans* in worked and painted wood when it becomes moistened again. In this case it is not a case of blue stain which occurred in tree stems or sawn timber but a new infection. Mycelium and sporophores growing on the wood surface can lead to paint flaking and decay if moisture content is allowed to increase further. A knowledge of the biology of blue-stain fungi is

Table 5.11. Overview of some wood-staining fungi

Color of Stain	Staining fungus	Pigment formation	Preferred wood species
Blue	<i>Ceratocystis</i> spp.	Melanine-like pigments in the hyphae	Softwoods
Brown	<i>Discula</i> spp.	Pigments, also extracellular	Softwoods such as pine, spruce, rarely larch, pine sapwood preferred
Red	<i>Fusarium</i> spp.	Naphthoquinone derivatives, also extracellular	Ash, maple, poplar, pine
Pink	<i>Arthrographis</i> spp.	Naphthoquinone derivatives, also extracellular	Softwoods such as pine and spruce, hardwoods such as oak and birch, sapwood and heartwood
Green	<i>Chlorociboria</i> spp.	Xylindein (naphthoquinone derivative), also extracellular	Hardwoods such as beech, maple, red oak, and poplar

important for conservation treatments of wood artifacts. The discoloration of blue stain is irreversible; bleaching has little effect except for some lightening of the color. Wood attacked by blue-stain fungi is characterized by variable permeability to liquids.

Attack of blue stain can be avoided by harvesting live, healthy trees, by winter felling, rapid drying, suitable storage and preventive construction methods or by chemical methods. Millwork such as doors and windows can be treated with preservatives either directly or by incorporation into primers of finishing systems (cf. Chap. 7).

Other types of staining fungi can cause various discolorations in wood (Table 5.11; Rypáček 1966; Scheffer 1973). The pigments formed by several species have been characterized as naphthoquinone derivatives (cf. Sect. 5.2.7). The pigments are formed in the hyphae and also secreted extracellularly. The discolorations may be coffee brown (*Discula* spp.), red (*Fusarium* spp.), pink (*Arthrographis* spp.) or blue-green (*Chlorociboria* spp.). The discolorations are irreversible and often very persistent.

Surface Molds

Discoloration of wood can also be caused by mold fungi which colonize unfinished and painted wood surfaces when air humidity and wood moisture content are high. The mostly colorless hyphae do not affect wood strength

since there is almost no penetration into the wood, and they also do not secrete any pigments. Surface discoloration is caused primarily by the large quantities of colored spores which are formed.

The mold fungi do not represent a taxonomic entity of a systematic group, but are composed of fungi within the Ascomycota and Deuteromycota. In many cases the fast-growing mold fungi are the first wave of attack, followed by staining and decay fungi as wood destruction progresses. They possess a broad spectrum of physiological capabilities, whereby they can colonize various materials and can damage not only wood surfaces but also varnishes and paints. Mold fungi have a characteristic moldy odor, and some species can have detrimental effects on health (cf. Sect. 5.2.10). Florian (1997) gives an overview of surface molds on various heritage objects.

5.2.6

Wood-Destroying Fungi

5.2.6.1

Basidiomycota

Brown-Rot Fungi (Brown Rotters)

Coniophora puteana (Schum.: Fr.) P. Karsten

Synonyms and Common Names. *Coniophora cerebella*, cellar fungus.

Systematics. Hymenomycetes, Aphyllophorales, Coniophoraceae.

Distribution. Temperate zones of Australia, Europe (Germany, United Kingdom), USA.

Occurrence. Mainly in wood in buildings; can also occur outdoors; widespread in mines; attacks mostly softwoods.

Type of Decay. Brown rot largely in the form of very small, shiny cubical rot.

Distinguishing Features. Surface mycelium not well developed, inconspicuous, delicately fluffy, yellowish; strand mycelium very fine, brown to black, resembles spider webs, firmly attached to the wood and difficult to detach; fruit bodies, which are rarely formed, are mostly elongated, sometimes oval, resemble crusts and are hard to detach, about 1–3 mm thick, fruit layer (hymenium) dark olive-brown with coarse warts when aged, and surrounded by a white to pale yellow margin about 10 mm wide (Fig. 5.28A); spores are yellowish, elliptical $10\text{--}16 \times 6\text{--}8\mu\text{m}$; hyphae are $2\text{--}10\mu\text{m}$ in diameter in cultures, with double and multiple clamp connections, but lacking clamp connections inside wood.

Growth and Decay Conditions. Optimal conditions at 23°C and wood moisture content of 50–60%; can grow very fast at 6–7 mm/day; is a “wet rot” which becomes inactive at low levels of wood moisture content.

Special Characteristics. Green building timbers are attacked very quickly (new construction fungus); outdoors it may occur together with soft rot; in building timbers associated with attacks by *Xestobium rufovillosum*, the death watch beetle; the most common decay fungus in buildings in the United Kingdom; high threshold for biocides such as zinc and cadmium compounds in wood preservatives (Eaton and Hale 1993). Duncan and Lombard (1965) describe *Coniophora puteana* as one important fungus associated with principal decays in wood products in the United States.

Serpula lacrymans (Wulfen: Fr.) Schroeter

Synonyms and Common Names. *Serpula lacrimans*, *Merulius lacrymans*, *Merulius domesticus*, “the true dry rot fungus”.

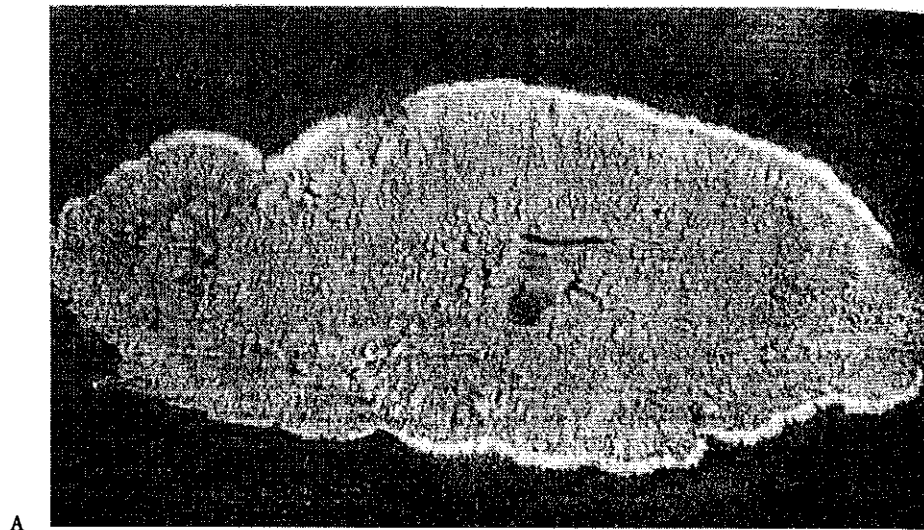
Systematics. Hymenomycetes, Aphyllophorales, Coniophoraceae.

Distribution. Temperate and cooler zones in Africa, Australia, Europe (Germany, United Kingdom, Denmark), India, Japan, Russia; not common in North America.

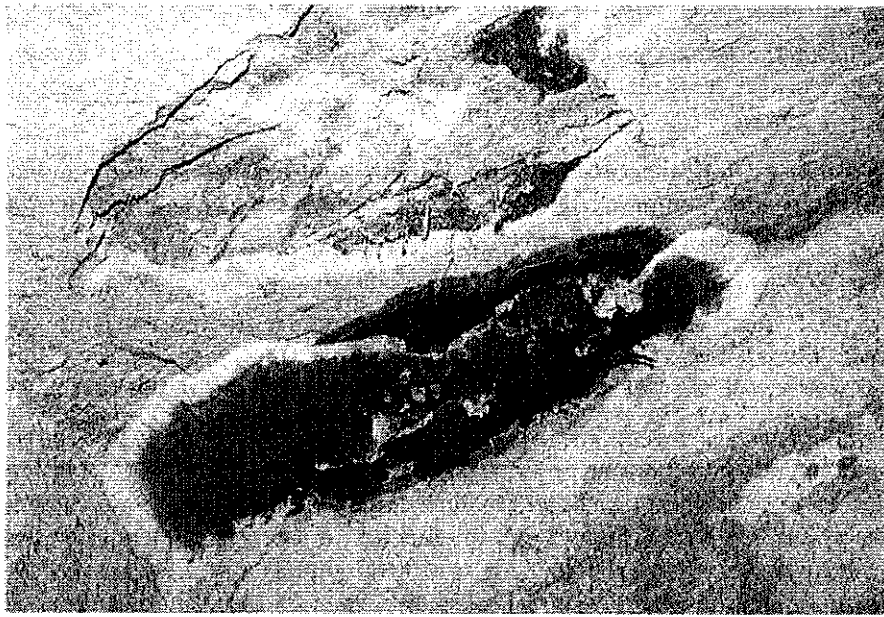
Occurrence. Typical decay fungus for wood in buildings; is often found in old buildings with basements, in churches, and half-timbered buildings; attacks mostly softwoods, seldom hardwoods.

Type of Decay. Brown rot; wood breaks up into relatively large cubes (side length 50 mm) compared with other brown rotters; fracture surfaces are short-fibered and smooth; in damp conditions mycelium forms on the wood surface; wood becomes deformed, the surface resembling a washboard.

Distinguishing Features. Surface mycelium is white, whitish gray to gray, often with lemon yellow or wine red interference spots, forms coatings resembling fleece, cotton, skins, or kid leather which can be pulled off the wood. Strand mycelium is typically up to 8 mm in diameter and several meters long; the strands are gray and limp and can grow through masonry; they are flexible when wet and break with a cracking sound when dry. Fruit bodies are oval and flat or crusty, 100–1000 mm in diameter and can be readily detached; the fruit layer (hymenium) is olive brown, in folds, up to 20 mm thick, and is surrounded by white, warty additional growth 10–40 mm wide, resembling a fried egg (Fig. 5.28B). Older fruit bodies may be attacked by mold fungi. Spores are rust brown, elliptical with a pointed extension at one end, $9\text{--}12 \times 4\text{--}6\mu\text{m}$. Spore formation is positively influenced by light. Hyphae in wood are $2\mu\text{m}$ in diameter on average, and form medallion clamps. Water drops may form on their ends, hence the name lacrymans (the “teary” one).



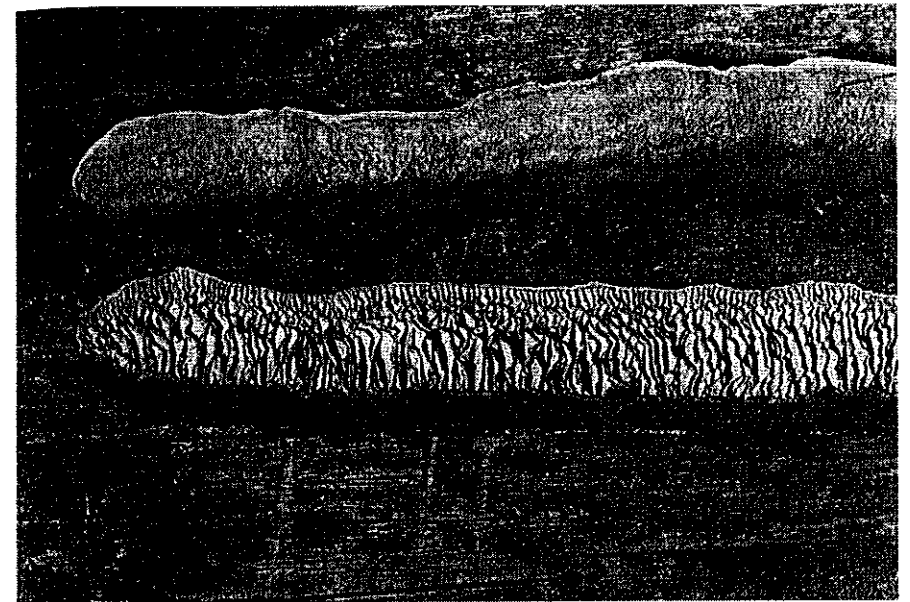
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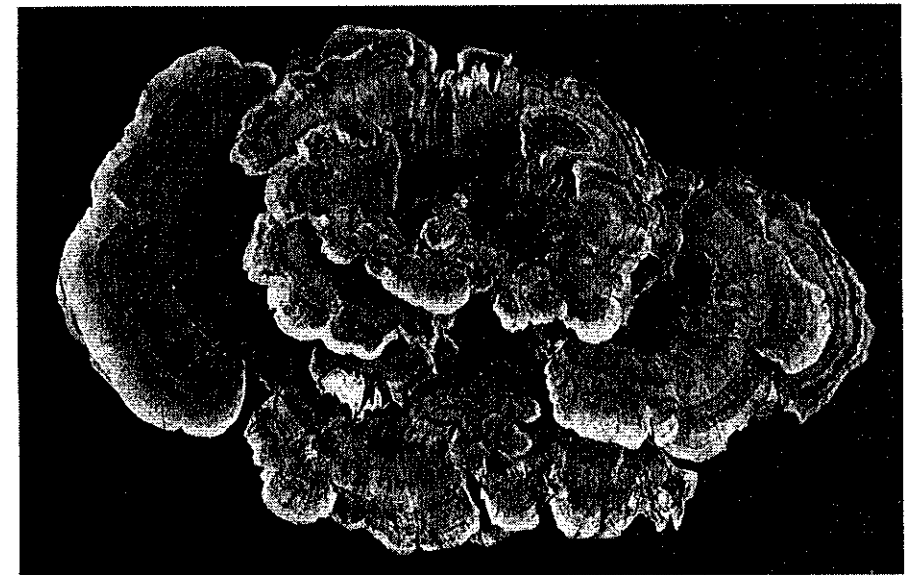
B

Fig. 5.28. Fruit bodies of wood-decay fungi. A *Coniophora puteana*. B *Serpula lacrymans*. C *Gloeophyllum* spp. D *Trametes versicolor*. (A Courtesy of G. Binker)

Growth and Decay Conditions. Optimum temperature at 21°C, above 28°C growth ceases; a wood moisture content of 40–60% is required only for spore germination and in the initial stages of development; the fungus can transport water, sugar, nitrogen compounds and inorganic nutrients especially via vascular hyphae in the strands to dry wood (Eaton and Hale 1993). Growth can be very rapid at 9 mm/day, especially in stagnant air.



C



D

Fig. 5.28. Continued

Special Characteristics. *Serpula lacrymans* is considered the fungus that causes the greatest economic damage to buildings in Europe. Because of its hidden growth, active infestation is often not discovered for a long time. In buildings with active attack a typical fungus odor can be present. Important causes of attack are construction and other defects which lead to elevated wood moisture content. Since the fungus is capable of transporting water and

therefore can attack wood with a moisture content of less than 20%, it has been termed "dry rot" and "water conducting" fungus. In Europe *Serpula lacrymans* first appears in the literature at about the time bricks and mortar were added to wood in house construction (Bech-Andersen and Elborne 1999), which may be due to its dependence on divalent metal ions such as calcium available from mortar (cf. Physiology). The fungus may be especially rare in the USA because so many houses are built entirely of wood. *Serpula lacrymans* is very sensitive to heat and to biocides. Remedial treatments have to be carried out very carefully because of its biological characteristics. In addition to eliminating the source of moisture in the building, affected wood members must be removed to 1 m along its length beyond visible attack. Organic materials must be removed within a radius of 1.5 m of the decayed area (DIN 68800 Part 4/1992). Since the fungus can also spread over inorganic materials, masonry must be included in the treatment. It is important that adjacent rooms and living quarters are also investigated (Jennings and Bravery 1991). In Europe hot air treatments are increasingly used, especially in historic buildings in order to save building members (cf. Chap. 9). The possibility of induced thermotolerance of *Serpula lacrymans* following exposure to sublethal temperatures has been raised (White et al. 1995). More sophisticated control methods such as environmental control or biocontrol are necessary (Palfreyman et al. 1995). For viability and genetic studies see Section 5.2.8. Investigations of the viability of the hyphae of *Serpula lacrymans* with fluorescein-diacetate (FDA) have shown that individual hyphae in strand mycelium can survive for months under dry conditions (Huckfeldt et al. 2000). This fungus is especially dangerous because of its capacity for extended periods of dry dormancy. The asexual conidia in particular could be identified as the possible cause with the aid of the FDA test (cf. Sect. 5.2.8). Detailed discussions of *Serpula lacrymans* can be found in Seehann and Hegarty (1988), Schmidt and Moreth-Keberník (1991), Jennings and Bravery (1991), Palfreyman et al. (1995) and Ridout (1999).

***Antrodia vaillantii* (DC.: Fr.) Ryv.**

Synonyms and Common Names. *Poria vaillantii*, *Fibroporia vaillantii*, white pore fungus, mine fungus.

Systematics. Hymenomycetes, Aphyllophorales, Coriolaceae.

Distribution. Widely distributed in temperate as well as tropical zones of Africa, Asia, Australia, Europe, but less well known in USA.

Occurrence. Typical fungus in mines and in buildings with very damp conditions, in storage yards, and especially with ground contact in the soil and air transition zone; attacks mainly softwoods.

Type of Decay. Brown rot; cubical cracks are not as deep as with *Serpula lacrymans* but cubes are larger than with *Coniophora puteana*.

Distinguishing Features. Surface mycelium is pure white, never with yellow spots, and growth resembles ice crystals. Strand mycelium is white, stringy, smooth, and remains flexible when dry (in contrast to *Serpula lacrymans*). Strands can grow over masonry, but hyphae cannot penetrate well through it. Can be detached from its substratum. Fruit bodies are only rarely found in buildings; they form white spots, knobs or crusts; the fruit layer (hymenium) has pores of irregular, often angular shape and size (0.3–1.5 × 0.2–0.6 mm). Spores are hyaline, ellipsoid to kidney-shaped (Langendorf 1988), 4.5–8 × 2.5–5 µm. Hyphae are 2–5 µm in diameter; will form medallion clamps occasionally.

Growth and Decay Conditions. Temperature requirements are higher than for *Serpula lacrymans* and *Coniophora puteana* (Bech-Andersen 1995); optimal conditions are 26–27 °C and a wood moisture content of 35–45%; is a "wet rot" which can survive long periods of dormancy due to dryness.

Special Characteristics. The common name white pore fungus is also applied to other species of brown rot attacking softwoods, but they have the same moisture requirements. They merit the same concerns in wood preservation, so that an exact identification is not necessarily required. Separation of the pore fungi is possible by electrophoresis (Schmidt and Moreth-Keberník 1993). According to Schmidt (1994), *Antrodia vaillantii* has a high tolerance to preservatives containing copper because of its secretion of oxalic acid. Tolerance to arsenic has also been reported.

***Daedalea quercina* (L.: Fr.) Pers**

Synonyms and Common Names. *Lenzites quercinus*, *Trametes quercina*, maze gill.

Systematics. Hymenomycetes, Aphyllophorales, Coriolaceae.

Distribution. In temperate zones worldwide: Europe, Caucasus, North and Central Asia, North America, North Africa.

Occurrence. Typical decay fungus of hardwoods; attacks predominantly oak wood used outdoors and exposed to the weather, such as in wooden boats, exposed beams, railroad ties, bridge timbers or piling. Occasionally it is found in window frames and half-timbering in buildings.

Type of Decay. Causes intensive brown rot in the otherwise durable heartwood of oak or chestnut. The affected wood turns gray at first and later brown.

Distinguishing Features. Surface mycelium is absent because it is a typical substrate fungus (Grosser 1985); but sometimes white to yellowish sheets of mycelium can be found inside checks or splits. Fruit bodies are bracket-shaped with faint zones, uneven brownish-gray surfaces and distinct edges. The underside has grayish-yellow to wood-colored, coarse, branched lamel-

lae that form labyrinthian passages (hence the name maze gill). In the zone at the edge of the cap are round pores. The bracket is corky, and can reach an age of 10 years. In the absence of light, fruit bodies are formed which are crusty or knobby. Spores are ellipsoid, flattened on one side, $5.5\text{--}7.5 \times 2.5\text{--}3\text{ }\mu\text{m}$. Hyphae are hyaline, with clamp connections.

Growth and Decay Conditions. Optimum temperatures are $23\text{--}29\text{ }^{\circ}\text{C}$ (Langendorf 1988), optimum moisture content about 40%; the fungus lives primarily as a saprophyte.

Gloeophyllum spp.

Three species of this genus are of importance; they are discussed together because of their similar biology: (1) *Gloeophyllum abietinum* (Bull.: Fr.) P. Karsten; (2) *G. sepiarium* (Wulfen: Fr.) P. Karsten; (3) *G. trabeum* (Pers.: Fr.) Murr.

Synonyms. (1) *Lenzites abietina*, (2) *Lenzites sepiaria*, (3) *Lenzites trabea*.

Systematics. Hymenomycetes, Aphyllophorales, Coriolaceae.

Distribution. Cosmopolitan; Australia, Asia, Europe (but limited occurrence in the United Kingdom), New Zealand, North America (are major decay fungi in buildings in California), South Africa (Eaton and Hale 1993).

Occurrence. These are the most severe wood-destroying fungi on felled logs, stored timber, wood in use and softwood that has been rewetted, such as utility poles, fencing, railroad ties, roof framing, mine timbers, bridge timbers, cooling tower parts, and wooden boats. Trapped moisture due to poor construction practices makes *Gloeophyllum* spp. the most important decay fungus in softwood windows (Grosser 1985) and is therefore also referred to as the "wooden window fungus". Occurrence is often species-specific, i.e., (1) in spruce and true fir, (2) in pine, and (3) in softwoods and hardwoods.

Type of Decay. Brown rot beginning unevenly in the interior of the wood, leaving the surface layers mostly unaffected. The wood separates along the growth rings, with many cubical cracks, and emits a sweet, tar-like odor. Wooden members undergo little overall deformation. When fruit bodies become evident, the wood is usually already largely destroyed.

Distinguishing Features. Surface mycelium is not found on areas exposed to light. In darkness and high relative humidity occasionally umber-colored, dry, felted mycelium with strand formation occurs (similarly in pure culture); it is difficult to detach from the substratum. Substratum mycelium is white and fluffy. Fruit bodies in light conditions, in their normal or typical form, are usually 1 year old. They can be shaped like strips, brackets, or roof tiles or can occur in rows (cf. Fig. 5.28C). The substance of the fruit bodies is leathery and tough but flexible. Most often they are found at drying checks or splits. The fruiting layer (hymenium) on the underside usually has lamellae

resembling gills (hence the common name gill fungi) oriented with the long axis of the fruit body which are connected pore-like at the edges. The upper surface of the brackets is usually marked with concentric zones and is furrowed. The three species are distinguished by the color and number of lamellae or gills: in *G. abietinum* they are gray with light borders, 8–12 lamellae/10 mm, smaller than in *G. sepiarium*, often resupinate (cf. Fig. 5.28C) (i.e., grown with its under side attached to the wood); in *G. sepiarium* they are light to dark brown with reddish borders, 12–20 lamellae/10 mm; and in *G. trabeum* cinnamon to ochre with irregular light borders, 20–40 lamellae/10 mm. In dark, damp conditions various forms of abnormal fruit bodies may be found. They are felt-like, soft, dark brown structures in the shape of cones, mesentery-like pads, small trees or antlers. Spores are hyaline, cylindrical, in *G. abietinum* $5.8\text{--}13 \times 3\text{--}4.5\text{ }\mu\text{m}$. Hyphae are hyaline, with clamp connections, in *G. abietinum* $2\text{--}5\text{ }\mu\text{m}$ in diameter.

Growth and Decay Conditions. Optimum conditions are temperatures of $26\text{--}35\text{ }^{\circ}\text{C}$ and wood moisture contents of 40–60%; they are typical "wet rot" fungi which develop especially well in the presence of trapped moisture.

Special Characteristics. Due to their heat resistance and ability to survive in dry conditions, *Gloeophyllum* spp. can survive in wood windows heated and dried by direct exposure to sunlight (Theden 1972). According to Eaton and Hale (1993), *G. trabeum* can survive for 10 years in wood with 12% moisture content. Attack of very wet wood is also possible. In structures in California *Gloeophyllum* spp. were the fungi most frequently isolated from decay in wood exposed above-ground. The same fungi were present in the green lumber from which the buildings were built (Wilcox and Dietz 1997). This suggested the possibility that most of the fungi responsible for structural decay were present in the green lumber when the structure was built. *Gloeophyllum* spp. at times can be noticeably tolerant to wood treated with creosote, PCP or CCA (Schmidt 1994).

Lentinus lepideus (Fr.: Fr.)Fr.

Synonyms and Common Names. *Neolentinus lepideus*, stag's horn fungus, scaly Lentinus.

Systematics. Hymenomycetes, Aphyllophorales, Polyporaceae.

Distribution. Temperate zones of the Northern and Southern Hemispheres; widespread in Europe, North America, and Russia.

Occurrence. Timber storage yard rot in softwoods, mainly in railroad ties, utility poles, piling, bridge timbers (at soil/air/water contact), mine timbers, and in buildings in very moist areas such as beam ends.

Type of Decay. Intensive brown rot in otherwise durable heartwood of pine. Damp wood has vanilla-like odor, or that of balm of Peru, sweet balm, or perfumed resin (Bech-Andersen 1995).

Distinguishing Features. Surface mycelium is whitish resembling ice crystals, and is formed rarely, only at high moisture content of substrate and air. Strand mycelium is brownish, resembling ice crystals, up to 3 mm thick. Substrate mycelium is whitish in destroyed wood, and is also formed only at high relative humidity. The normal or typical light form of the fruit body has a typical mushroom-like cap, is ivory with dark scales on the upper surface (hence the name scaly *Lentinus*), leathery, and tough. The underside has yellow lamellae which extend down the stem and have a finely serrated edge. The abnormal form of the fruit body produced in the dark is antler-like with white tips, hence the name stag's horn fungus, and is sterile. Spores are hyaline, elongated ellipsoid with a smooth surface, $10\text{--}15 \times 4\text{--}5 \mu\text{m}$ (Langendorf 1988). Hyphae are colorless, irregularly divided, with clamp connections and medallion clamps, $1\text{--}2.5 \mu\text{m}$ wide (Bech-Andersen 1995).

Growth and Decay Conditions. At optimum temperatures of $27\text{--}33^\circ\text{C}$ and optimum wood moisture content of 30–60% a growth rate of 5.3–10 mm/day is reached.

Special Characteristics. *Lentinus lepideus* is especially dangerous because of its high resistance to heat and dryness, so that it can also occur in wood exposed to direct sunlight such as railroad ties, exposed beam ends, and roof timbers. Since the fungus mainly causes brown rot in the heartwood, it can destroy the heartwood of pine utility poles and railroad ties which cannot be treated with preservatives. The fungus is highly resistant to coal tar preservatives (e.g., creosote), which should be considered in the treatment of railroad ties, but it is very sensitive to other biocides such as sodium fluoride and borates. *Lentinus lepideus* can also be found in wood-based materials (Eaton and Hale 1993).

***Paxillus panuoides* (Fr.: Fr.)Fr.**

Synonyms and Common Names. *Tapinella panuoides*, stalkless *Paxillus*, mine fungus.

Systematics. Hymenomycetes, Agaricales, Paxillaceae.

Distribution. Temperate zones.

Occurrence. Timber storage yard rot, but also in very moist wood in use, such as railroad ties, bridge timbers, wet balcony members; is also found in mines below ground (cf. common name), in basements, stables, and wet rooms.

Type of Decay. Typical brown rot in softwoods, especially in pine; the infested wood turns yellow at first, later orange brown to red brown (typical distinguishing feature), and only then forms cubicle cracks where the longitudinal cracks are more pronounced than the perpendicular ones.

Distinguishing Features. Surface mycelium is pale yellow to light ochre, thin, and cannot be detached from the wood. Strand mycelium is clay colored, the

diameter of string and resembles ice crystals (never blackish, in contrast to *Coniophora puteana*). Fruit bodies are clay colored and shell to fan shaped, and have a form of brim with rolled-in edges, stalkless (cf. common name) or with a short, eccentric stalk laterally attached to the wood. On the underside are closely spaced, forked, clay colored lamellae which are connected at the base by cross strips and are often strongly crimped. Fruit bodies are soft and fleshy, but fragile when dry. They occur throughout the year. Even in darkness, normally shaped, spore forming fruit bodies are produced, a capability possessed by few fungi, which permits *Paxillus panuoides* to spread rapidly inside mines through spore emission. Spores are colorless to pale yellow, mildly elliptical with a smooth surface, measuring $4.5\text{--}6 \times 3\text{--}4 \mu\text{m}$ (Langendorf 1988). Hyphae are colorless or brownish, with clamp connections and are $4\text{--}6 \mu\text{m}$ in diameter (Bech-Andersen 1995).

Growth and Decay Conditions. *Paxillus panuoides* is a "wet rot" fungus which requires 50–70% wood moisture content and a temperature of $23\text{--}30^\circ\text{C}$. It is capable of going into dormancy in periods of drought.

Special Characteristics. In buildings *Paxillus panuoides* often occurs together with *Coniophora puteana* because of similar physiological growth conditions. As early as 1793 Alexander von Humboldt described cases of attack by *Paxillus panuoides* in timbers inside mines in Saxony.

White-Rot Fungi (White Rotters, Simultaneous Rotters)

***Donkioportia expansa* (Desm.) Kotl. & Pouzar**

Synonyms. *Poria megalopora* (Persoon) Cooke, *Poria expansa*, *Fomes expansus*, *Phellinus megaloporus*.

Systematics. Hymenomycetes, Aphyllophorales, Coriolaceae.

Distribution. Europe, mainly Belgium, France, and England, but recently also in Germany (Ritter 1992; Kleist and Seehann 1999); in North America in Ohio and in Ontario.

Occurrence. Mostly in buildings with long-standing defects in roof and ceiling construction. Occurs in beams and other structural members in basements and floor systems, in parquet flooring and in windows. Decay is limited to moist zones, in hardwoods, largely in oak even in the heartwood, and especially in ceiling beams in half-timbered buildings (Ritter 1992); it can also attack other wood species (Buchwald 1986; Kleist and Seehann 1999).

Type of Decay. Causes a fibrous white rot, which often cannot be diagnosed until the wood is split open. The wood appears decayed in stripes, where white, decomposed fibers alternate with brown zones and sound wood (Grosser 1985). Oak heartwood is destroyed completely, leaving only the wood rays. If the fungus attacks softwood the surface is often left intact, so that

infestation is often not discovered (Kleist and Seehann 1999). Although a white-rot fungus, *Donkioporia expansa* produces black zones between substrate and fungal mycelium caused by the deposition of melamines.

Distinguishing Features. Surface mycelium inconspicuous, located between the wood and fruit body, attached firmly, yellowish white. Strand mycelium is absent, and substrate mycelium is not macroscopically visible. Fruit bodies are perennial, woody, brownish, very large with a diameter of 150–250 mm and a thickness of 25 mm, always spread out with one or more layers of tubes, resupinate. On vertical substrates fruit bodies with wavy or step-like protruding tubes can also be found. The pores are gray to ochre brown; fracture surfaces of tubes are yellow to tobacco color (Grosser 1985). Characteristic are the honey-brown, gummy drops which form at the edge of the fruit bodies and leave black hollows after they dry out (Kleist and Seehann 1999). Spores are hyaline, ellipsoid, $4.5\text{--}5.5 \times 3.2\text{--}3.7\mu\text{m}$. In wood $1\text{--}4\mu\text{m}$ thick, hyaline to yellowish clamp hyphae can be found (Cartwright and Findlay 1969).

Growth and Decay Conditions. Optimum temperature is 27°C ; the fungus only occurs in very moist wood at a moisture content of 40–60%. Even very high wood moisture contents of as much as 150%, e.g., in cooling towers, do not inhibit growth (van Acker and Stevens 1996). In regard to intensity of destruction and ecological behavior, *Donkioporia expansa* is comparable to *Coniophora puteana* and *Antrodia vaillantii*. Among the decay fungi in buildings, *Donkioporia expansa* is in second place in Germany and third in Belgium (Kleist and Seehann 1999).

Special Characteristics. With its porous surface, *Donkioporia expansa* is reminiscent of *Antrodia vaillantii*, but the pores are not white but gray to ochre brown (Kleist and Seehann 1999). Attacked wood is readily colonized by species of the Anobiidae family, especially by *Xestobium rufovillosum*. The best known case is the roof structure of the Palace of Versailles, which was documented in detail in a 1922 publication (Grosser 1985). Since this fungus does not produce any strand mycelium, it cannot spread to neighboring dry wood; it therefore depends on areas which are moistened directly. Control treatments of affected wood members should be the same as for other “wet rot” fungi.

Trametes versicolor (L.: Fr.) Pilát

Synonyms and Common Names. *Polyporus versicolor*, *Coriolus versicolor*, *Polystictus versicolor*, many zoned polypore, varicolored bracket, rainbow fungus.

Systematics. Hymenomycetes, Aphyllophorales, Coriolaceae.

Distribution. Cosmopolitan, especially in temperate zones.

Occurrence. Timber storage yard rot, found in wood in use outdoors without soil contact, in piled lumber, railroad ties, piles, wood used in gardens; it

attacks hardwoods, especially beech and oak. The fungus is sometimes found in mines but not in buildings.

Type of Decay. Causes white rot of the simultaneous rot type. In the initial stages black zone lines may be formed, resulting in a marble-like appearance (cf. Sect. 5.2.5.1).

Distinguishing Features. Surface mycelium is not formed (substrate fungus). Fruit bodies (cf. Fig. 5.28D) are annual brackets up to 3 mm thick and 60 mm in diameter, usually arranged above each other like roof tiles. The upper surface is velvety with a silky luster, bearing concentric zones of various coloration (cf. the name) such as yellowish, brownish, reddish, gray, blackish; the outermost zone is often whitish. On the underside are whitish pores of 0.2–0.3 mm diameter (Langendorf 1988). The initial color variations are only faintly recognizable when the fruit bodies have dried out. Spores are cylindrical, measuring $6\text{--}7 \times 1.5\text{--}2\mu\text{m}$ (Bech-Andersen 1995). Hyphae are thin-walled, $1.5\text{--}3.5\mu\text{m}$ wide, with clamp connections (Bech-Andersen 1995).

Growth and Decay Conditions. Optimum growth conditions are temperatures of $24\text{--}33^\circ\text{C}$ and a wood moisture content of 40–45%, but the latter may also be higher (80–120%; Bech Andersen 1995). It is capable of dry dormancy.

Special Characteristics. *Trametes versicolor* is sensitive to inorganic wood preservatives such as those containing copper or zinc compounds, but is more resistant to organic biocides. It is a typical decay fungus for stored roundwood.

Schizophyllum commune Fr.: Fr.

Systematics. Hymenomycetes, Polyporales, Schizophyllaceae.

Distribution. Cosmopolitan, in temperate and in tropical zones.

Occurrence. In stored hardwood containing bark, mainly in beech; common in utility poles and in cooling towers, but not in buildings. In tropical conditions wood is attacked very quickly; softwoods and even woods of high natural durability, as well as wood-based materials can be attacked (Eaton and Hale 1993).

Type of Decay. Typical white rot.

Distinguishing Features. Surface mycelium is not formed (substrate fungus). Fruit bodies are small (10–40 mm), shell-shaped, leathery brackets, and usually occur in large numbers. The upper surface is light gray, felt-like, and zoned, and the edges are rolled inward. The underside does not have a true hymenophore, but violet pseudolamellae which are split. The lamellae can undergo hygroscopic movement in response to changes in relative humidity. Spores are hyaline, smooth, and cylindrical measuring $3\text{--}6 \times 1\text{--}2\mu\text{m}$ (Langendorf 1988); data for hyphae not available.

Growth and Decay Conditions. Requires medium to high wood moisture content and optimum temperatures of 30 °C, and can survive strong exposure to direct sunlight and temporary drying of the wood by dormancy.

Special Characteristics. *Schizophyllum commune* is a typical decay fungus in stored roundwood.

Phanerochaete chrysosporium Burds.

Systematics. Hymenomycetes, Aphyllophorales, Corticiaceae; produces imperfect fruiting forms: *Chrysosporium lignorum*, *Sporotrichum pulverulentum* (Eaton and Hale 1993).

Distribution. Widely distributed in the USA, in Europe, especially the United Kingdom, and in Russia.

Occurrence. In chip piles of the pulp industry and wood-based materials, in both softwood and hardwood.

Type of Decay. Typical white rot.

Distinguishing Features. Fruit bodies are bark-shaped, and spores are numerous.

Growth and Decay Conditions. Optimum growth conditions at a temperature of 39°C; it is a very heat-tolerant species with strong mycelial growth even at 40°C, and the maximum temperature is only reached at 50°C.

Special Characteristics. The physiology and biochemistry of this fungus have been studied in detail in view of its cellulose, hemicellulose, and lignin degradation (Zabel and Morrell 1992; Eaton and Hale 1993; Schmidt 1994; Bruce and Palfreyman 1998). *Phanerochaete chrysosporium* is being tested in the USA for biological pulp production. It also attacks persistent environmental poisons like DDT, which is of importance for the decontamination of wood waste (Schmidt 1994).

Pleurotus ostreatus (Jacq.: Fr.) Kummer

Common Names. Oyster fungus, oyster mushroom.

Systematics. Hymenomycetes, Polyporales, Polyporaceae.

Distribution. Cosmopolitan.

Occurrence. Saprophyte mainly on hardwoods, especially beech; in recent years also in wood-based materials such as plywood and particleboard; has also been found in buildings.

Type of Decay. Typical white rot.

Distinguishing Features. Forms leathery, white substrate mycelium in decayed wood (Bech-Andersen 1995). Fruit bodies are cap-shaped with a lateral stem;

the caps are shaped like shells or tongues, and are blue-gray, yellow to gray-brown. The lamellae on the underside of the cap are whitish to light gray and extend down the stem. Spores are colorless, cylindrical, and smooth, measuring $8-12 \times 3-4.5 \mu\text{m}$ (Langendorf 1988). Hyphae inside the wood are colorless, thin-walled, and $1-3 \mu\text{m}$ wide (Bech-Andersen 1995).

Growth and Decay Conditions. Optimum temperatures are at 27°C, at which mycelium can grow up to 7.5 mm/day; it is a "wet rot" fungus requiring wood moisture contents up to 80% (Bech-Andersen 1995); the fungus is not tolerant to dry conditions, i.e., the fleshy fruit bodies lose their function when they dry out.

Special Characteristics. The oyster mushroom is edible and is cultivated for food. Flooring contaminated with poisonous substances can sometimes be decontaminated with straw infected with *Pleurotus ostreatus* (Schmidt 1994).

5.2.6.2

Ascomycota and Deuteromycota

Soft-Rot Fungi

Chaetomium globosum Kunze

Systematics. Ascomycota, Pyrenomycetes, Chaetomiaceae.

Distribution. Cosmopolitan.

Occurrence. Typical terrestrial soft rot. Wood in use outdoors, directly on or just below the soil surface, is especially at risk. Cultural property exposed to the elements is also often destroyed by this fungus. Occurs in both softwoods and hardwoods, and in soil contact can also attack woods of high natural durability such as bongossi and teak.

Type of Decay. Causes typical soft rot of Type I. Fungal growth takes place mainly in the S 2 layer of wood cells, which is only visible microscopically. When moist, the wood is greasy and colored black; when dry the latewood is darker. Fractures of the wood are shell-shaped. Severely damaged wood is sharply demarcated from sound wood.

Distinguishing Features. Mycelium on the wood surface is stringy. Fruit bodies are dark green, bottle-shaped, about 1 mm long (perithecia) with wavy hairs on the surface which can be seen with a hand lens.

Growth and Decay Conditions. Requires a wood moisture content above 80% (Langendorf 1988) and aerobic conditions. At 30°C *Chaetomium globosum* causes serious strength losses (Gersonde and Kerner-Gang 1976). In birch, for instance, after 2-week exposure and a mass loss of 6%, the impact bending strength was reduced by 59%. This fungus exhibits very high cellulolytic activity which is influenced by the nature of the lignin in a given species of wood.

It has very high tolerance to wood moisture, and even a moisture content of 200% does not inhibit its destructive activity, provided there is still sufficient air space to provide aerobic conditions. The fungus can grow on substrates with pH in the range from 3–11.

Special Characteristics. *Chaetomium globosum* has been used for many years as a standard fungus for testing preservatives against soft rot. Its spores remain viable for many years. The fungus is more resistant to chromium-fluorine salts, which are effective against brown-rot and white-rot fungi, but is sensitive to copper compounds.

Other Species of Soft-Rot Fungi

It is impossible to list all other species of fungi which cause soft rot, but compared with *Chaetomium globosum*, their growth rate is much lower. Often several species participate simultaneously in the wood destruction.

Phialophora spp. (also known as *Lecythophora* spp.) of the Deuteromycota are common in softwoods in contact with the ground, but also in wood in use without such contact.

Monodictys spp. of the Deuteromycota are widespread in hardwood and softwood in fresh water rivers and in cooling towers. Their growth rate is very low.

Humicola spp. of the Deuteromycota are common in temperate and cold coastal regions. The genera *Paecilomyces* and *Thielavia* are also found relatively often.

5.2.7

Staining Fungi and Surface Molds

5.2.7.1

Ascomycota and Deuteromycota

Sap-Stain Fungi on Freshly Felled Timber

Ceratocystis coerulescens (Münch) Bakshi

Systematics. Ascomycota, Plectomycetes.

The genus *Ceratocystis* contains 59 known species of the perfect state. Imperfect states of this genus are also known, e.g., *Chalara* spp., which are classified with the Deuteromycota, Hyphomycetes, and also colonize lumber (Eaton and Hale 1993).

Ophiostoma spp. is considered an independent genus with the imperfect state *Graphium* spp.

Distribution. Temperate zones.

Occurrence. In freshly felled logs (primary blue stain) or poorly stored lumber (secondary blue stain), often in damaged forest areas; rarely found in wood in buildings; occurs mainly in softwoods.

Type of Damage. The sapwood is stained in blue-black streaks, but the heartwood is not affected. The attack starts from the wood surface, and penetrates quickly into the interior via the rays. Wood strength is hardly affected, but infestation can lead to uneven penetration of wood preservatives, can slow down the drying process, and the change in appearance can seriously devalue premium grades of softwood lumber.

Distinguishing Features. Substrate mycelium can be recognized under the light microscope as fairly thick, brown septate hyphae 1–8.5 µm wide (Bech-Andersen 1995). They are visible, without the application of stains, in the ray parenchyma cells and occasionally in longitudinal tracheids and wood fibers. The hyphae penetrate wood through the pits, or bore through the cell wall. Characteristically, hyphae are swollen before entering the wall, but narrow down to penetrate the wall via a fine bore hole. The fruit bodies of the perfect fruit form, ascocarps, are blue to black bottle-shaped forms (perithecia) of approximately 0.2 mm diameter on the wood surface. Spores are small, unicellular, and hyaline, $2.5\text{--}5.5 \times 1.5\text{--}2.5 \mu\text{m}$ (Langendorf 1988).

Growth and Development. The fungi thrive outdoors at wood moisture contents of 30–150% and temperatures of 20–30°C. Growth is favored by stagnant air. The fungi take nourishment from carbohydrates freely accessible in the wood cell lumina.

Other Species of Sap-Stain Fungi on Freshly Felled Timber

Other species found on freshly felled wood are *Phoma* spp., and *Cladosporium* spp.; in tropical areas *Lasiodiplodia theobromae* has been identified in hardwoods.

Blue-Stain Fungi on Wood in Service

Aureobasidium pullulans (de Bary) Arnaud

Synonyms. *Pullularia pullulans*.

Systematics. Deuteromycota, Blastomycetes.

Distribution. Cosmopolitan; North America, Europe, Australia.

Occurrence. In painted wood in use that periodically becomes wet; wood outdoors exposed to the elements; half-timbering and outdoor wooden sculptures; often in the sapwood of softwoods such as pine, and in the wood of hardwoods that do not form heartwood such as abachi.

Type of Damage. Black discoloration in streaks on the wood surface; paint and varnish films lift due to mycelial growth in the wood and spore forma-

tion on its surface. The mycelium of *Aureobasidium pullulans* penetrates about 1 mm into the wood surface and colonizes the lumina of the cells. Deeper penetration (>2.5 mm) takes place via the rays.

Distinguishing Features. The hyphae are pigmented irregularly and characteristically swollen. Perfect states are not known for this fungus, but its imperfect states consist of hyaline, conidiogenic cells which produce large quantities of conidia (also called blastospores). The conidia are unicellular, hyaline, and elliptical.

Growth and Development. *Aureobasidium pullulans* requires periodic recurrent wetting of the wood, the optimum being 30–80% wood moisture content. It can survive for 1 year on sound wood that has been dried to 12% moisture content. Wood surfaces become infected by conidia or by mycelium. The fungus is ubiquitous on cellulosic substrates, one reason being that it is capable of forming cellulase, pectinase, and laccase in response to the nourishment available. Optimum temperature for mycelial growth has been reported as 25°C; other studies have shown that *Aureobasidium pullulans* has a certain temperature and pH tolerance. As a typical fungus on coatings, it can also take nourishment from detritus sources (Zabel and Morrell 1992).

Special Characteristics. In cultures on nutrient agar the fungus is slimy, yeast-like, and turns black.

Other Species of Blue-Stain Fungi on Wood in Service

Other species found on wood in service are *Cladosporium* spp., *Alternaria* spp., *Stemphylium* spp. and *Sclerophoma* spp.

Other Wood-Staining Fungi (cf. Table 5.11)

Discula spp.

Systematics. Deuteromycota.

Distribution. Central Europe.

Occurrence. Massive attack of softwoods on sandy forest sites; pine sapwood is especially affected.

Type of Damage. Coffee-brown discoloration of pine sapwood, especially around the rays; no effect on wood strength.

Distinguishing Features. In the wood the hyphae grow through the pits, and occasionally through the cell walls.

Growth and Development. Optimal growth conditions are at 30°C and approximately 100% wood moisture content. The fungus takes its nourishment from cell contents of the ray parenchyma.

Special Characteristics. The fungus secretes extracellular pigments which impart a coffee-brown color to the wood.

Arthrographis cuboidea (Sacc. & Ellis) Sigler

Systematics. Deuteromycota.

Distribution. North America.

Occurrence. Widespread in the forest and in storage yards; attacks both softwoods and hardwoods.

Type of Damage. The wood is stained noticeably pink; there is no effect on wood strength.

Growth and Development. The fungus colonizes and stains the wood; unlike other wood-staining fungi it attacks sapwood and heartwood of both softwoods and hardwoods.

Special Characteristics. The mycelium of *Arthrographis cuboidea* forms an extracellular red pigment in the wood; according to Golinski et al. (1995), it is a naphthoquinone derivative. Similar derivatives have also been found in the red stains of pine by *Fusarium* spp.

Chlorociboria aeruginosa (Pers.: Fr.) Seaver ex Ramamurthi, Korf & Batra

Synonym. *Chlorosplenium aeruginosum*.

Systematics. Ascomycota, Helotiales, Dermateaceae.

Distribution. Cosmopolitan; Europe; North, Central, and South America; the Caribbean, and Japan.

Occurrence. On moist pieces of hardwood, often those with white rot, especially beech, red oak, birch, poplar, maple, and alder.

Type of Damage. The affected wood turns an intense green color. However, the term "green decay" is incorrect since the fungus primarily discolors the wood.

Distinguishing Features. The green hyphae of the substrate mycelium and the cell walls stained green are readily visible under the light microscope. At high relative humidity and high wood moisture content fruit bodies form cup-shaped, dark to blue-green apothecia about 3 mm in diameter. "Aeruginosa" means deep green with a touch of blue in Latin, and refers to the color of the fruit bodies. The spores are hyaline and ellipsoid.

Growth and Development. In moist wood, and sometimes also in wood attacked by white-rot fungi, the hyphae grow especially in the ray parenchyma cells. They take their nourishment mainly from the cell contents and hardly affect wood strength. The hyphae die off in dry wood.

Special Characteristics. *Chlorociboria aeruginosa* produces an extracellular, lightfast pigment which permanently stains the cell walls. The pigment is a naphthoquinone derivative named xylindein. This unusual wood stain has a long history: artisans in Europe have used pieces of wood naturally stained blue-green for relic boxes in the eleventh and twelfth centuries, and later in the Renaissance for marquetry, paneling, and furniture (Blanchette et al. 1992; Michaelsen et al. 1992; Flade and Unger 1997). Inlays of wood stained by the fungus in furniture can be distinguished from wood stained with indigo dyes by the uneven coloration of the former.

Surface Molds

Trichoderma spp.

Systematics. Deuteromycota, Hyphomycetes. *Trichoderma* is the imperfect state of *Hypocrea* (Ascomycota, Pyrenomycetes, Hypocreales; Eaton and Hale 1993). The taxonomy of *Trichoderma* is not clear; past isolations were given as *T. viride* Pers., but newer studies have also identified *T. aureoviride*, *T. harzianum*, and *T. koningii* as growing on wood.

Distribution. Cosmopolitan, in temperate zones but also in the tropics.

Occurrence. On the surface of softwoods and hardwoods stored in moist conditions, especially on the sapwood.

Type of Damage. Whitish green discoloration from mycelial growth and spore formation.

Distinguishing Features. Surface mycelium grows very rapidly as a thin, whitish layer and forms conidiophores shaped like little trees with bunches of conidia at the tips. The mass of conidia forms a typical green mat on the wood surface.

Growth and Development. Optimum development takes place at high wood moisture content and high relative humidity (about 95%), warm conditions and stagnant air. Starch and soluble sugars in the parenchyma cells closest to the surface serve as nourishment.

Special Characteristics. *Trichoderma* spp. has been studied extensively since about 1982 with respect to its physiological capabilities. The capability for production of cellulase and the consequent cavity formation, e.g., in birch, appears to depend on the particular strains used (Eaton and Hale 1993). Some species of *Trichoderma* are resistant to biocides which are effective against blue stain, which can be a problem when treated wood becomes wet for extended periods allowing growth of mold fungi.

The inhibiting and lethal effects of *Trichoderma* species on Basidiomycota (Schmidt 1994) have been investigated since as early as 1934 with regard to biological control (cf. Chap. 10). Zabel and Morrell (1992) have infected heart-

wood with *Trichoderma* spp. in order to improve its treatability and lower its pH.

Gliocladium spp.

Systematics. Deuteromycota, Hyphomycetes. *Gliocladium* is also an imperfect state of *Hypocrea* (Ascomycota, Pyrenomycetes, Hypocreales).

Distribution. Cosmopolitan, in temperate zones but also in the tropics.

Occurrence. On the surface of softwoods and hardwoods stored under moist conditions.

Type of Damage. Wood is discolored white, green, or pink by mycelial growth and spore formation.

Distinguishing Features. The surface mycelium is slimy; single-celled conidia are formed at the tips of penicillate conidiophores. The pink conidia of *Gliocladium roseum* form aggregations on the wood surface.

Growth and Development. Optimum development occurs at high relative humidity, high wood moisture content, and stagnant air. Spores can germinate within a few minutes.

Other fungi that color wood surfaces are *Aspergillus niger* (black) and *Penicillium* spp. (green). *Paecilomyces variotii* causes a mainly yellow discoloration of wood surfaces, especially in oak.

5.2.8

Viability Tests of Fungi

For the treatment of wooden objects which have been attacked by brown-rot fungi, especially by *Serpula lacrymans*, the viability of the fungal mycelium before and after control measures is of great importance. If an attack has already died out, conservation treatments of works of art and cultural property can be done with less expense and more conservatively (Steinfurth 1997). Whereas the mycelium of *Serpula lacrymans* can be discerned readily under the light microscope, it is difficult to distinguish between living and dead mycelium. The following test methods are being used.

5.2.8.1

Growth Test

Pieces of infected wood are placed on an artificial food source such as agar-agar or into a moist chamber, and are cultivated under optimum conditions. Mycelial growth or mass loss of the wood are then determined. However, the mycelium of *Serpula lacrymans* collected under practical conditions is not sterile and is often infected with mold fungi which overwhelm everything else during culturing, making exact determinations difficult.

5.2.8.2

Color Indicators

Measurement of Changes in pH

Brown-rot and white-rot fungi liberate organic acids such as oxalic acid during wood decay, which alter the acidity of the substrate and lower its pH. Optimum pH levels are lower for brown rot than for white rot. Changes in pH caused by fungi can be determined by color indicators. Bromophenol blue and bromocresol green have been found suitable; they are sprayed on the wood in a 0.04% solution in ethanol diluted with equal parts of water. A change in color of bromocresol green from blue to green or yellow then indicates infection with wood-destroying fungi (Peek et al. 1980). This sensitive method is useful for early detection especially of brown rot, but can also be used to determine the viability of *Serpula lacrymans* or *Coniophora puteana* (Bruhn 1993; Weiß et al. 2000), since dead mycelium will not lead to color changes. Besides using color indicators, the concentration of oxalic acid in wood can also be determined directly, and this can be used, for example, to follow the spread from the initial point of attack of *Serpula lacrymans* in a historic object (Bruhn 1994).

Staining of Fungus Cells

This method is based on preferential staining of the cell contents of living mycelium cells, the cell plasma, which decomposes autolytically after the cell dies. The stain Janus green B assures uniform staining of living cell plasma (Koch et al. 1989), turning the mitochondria (enzyme reservoirs) dark blue while imparting little or no change to color of the cell walls of wood and fungi.

Dyeing of Fungal Hyphae with Fluorescein-Diacetate (FDA)

Fungal hyphae can also be dyed in vivo with FDA and made visible in a confocal laser scanning microscope. This method can be used for the detection of living hyphae in surface as well as in substrate mycelium in wood (Huckfeldt et al. 2000).

5.2.8.3

Determination of Adenosin Triphosphate (ATP)

ATP is the most important intracellular agent of storage and transfer of energy in intermediate cell metabolism, and its presence indicates active, living cells. In the case of wood attacked by *Serpula lacrymans*, the ATP is extracted with 80% dimethyl sulfoxide for 30 min at 20°C. The ATP content is measured using the luciferin-luciferase complex obtained from the firefly, *Photinus pyralis*, in a luminometer (Kjerulf-Jensen and Koch 1992).

5.2.8.4

Immunological Determination

This method, which Palfreyman et al. (1991) attempted to use on historical ship timbers can detect early stages of brown rot before mass loss in wood occurs based on the production of antibodies. If an antigen, such as a protein extract of *Serpula lacrymans*, is injected into a mammal such as a rabbit, antibodies will be formed. The antiserum contains these specific antibodies against *Serpula lacrymans* which are applied to the new *Serpula lacrymans* strain found at the location undergoing control treatment. The detection is made by fluorescence in combination with a fluorescence dye such as fluoro-chrome (Koch 1990; Toft 1992).

5.2.8.5

Detection of Volatile Organic Compounds (VOC)

Serpula lacrymans and other fungi emit volatile metabolites into the environment during their life processes, which can be identified by using a combination of a gas chromatograph and a mass spectrometer (GC/MS; Bjurman and Kristensson 1992; Esser and Tas 1992). Investigations of fungus cultures have shown that, in principle, fungal species can be distinguished based on their volatile metabolites which can be used as selective models for identification. Wood attacked by fungi may also emit specific VOC. A further possibility is the use of electronic noses, which work with chemical sensors and can recognize the various groups of VOC given off by individual fungi and by wood (Nilsson 1996).

All of the above methods have been used on separate samples in the laboratory. Rapid methods for the detection of living, active decay in situ are still under development.

5.2.9

Attack on Consolidants and Coatings for Wood

The enzymes of living fungus cells can cause damage to natural and synthetic polymers. Generally, enzymes are highly specific with regard to substrate and action, such as splitting of natural macromolecules, but nevertheless fungi are also capable of attacking other substrates such as synthetic polymers. The fungal attack is facilitated by high relative humidity, a temperature of 35–37 °C and pH values in the weakly acidic range. Pure acrylic resins are largely resistant to brown-rot fungi such as *Coniophora puteana* and soft-rot fungi such as *Chaetomium globosum* because they cannot use the resins as a source of carbon (Unger and Unger 1995), but exceptions are possible through the separation of plasticizers. Compared with acrylics, poly(vinyl acetate) products are much less resistant to fungi. Natural polymers and their semisynthetic

derivatives such as gelatine, starch, and cellulose ether show more instability in the face of fungus attack than synthetic polymers.

The consolidation of deteriorated portions of wood objects can be done either with soluble polymers or with suitable monomers (cf. Chap. 11). Polymer solutions do not penetrate into the wood structure as well as monomers, so that in many cases only regions near the surface are impregnated. Consolidated wood will generally take up moisture (e.g., from the air) more slowly and give it up again at a reduced rate. On the one hand, the reduced porosity and reduced rate of moisture uptake are detrimental to fungal attack, which should manifest itself in increased biostability. On the other hand, moisture once taken up remains in the material longer, so that after initial infection the fungi could be expected to spread more rapidly than in untreated wood. It is known that linden wood impregnated with 5, 10, and 20% solutions of Paraloid B72 is not resistant to the brown rotters *Coniophora puteana*, *Antrodia vaillantii* and *Lentinus lepideus* and that a mass loss of >10% is incurred, which is often greater than in untreated control specimens (Paciorek 1993).

When hardwoods such as birch or alder are impregnated with methyl methacrylate (MMA) and the monomer is subsequently polymerized in situ, the resulting wood-plastic combination is nearly, but not entirely, resistant to brown rotters. Mass loss of the modified wood was about 1–2% (Aho and Vihavainen 1972). The observed differences in the behavior of hardwoods treated with acrylics can probably be attributed to the much lower amounts of Paraloid B72 that are taken up by the wood, compared with the 40–60% loading, based on the untreated wood, of poly(methyl methacrylate) (PMMA), and to more uniform distribution of PMMA in the treated wood. However, even PMMA is deposited only in the cell lumens, so that after a fungus infection the cell walls can be destroyed. Wood treated with solutions of poly(vinyl acetate) (PVA) or with vinyl acetate monomer in combination with styrene is very susceptible to brown-rot fungi.

Wood specimens treated with various solutions of acrylic resins did not show any mold formation after 120 days (Lehmann 1984), but shellac, bees wax, dammar and epoxy resins start to get moldy after 20–40 days. Epoxy resins are generally considered very mold resistant, so that these particular test results may be due to the specific type of epoxy and hardener. Results of tests on the behavior of wood decayed by brown rot, consolidated, and then again exposed to brown-rot fungi, were published by Unger et al. (2000). Surface coatings containing animal glue or whole egg are very susceptible to mold at relative humidities of >80% and poor air circulation. Synthetic binders can also be colonized superficially by mold fungi and/or bacteria.

5.2.10

Dangers to Health from Wood-Destroying Fungi

The question of endangerment of human health by fungi is especially significant during conservation treatments of individual objects or interior spaces, and this has been the subject of a number of reports (Pantke and Kerner-Gang 1988; Hödl 1994a,b). According to Schmidt (1994), about 200 different species of fungi sometimes secrete highly toxic mycotoxins. Benko (1992) has identified 24 mold fungi found on wood which can trigger pathogenic effects in people. This includes mesophilic (22–25 °C) as well as thermotolerant (37 °C) genera and species which are also found in interior spaces. On painted wooden window frames, for instance, the genera *Penicillium*, *Cladosporium*, and the *Alternaria* complex can be found. Interior wood trim is colonized by *Aspergillus versicolor* and *Trichoderma viride*, and *Stachybotrys chartarum* can be found on gypsum wall board with paper faces. In susceptible people, pathogenic mold fungi can trigger the following reactions: allergies of immediate and delayed types, the sick building syndrome (SBS), and mycotoxicosis. Allergic reactions primarily affect the skin but also affect the respiratory system. For SBS, irritation of mucous membranes, headaches, fatigue, and impaired concentration and memory are typical. In cases of mycotoxicosis, the ingestion of toxin containing spores can lead to outright poisoning.

Aspergillus fumigatus and *Aspergillus niger* are examples of thermotolerant mold fungi found in interior spaces which can trigger allergies, and play a particular role in lung mycosis. Certain species of the genera *Stachybotris*, *Fusarium*, and *Trichoderma* are among those found on wood and are potential producers of mycotoxins. *Chaetomium globosum* is a soft-rot fungus suspected of causing skin disease. The white-rot fungus *Schizophyllum commune* reportedly causes various symptoms of illness in people by ingestion of basidiospores (Benko 1992). Breathing in large quantities of the spores of the brown rotter *Serpula lacrymans* probably also induces allergenic effects in some people.

When handling fungus-infected objects, disposable gloves, disposable respiratory masks that cover mouth and nose completely, a closed lab coat and a hair protector should be used. The conservation work on fungus-infected objects should be carried out in safety cabinets, such as laminar air-flow boxes with suitable filters, which are capable of trapping spores and mycelium fragments. When the work is done, hands and all work surfaces should be disinfected thoroughly, using disinfecting soap and paper towels for the hands. Subsequently, protection of the skin with a suitable cream is recommended. Work surfaces should be subjected to a scrubbing disinfection. If the presence of fungi pathogenic to humans is suspected, it is advisable to consult a mycologist for identification of the fungus species so that a better judgment of the extent of the danger can be made.

5.3 Bacteria

Overview

Compared with insects and fungi, bacteria are much less important as agents of wood deterioration. Wood strength is reduced only somewhat, or reduced at a much slower rate. However, bacteria can cause color changes in wood. Accelerated decomposition of wood is possible by the simultaneous attack by bacteria and fungi. Wood treated with preservatives, even at high preservative retention, is not always resistant to bacteria. Since bacterial cells divide rapidly in optimum conditions, they can penetrate through the wood quickly, when aided by water transport. Bacteria will attack the various structural elements of wood differently (Schmidt and Liese 1994). Since the type of damage in wood caused by bacteria is the most important consideration in the conservation of wooden objects, the different kinds of bacteria (Fig. 5.29, Fig. 5.30) are discussed not according to their biological systematics, but according to the structural damage pattern (Eaton and Hale 1993).

5.3.1

Bacteria Destroying Pit Membranes

Bacteria can destroy the pit membranes of tracheids and ray parenchyma in archaeological wet wood or logs stored in water or on water spray decks. Soft-

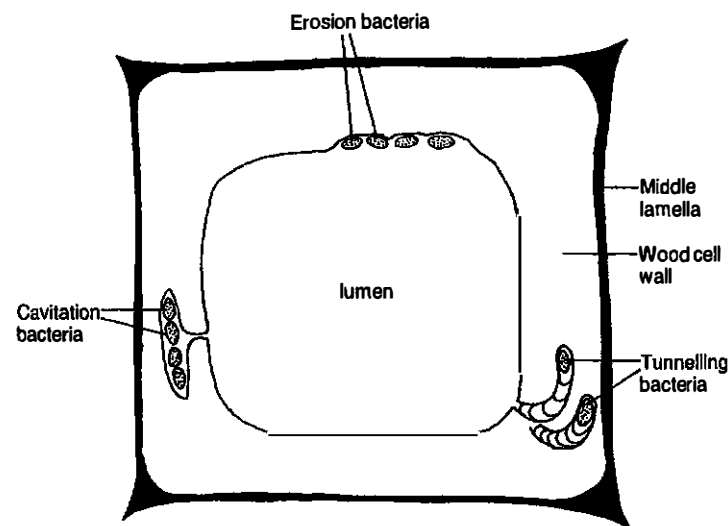


Fig. 5.29. Overview of an attack of the wood cell wall by bacteria. (After Eaton and Hale 1993)

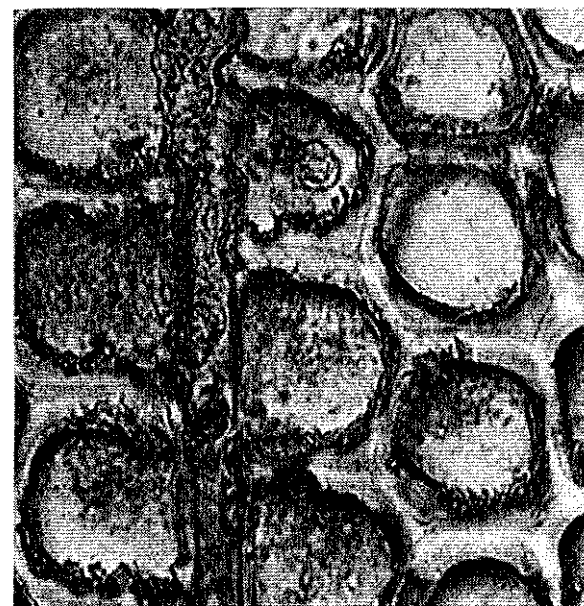


Fig. 5.30. Microscopic view of damage in wood caused by erosion bacteria. (Courtesy of T. Nilsson)

woods are affected more than hardwoods, and sapwood more than heartwood. Destruction of pit membranes increases porosity and improves the permeability to fluids (Blanchette et al. 1990). When logs stored under such conditions are sawn into lumber, excessive absorption of wood preservatives can subsequently take place. Such excess absorption can be the cause of failure of paint and varnish coatings for wood.

5.3.2

Bacteria Destroying Wood Cell Walls

These bacteria are further subdivided according to the microscopic structure of their attack, into erosion bacteria, tunnelling bacteria, and cavity-forming bacteria (Daniel and Nilsson 1998; cf. Fig. 5.29).

Erosion bacteria (cf. Fig. 5.30) attack the S3 layer of the wood cell wall from the lumen, and subsequently decompose the S2 layer. If the attack occurs in waterlogged wood under anaerobic conditions, the decomposition of the S2 layer is uneven (Nilsson 1999). In most cases, even in advanced decomposition, the middle lamella remains intact. Both softwoods and hardwoods are attacked.

Tunnelling bacteria penetrate the S2 layer of the wood cell wall, each tunnel being headed by a single bacterium. Division of the bacteria increases the

number of tunnels rapidly, and a branched tunnel system is formed. The middle lamella and the S3 layer may remain largely intact.

Cavity-forming bacteria, like the tunneling bacteria, attack the S2 layer. They form angular cavities which extend at right angles to the long axis of the fibers.

5.4 Marine Borers

Overview

The most important wood-destroying marine borers are found among the Bivalvia and the Crustaceae (Grosser 1985; Richardson 1993).

The Teredinidae (shipworm) family of the Bivalvia includes dangerous pests of objects such as shipwrecks in salty ocean water. The Teredinidae are elongated, whitish animals which depart significantly from the typical bivalve shape. Their distribution depends on the salt content of the water and its temperature. Warm climates favor their life processes, while cold temperatures slow down their activity. The most important species belong to the genera *Teredo* and *Bankia*. Adults of the genus *Bankia* are significantly larger, at a length of 1500–1800 mm, than those of the genus *Teredo* which grow to a length of 300–600 mm, although shipworms 2 m long have been recorded.

The gribble, family Limnoridae of the Crustaceae, do not penetrate into wood as deeply as the Teredinidae, and destroy it much more slowly. Their tunnels extend parallel to the wood surface, and as the outer layers are lifted off by wave action, the gribble gradually burrow more deeply into the wood.

5.4.1 Teredinidae

Teredo navalis L.

Common Name. Shipworm.

Systematics. Bivalvia, Teredinidae.

Distribution. Coastal waters of warm and temperate zones.

Type of Damage. The wood is gnawed on the surface and is studded with circular bore holes 6–8 mm in diameter (Fig. 5.31); heavily damaged wood appears sieve-like in cross section. Heartwood is also attacked. The interior of the bore holes contains characteristic calcium deposits.

Distinguishing Features. The shipworm has a worm-like, extended, whitish body and deposits calcareous material on the surface of the bore hole. At the head portion are shell-like valves in a circular arrangement. The serrated edges of these shell-like valves serve as the boring utensil with which the shipworm can rapidly bore into the wood. At the rear end are two snout-like

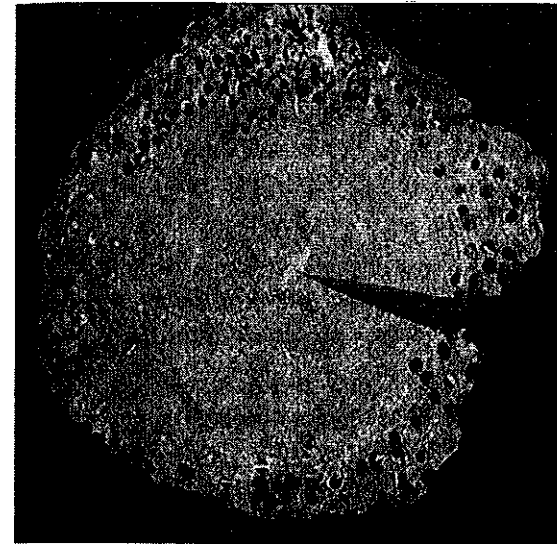


Fig. 5.31. Type of damage caused by *Teredo navalis*

hoses (siphons) which extend into the ocean water. Adults are about 200–450 mm long.

Development. The shipworms are bisexual and produce annually 1–5 million eggs in three to four batches. After fertilization in the womb, larvae develop within 14 days, and are then expelled into the ocean water. The larvae, 0.3 mm long, attach themselves to wood after 1–3 weeks and begin to scrape. When the shell-like valves have developed into a boring utensil, shipworms can penetrate into the wood. About 23 days after attachment their final shapes are formed, and rapid growth in length takes place. In contrast to other bivalves, the shipworm uses the bore chips as a food source. Shipworms live 1–3 years. They attack softwoods as well as hardwoods, and require a salt content in the water of 0.9–3.5%.

Other species belong to the *Bankia* genus.

5.4.2 Limnoridae

Limnoria lignorum Rathke

Common Name. Gribble.

Systematics. Crustaceae, Limnoridae.

Distribution. Coastal waters of cold and temperate zones (North Sea coast, northeast and northwest coasts of North America), central Europe.

Occurrence. In both softwoods and hardwoods of marine structures and in boats and shipwrecks.

Type of Damage. Round, winding bore tunnels which usually follow the earlywood layers of softwoods. The tunnels do not penetrate more than 20 mm into the wood, and have holes which serve for water exchange. The wood is destroyed layer by layer from the outside, and the destroyed and flaking layer can reach a depth of 6–12 mm in 1 year.

Distinguishing Features. Gribbles are flattened, isopod-like creatures which are yellow-brown in color and can roll themselves up. They have strong, sharp mandibles with sharp edges, and in central Europe are 4–5 mm long.

Development. Wood serves both as a food source and as a breeding shelter. The animals usually live in pairs for about 1 year in a borehole of 1.5–2 mm diameter. They require water with a salt content of 1.5%. *Limnoria lignorum* is a cold-water species which does not develop well above 20°C. Breeding begins when temperatures reach 9–10°C (Eaton and Hale 1993).

Other species include *Limnoria tripunctata*, and *Limnoria quadripunctata*.

References

- Aho V, Vihavainen T (1972) Decay tests on wood-polymer combinations (finn.). Staatliches Institut für technische Forschung (ed) Finnland, Schriftenreihe 1, Holz 56, Helsinki
- Bavendamm W (1928) Über das Vorkommen und den Nachweis von Oxydasen bei holzzerstörenden Pilzen. Z Pflanzenkr Pflanzenschutz 38:257–276
- Bech-Andersen J (1995) The dry rot fungus and other fungi in houses. IRG/WP/95-10124
- Bech-Andersen J, Elborne SA (1999) The dry rot fungus (*Serpula lacrymans*) in nature and its history of introduction into buildings. IRG/WP/99-10300
- Becker G (1963) Holzbestandteile und Hausbocklarven-Entwicklung. Holz Roh Werkst 21: 285–289
- Belmain SR, Simmonds MS, Blaney WM (1999) The deathwatch beetle, *Xestobium rufovillosum*, accommodated in all the best places. Proceedings of the 3rd International Conference on Urban pests (ICUP) 19–22 July 1999, Prague, Czech Republic
- Benko R (1992) Wood colonizing fungi as a human pathogen. IRG/WP/92-1523
- Binker G (1996) Insektenfallen gegen Anobienbefall. Restauro 102(6):400–405
- Bjurman J (1984) Conditions for basidiospore production in the brown-rot fungus *Gloeophyllum sepiarium* in axenic culture. IRG/WP/1232
- Bjurman J, Kristensson J (1992) Analysis of volatile emissions as an aid in the diagnosis of dry rot. IRG/WP/92-2393
- Blanchette RA (1998) A guide to wood deterioration caused by microorganisms and insects. In: Dardes K, Rothe A (eds) The structural conservation of panel paintings. Proceedings of a Symposium at the J. Paul Getty Museum, 24–28 April 1995. The Getty Conservation Institute Los Angeles 1998, pp 55–68
- Blanchette RA, Nilsson T, Daniel G, Abad D (1990) Biological degradation of wood. In: Rowell RM, Barbour RJ (eds) Archaeological wood: properties, chemistry, and preservation. American Chemical Society, Washington, DC. Adv Chem Ser 225:141–174
- Blanchette RA, Wilmering AM, Baumeister M (1992) The use of green-stained wood caused by the fungus *Chlorociboria* in intarsia masterpieces from the 15th century. Holzforschung 46:225–232
- Bruce A, Palfreyman JW (1998) Forest products biotechnology. Taylor & Francis, London

- Bruhn S (1993) Activity proof of *Serpula lacrymans* and *Coniophora puteana* at the site of attack. WKI Short Rep 20
- Bruhn S (1994) Methode zur Bestimmung der Ausbreitung des Echten Hausschwammes am Beispiel der Schrotholzkirche in Wespen. Holz-Zentralblatt 136:2276
- Buchwald G (1986) On *Donkioportia expansa* (DESM.)KOTL. & POUL. IRG/WP/1285
- Cartwright KStG, Findlay WPK (1969) Decay of timber and its prevention, 2nd edn. HMSO, London
- Cassens DL, Feist WC, Johnson BR, De Groot RC (1995) Selection and use of preservative-treated wood. Forest Products Society, Madison, Publ 7299
- Creefield JW (1996) Wood destroying insects. Wood borer and termites, 2nd edn. CSIRO Publishing, Collingwood, Victoria, Australia
- Cymorek S (1984) Schadinsekten in Kunstwerken und Antiquitäten aus Holz in Europa. Holzschutz – Forschung und Praxis, Symposium 1982, DRW, Leinfelden-Echterdingen, pp 37–56
- Daniel G, Nilsson T (1998) Developments in the study of soft rot and bacterial decay. In: Bruce A, Palfreyman JW (eds) Forest products biotechnology. Taylor & Francis, London, pp 37–62
- DIN 68800 part 4 (1992) Wood preservation; measures for the eradication of fungi and insects
- Dominik J, Starzyk JR (1983) Ochrona drewna. Owady niszczące drewno. Państwowe Wydawnictwo Rolnicze i Leśne, Warszawa
- Duncan CG (1960) Wood-attacking capacities and physiology of soft-rot fungi. Forest Products Laboratory, Madison, no 2173
- Duncan CG, Lombard FF (1965) Fungi associated with principal decays in wood products in the United States. USDA Forest Service, Forest Products Laboratory Report no WO-4, Madison, WI
- Eaton RA, Hale MDC (1993) Wood: decay, pests and protection. Chapman & Hall, London
- Eriksson K-EL, Blanchette RA, Ander P (1990) Microbial and enzymatic degradation of wood and wood components. Springer, Berlin Heidelberg New York
- Esser PM, Tas AC (1992) Detection of dry rot by air analysis. IRG/WP 92-2399
- Falck R, Haag W (1926) Decomposition of lignin and of cellulose: two different processes by wood-destroying fungi. Ber 60B:225–232. In: Eaton RA, Hale MDC (1993) Wood: decay, pests and protection. Chapman & Hall, London
- Fengel D, Wegener G (1989) Wood. Chemistry, ultrastructure, reactions. De Gruyter, Berlin
- Findlay WPK, Savory JG (1954) Moderfäule. Die Zersetzung des Holzes durch niedere Pilze. Holz Roh Werkst 12:293–296
- Flade J, Unger A (1997) Die Späne-Marmorierung. Restauro 103:30–37
- Florian ML (1997) Heritage eaters. Insects and fungi in heritage collections. James & James, London
- Geis KU (1996) Unbemerkte Einbürgerung und Ausbreitung des nordamerikanischen Gruben-halsigen Splintholzkäfers, *Lyctus cavicollis* LeConte, in Mitteleuropa, nebst Anmerkungen zur möglichen Einschleppung zweier anderer nearktischer Lyctiden (Coleoptera, Lyctidae). Anzeiger Schädlingskd Pflanzensch Umweltsch 69:31–39
- Gersonde M, Kerner-Gang W (1976) A review of information available for development of a method for testing wood preservatives with soft rot fungi. Int Biodetn Bull 12:5–13
- Golinski P, Krick TJP, Blanchette RA, Mirocha CJ (1995) Chemical characterization of a red pigment (5,8-dihydroxy-2,7-dimethoxy-1,4-naphthalene-dione) produced by *Arthrographis cuboidea* in pink stained wood. Holzforschung 49:407–410
- Graf E (1992) Biologischer Holzschutz – Möglichkeiten und Grenzen. Vorträge der 19. Holzschutz-Tagung Rosenheim/Germany, 07./08.10.1992, pp 21–32
- Grosser D (1985) Pflanzliche und tierische Bau- und Werkholz-Schädlinge. DRW-Verlag Weinbrenner, Leinfelden-Echterdingen
- Hartig R (1874) Wichtige Krankheiten der Waldbäume. Springer, Berlin
- Hödl I (1994a) Konservierung von mikroorganismenbefallenen Archivalien im Steier-märkischen Landesarchiv. Restauratorenblätter 14:65–72

- Hödl I (1994b) Selbstschutz für Archivmitarbeiter. Restauratorenblätter 14:73–79
- Huckfeldt T, Kleist G, Quader H (2000) Vitalitätsansprache des Hausschwammes (*Serpula lacrymans*) und anderer holzerstörender Gebäudepilze. Z Mykol 66(1):35–44
- Jennings DH, Bravery AF (eds) (1991) *Serpula lacrymans* fundamental biology and control strategies. Wiley, Chichester
- Kempe K (1999) Dokumentation Holzschädlinge. Holzzerstörende Pilze und Insekten an Bauholz. Verlag Bauwesen, Berlin
- Kjerulf-Jensen Ch, Koch AP (1992) Investigation of microwave as a means of eradicating dry rot attack in buildings. IRG/WP/92-1545
- Kleist G, Seehann G (1999) Der Eichenporling, *Donkioporia expansa* – ein wenig bekannter Holzzerstörer in Gebäuden. Z Mykol 65:23–32
- Koch AP (1990) Dry rot – new methods of detection and treatment. BWPDA Record of Convention, The British Wood Preserving and Damp-proofing Association, London, 13 pp
- Koch AP, Kjerulf-Jensen Ch, Madsen B (1989) New experiences with Dry rot in Danish buildings, heat treatment and viability tests. IRG/WP/1423
- König E (1957) Tierische und pflanzliche Holzschädlinge. Holz-Zentralblatt Verlag, Stuttgart
- Kollmann F (1955) Technologie des Holzes und der Holzwerkstoffe, vol 1 and 2. Springer, Berlin
- Göttingen Heidelberg/Bergmann, München
- Krishna K, Weesner FM (eds) (1970) Biology of termites, vol II. Academic Press, New York
- Langendorf G (1988) Holzschutz. Fachbuchverlag, Leipzig
- Lehmann J (1984) Kriterien für die Auswahl von Harzen und Lösungsmitteln zur Festigung holzwurmgeschädigten Holzes. Arbeitsbl Restaur (2), Gruppe 8:112–121
- Lepesme P (1944) Les Coléoptères des denrées alimentaires et des produits industriels enheposés. Encyclop Entom Sér A XXII
- Liese J (1954) Holzschutz. Verlag Technik, Berlin
- Liese W (1955) On the decomposition of the cell wall by micro-organisms. Rec Br Wood Preserv Assoc:159–160
- Liese W (1970) Ultrastructural aspects of woody tissue disintegration. Annu Rev Phytopathol 8:231–258
- Liese W (ed) (1975) Biological transformation of wood by microorganisms. Springer, Berlin Heidelberg New York
- Liese W, Ammer U (1964) Über den Befall von Buchenholz durch Moderfäulepilze in Abhängigkeit von der Holzfeuchtigkeit. Holzforschung 18:97–102
- Mahler G (1992) Konservierung von Holz durch Schutzgas. Allg Forstz 47:1024–1025
- Meincke I, Theuerkauf H, Dietrich G, Hundt R, Kopprasch G, Kummer G, Stade R (1980) Wissenspeicher Biologie. Volk und Wissen, Berlin
- Merrill W, Lambert D, Liese W (1975) Important diseases of forest trees. By Dr. Robert Hartig 1874. Phytopathol Classics 12. Am Phytopathol Soc, St. Paul
- Michael E, Hennig B, Kreisel H (1985) Handbuch für Pilzfreunde, vol 4, Blätterpilze-Dunkelblättler. Fischer, Jena
- Michaelsen H, Unger A, Fischer C-H (1992) Blaugrüne Färbung an Intarsienhölzern des 16. bis 18. Jahrhunderts. Restauro 98:17–25
- Mori H (1975) List of damaging insects to cultural properties and conservation science against insect pests in Japan. Sci Pap Jpn Antiques Art Crafts 19:24–60
- Müller E, Loeffler W (1992) Mykologie, 5th edn. Thieme, Stuttgart
- Nilsson K (1996) Electronic noses for detection of rot in wood. IRG/WP/96-20098
- Nilsson T (1988) Defining fungal decay types – final proposal. IRG/WP/1355
- Nilsson T (1999) Microbial degradation of wood – a review with special emphasis on water-logged wood. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/ France 1998, ARC-Nucléart, Grenoble 1999, pp 66–70
- Noldt U, Fettköther R, Schröder F, Dettner K, Francke W (1995) Zur chemischen Kommunikation von holzerstörenden Bockkäfern. Tagungsband der 20. Holzschutz-Tagung Rosenheim/Germany, 18./19.10.1995, pp 157–170

- Noldt U, Tiedemann D (1998) Der Scheinbockkäfer *Nacerda melanura* (L.) (Oedemeridae) im Hamburger Hafen. BFH-Nachrichten 36:3
- Paciorek M (1993) Badania wybranych tworzyw termoplastycznych stosowanych do impregnacji drewna (A study of some thermoplastic resins used for wood impregnation). Studia i Materiały Wydziału Konserwacji i Restauracji Dzieł Sztuki Pięknych w Krakowie, Tom III
- Palfreyman JW, Button D, Glancy H, King B, Nicoll G, Smith GM, Vigrow A (1991) The detection and destruction of basidiomycetes in the timber of artefacts of historical or archaeological interest. In: Baer NS, Sabbioni C, Sors AI (eds) Science, technology and European cultural heritage, Proceedings of the European Symposium, Bologna, Italy, 13–16 June 1989. Butterworth-Heinemann, Oxford, 1991, pp 642–645
- Palfreyman JW, Philips EM, Stainer HJ (1996) The effect of calcium ion concentration on the growth and decay capacity of *Serpula lacrymans* (Schumacher ex Fr.) Gray and *Coniophora puteana* (Schumacher ex Fr.) Karst. Holzforschung 50:3–8
- Palfreyman JW, White NA, Buultjens TEJ, Glancy H (1995) The impact of current research on the treatment of infestations by the dry rot fungus *Serpula lacrymans*. Int Biodeter Biodegrad 35:369–395
- Pantke M, Kerner-Gang W (1988) Hygiene am Arbeitsplatz – Bakterien und Schimmelpilze. Restauro 94(1):50–58
- Peek R-D, Willeitner H, Harm U (1980) Farbindikatoren zur Bestimmung von Pilzbefall im Holz. Holz Roh Werkst 38:225–229
- Pinniger D (1990) Insect pests in museums. Archetype Publications Limited, Denbigh, Clwyd
- Pinniger DB, Child RE (1996) Woodworm – a necessary case for treatment? New techniques for the detection and control of furniture beetle. Proceedings of the 2nd International Conference on Insect pests in the urban environment, Heriot-Watt University, Edinburgh, Scotland, 7–10 July 1996, pp 353–359
- Pitman AJ, Jones AM, Jones EBG (1993) The wharf-borer *Nacerdes melanura* L., a threat to stored archaeological timbers. Stud Conserv 38:274–284
- Plarre R, Hertel H (2000) Incorporating of insect behaviour in standard tests of wood preservatives – a possible way to reduce pesticide loading. IRG/WP/00-20190
- Richardson BA (1993) Wood preservation, 2nd edn. E & FN SPON, London (AATA 32-2299)
- Ridout B (1999) Timber decay in buildings: The conservation approach to treatment. English Heritage & Historic Scotland E & FN SPON, London
- Ritter G (1992) Mykofloristische Mitteilung VII. Zur Verbreitung von *Donkioporia expansa* in den östlichen Bundesländern. Boletus 16(1):26–28
- Rustenburt G, Klaver CJ (1992) Standardization of sapstain tests – a challenge. IRG/WP/92-2403
- Rypáček V (1966) Biologie holzerstörender Pilze. Fischer, Jena
- Savory JG (1954) Breakdown of timber by Ascomycetes and Fungi Imperfecti. Ann Appl Biol 44:336–347
- Scheffer TC (1973) Microbial degradation and the causal organisms. In: Nicholas DD (ed) Wood deterioration and its prevention by preservative treatments. Syracuse University Press, Syracuse, pp 31–106
- Schmidt H (1962) Tierische Schädlinge in Bau- und Werkholz. Parey, Hamburg
- Schmidt O (1994) Holz- und Baupilze: Biologie, Schäden, Schutz, Nutzen. Springer, Berlin Heidelberg New York
- Schmidt O, Liese W (1994) Occurrence and significance of bacteria in wood. Holzforschung 48:271–277
- Schmidt O, Moreth-Kebernik U (1991) Old and new facts on the dry rot fungus *Serpula lacrymans*. IRG/WP/1470
- Schmidt O, Moreth-Kebernik U (1993) Differenzierung von Porenhäusschwämmen und Abgrenzung von anderen Hausfäulepilzen mittels Elektrophorese. Holz Roh Werkst 51: 143
- Schmidt O, Moreth U (1998) Genetic studies on house rot fungi and a rapid diagnosis. Holz Roh Werkst 56(6):421–425

- Schmidt O, Moreth U (1999) rDNA-ITS sequence of *Serpula lacrymans* and other important indoor rot fungi and taxon-specific priming PCR for their detection. IRG/WP/99-10298
- Seehann G, Hegarty BM (1988) A bibliography of the dry rot fungus, *Serpula lacrymans*. IRG/WP/1337
- Serdjukova IR, Toskina IN (1995) Some characters of biology and physiology of the common furniture beetle *Anobium punctatum* De Geer (Coleoptera, Anobiidae). Russian Entomol J 4(1-4):35-43
- Steinfurth A (1997) Echter Hausschwamm: Erfahrung, Wissensstand und Bekämpfung in Dänemark. Bautenschutz Bausanierung 20:16,18,21-23,25
- Su N-Y, Freytag E, Bordes ES, Dycus R (2000) Control of Formosan subterranean termite infestations using baits containing an insect growth regulator. Stud Conserv 45:30-38
- Sutter H-P (1986) Holzschädlinge an Kulturgütern erkennen und bekämpfen. Haupt, Bern
- Theden G (1972) Das Absterben holzerstörender Pilze in trockenem Holz. Mat Org 7:1-10
- Toft L (1992) Immunofluorescence detection of basidiomycetes in wood. Mat Org 27(1):11-17
- Toskina IN (1987) The influence of the past history of wood on its infestation by the common furniture beetle *Anobium punctatum* De Geer (Coleoptera, Anobiidae). In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6-11 Sept 1987, vol 3, pp 1207-1209
- Unger A (1990) Holzkonservierung. Schutz und Festigung von Holzobjekten. Callwey, München
- Unger A, Schiessl U, Unger W (1996a) Widersteht gefestigtes, insektenzerstörtes Holz von Kunstwerken einem erneuten Insektenangriff? Kunsttechnol Konserv 10:307-314
- Unger W (1995) Nutrition and climatic atmospheric conditions: decisive factors for the attack, infestation and spread of wood-destroying insects and fungi in architectural monuments. Arbeitshefte Bayer Landesamt Denkmalpflege 75:13-17
- Unger W, Unger A (1984) Zur Termitenresistenz von Platten und Elasten. Plaste Kautschuk 31:241-247
- Unger W, Unger A (1986) Was sind Anobien? Holztechnologie 27:255-257
- Unger W, Unger A (1995) Die biologische Korrosion von Konsolidierungsmitteln für Kunst- und Kulturgut aus Holz. Kunsttechnol Konserv 9:377-384
- Unger W, Fritsche H, Unger A (1996b) Zur Resistenz von Malmaterialien und Stabilisierungsmitteln für Kunst- und Kulturgut gegenüber holzerstörenden Insekten. Kunsttechnol Konserv 10:106-116
- Unger W, Fritsche H, Unger A (1997) The resistance of painting materials and consolidants against wood-destroying insects. IRG/WP/97-10239
- Unger W, Unger A, Schiessl U (1998) Reinfestation of consolidated ancient wood by insects. IRG/WP/98-10290
- Unger W, Unger A, Schiessl U (2000) On the resistance of consolidated ancient wood against *Serpula lacrymans* (Wulfen: Fr.) Schroeter. IRG/WP/00-10348
- Van Acker J, Stevens M (1996) Laboratory culturing and decay testing with *Physisporinus vitreus* and *Donkioportia expansa* originating from identical cooling tower environments show major differences. IRG/WP/96-10184
- Viitanen H, Ritschkoff AC (1991) Mould growth in pine and spruce sapwood in relation to air humidity and temperature. The Swedish University of Agricultural Sciences, Department of Forest Products, Uppsala, Report no 221
- Vité JP (1952) Die holzerstörenden Insekten Mitteleuropas. Textband. "Musterschmidt" Wissenschaftlicher Verlag, Göttingen
- Weidner H (1993) Bestimmungstabellen der Vorratsschädlinge und des Hausungeziefers Mitteleuropas, 5th edn. Fischer, Stuttgart
- Weiß B, Wagenführ A, Kruse K (2000) Beschreibung und Bestimmung von Bauholzpilzen, DRW-Verlag Weinbrenner, Leinfelden-Echterdingen

- White NA, Buultjens TEJ, Palfreyman JW (1995) Induction of transient thermotolerance in *Serpula lacrymans* and *Serpula himantoides* following exposure to supraoptimal (sublethal) temperature. Mycol Res 99(9):1055-1058
- Wilcox WW, Dietz M (1997) Fungi causing above-ground wood decay in structures in California. Wood Fiber Sci 29(3):291-298
- Zabel RA, Morrell JJ (1992) Wood microbiology. Decay and its prevention. Academic Press, London
- Zacher F (1950) Schädlinge in Haus und Hof. Deutscher Bauernverlag, Berlin

6 Diagnosis of Wood Condition

6.1

Introduction

Diagnostic investigations of wood have the following objectives:

1. Accurate determination of its properties,
2. Recording of the degree and extent of defects and damages,
3. Characterization of the nature and intensity of damage,
4. Determination of the cause of defects and damages,
5. Monitoring remedial treatments.

Test methods may be classified as destructive or nondestructive, recognizing that there may be destructive methods which inflict only minor damage and might thus be termed near-nondestructive. Both destructive and non-destructive methods are used for wood in scientific research and industrial quality control, but tests based on the destructive removal of test specimens from art objects and other cultural property can be acceptable only in rare, exceptional cases.

For cultural property, the determination of individual wood properties is of much less importance than the determination of the condition both before and after conservation and restoration treatments. Detection and evaluation of the condition of wood are also of great interest in forestry and the wood industry. In forestry, this would mean the early detection of internal decay and of bark or wood borers before they can cause catastrophic damage. In the wood industry, attention is paid to locating defects in logs or timbers, but also finding discolorations, decay, and insect damage. In the case of monuments and museum objects, the primary objective is the diagnosis of biological deterioration by fungi, bacteria, or insects. In archaeology not only biological deterioration, for example by fungi, bacteria, or marine borers, but also abiotic deterioration, for example by hydrolytic processes must be considered. Whether it be forestry, the wood industry, or cultural property, a common goal is to use methods which are as close as possible to being nondestructive in order to prevent further damage. Methods developed in forestry and the wood industry are on occasion used in modified form for art objects and other cultural property. The condition analysis of logs and lumber can be made by

mechanical, electrical, optical, acoustic, thermographic, radiographic, nuclear magnetic, chemical, and biological methods or possibly a combination of several of these methods (Table 6.1). For the conservation and restoration of wood objects, imaging methods are of particular interest, because for the conservator pictorial results are more instructive than measurement values and will facilitate well-directed action. Overviews of methods for the condition diagnosis of wood have been published by Kothe (1986), Steck and Görlacher (1986), Hailey and Morris (1987), Brandt and Rinn (1989), Niemz (1995), Unger and Unger (1995), and Tenisch (1999).

6.2

Mechanical Procedures

Increment cores, taken with an increment borer from structural timbers of historic buildings or from massive archeological objects, are useful for obtaining a variety of information. The cores can be dried at $103 \pm 2^\circ\text{C}$ to constant mass to determine the moisture content. In the case of highly resinous wood or wood treated with preservatives, the extraction or distillation method is used, where the cores are chipped and the moisture is evaporated in the presence of a solvent such as xylene or toluene. The vapor is condensed and accumulated in a graduated tube for measurement. Cores can also be used for mechanical strength tests such as compression tests, and for microscopic investigation of biotic and abiotic damage. Cores can also be chipped and used for a variety of chemical analyses, including analysis for wood preservatives. Depth of penetration and distribution of active ingredients may also be determined.

For the estimation of current strength of wood objects a variety of instruments are used which work with steel needles or thin drills. The portable pilodyn which was developed in Denmark shoots a steel needle of a diameter of 0.5–3 mm by means of a spring of specified energy into the wood. The depth of penetration is read on a scale attached to the instrument, and represents a measure of the strength or hardness of the wood. If insect damage or decay is present, the needle will penetrate significantly deeper. Informative measurements on old structural timbers of oak, pine and fir have been made by Görlacher (1987). Clarke and Squirrell (1985) and Mouzouras et al. (1990) mapped regions of differing strength of waterlogged wood from the *Mary Rose*, the flagship of Henry VIII, with the pilodyn. The latter can also be used under water.

Other devices are based on the principle that the resistance met by a needle pushed into wood at a constant feed rate is proportional to the strength of the wood at the point of the needle (Brandt and Rinn 1989; Chagneau and Levasseur 1989). The resistograph, which was developed in Germany, consists of a drill, a battery, a built-in printer and computer memory (Fig. 6.1). The needle drills can reach a depth of up to 1 m at a feed rate of up to 500 mm/min. The bore holes have a diameter of 1–3 mm and are self-closing since the chips

Table 6.1. Inspection methods for wood

Method	Procedure	Property tested	Preferred application	Advantages	Disadvantages
Mechanical	Increment cores	Moisture content, density, mechanical properties, biological deterioration, assay of preservatives	Trees, wood in structures	Simplicity, handy instruments, low cost	Destructive, results for limited locality only
	Measure depth of penetration (e.g. pilodyn)	Density, hardness, biological deterioration	Wood in structures, waterlogged wood finds	Simplicity, in situ measurement, handy instrument, low cost, nearly nondestructive	Destructive, properties not measured exactly, large scatter of data
	Measure resistance to boring (e.g. resistograph)	Density, biological deterioration	Trees, wood in structures	Easy to use, portable instrument, costs not high, in situ measurement, printed data plots	Destructive, properties not measured exactly, detection of decayed areas dependent on point of test
Electrical	Determination of electrical resistance or conductivity, dielectric constant, and use of microwaves	Moisture content (presence of decay)	Trees, wood in structures, cultural property	Nondestructive or nearly so, easy to use, low cost, in situ measurement, handy devices	Less accurate than the oven-dry method
Optical	Visual	External biodeterioration	Trees, wood in structures	Nondestructive, in situ measurement	Subjective evaluation
	Light and electron microscopy	Biological damage, chemical degradation, deposits of consolidants	Wood in structures, waterlogged wood finds	More accurate diagnosis, detection of early stages, photographic record	Destructive (samples are removed), preparation can be time consuming and instruments costly, laboratory method
	Endoscopy	Biological deterioration	Hidden spaces in buildings	Relatively simple, in situ inspection, photographic record	Destructive, bore holes required

Table 6.1. Continued

Method	Procedure	Property tested	Preferred application	Advantages	Disadvantages
Acoustic	Holography	Cracks, delaminations, decay	Cultural property	Nondestructive, photographic record	Laboratory method, not yet fully developed
	IR spectroscopy	Moisture content, deterioration	Art and archaeology objects	Nondestructive or nearly so, printed record	Laboratory method, only moisture content on surfaces can be tested
	Speed of ultrasound	Wood defects, decay areas, insect damage	Wood processing, wood in structures	Nondestructive, in situ measurement, handy instruments	Object must be accessible and density of sound wood must be known, coupling difficult with uneven surfaces (sculptures)
	Acoustic emission	Decay, internal stresses, active insect infestation	Wood in structures, cultural property	Nondestructive, in situ measurement, practical instruments for termites available	Laboratory method for house longhorn beetles
Thermographic	Measurement of heat radiation	Knots, decay, insect damage, moisture content differences, delaminations	Wood in structures, cultural property	Nondestructive, in situ measurement, handy instruments, imaging	Heating of cultural property problematic, resolution still insufficient
Radiographic	Conventional X-rays	Macroscopic wood structure, density, decay, insect damage	Movable cultural property, testing wood preservatives	Nondestructive, imaging	Resolution of mobile instruments still insufficient, laboratory method
	Computer-tomography	Decay, density, moisture content, deposits of consolidants	Trees, movable cultural property, waterlogged wood finds	Nondestructive, imaging (3-D reconstruction), transportable instruments available	Very high costs, expensive equipment, requires accessibility from all sides

Table 6.1. Continued

Method	Procedure	Property tested	Preferred application	Advantages	Disadvantages
Nuclear magnetic	Gamma-ray densitometry	Moisture content, density, decay	Wood drying, wood in structures	Nondestructive	Expensive equipment, transportable instruments still under development
	Neutron radiography	Moisture content	Wood processing	Nondestructive	Data density-dependent
	Tomography	Moisture content and distribution, consolidant distribution	Waterlogged wood finds, possibly trees	Nondestructive, imaging	Very expensive equipment, not transportable
	Chemical/biological	Decay, especially <i>Serpula lacrymans</i>	Wood in structures	Detects early stages of decay, identifies decay fungus species	Destructive (samples must be removed), laboratory methods

remain inside. The power consumption of the driver motor is a measure of wood density along the bore path, and is printed out in the form of a 'den-drogram' (Fig. 6.2). One operator can use this portable device to investigate the safety and load capacity of structural wood elements and to estimate residual strength of wood damaged by decay and insects. Panter and Spriggs (1997) use the Sibert decay detecting drill, a hand-held probe for assessing waterlogged wood degradation.

Hamm (1995) developed a densitometric method for determining wood density of standing trees, which is based on the volume ratio of increment cores before and after radial compression in a special cylinder. A semi-portable (16kg) prototype could produce results in 30s. This device also has potential for use on large timbers of waterlogged wood. Since the method is based on the assumption of constant density of water-saturated wood substance, it could not be used for dry wood.

6.3 Electrical Methods

Electrical methods include measurements of electrical resistance, conductivity, and the dielectrical constant of wood. They serve primarily for the determination of moisture content in wood (Skaar 1988; Vermaas 1996), but have

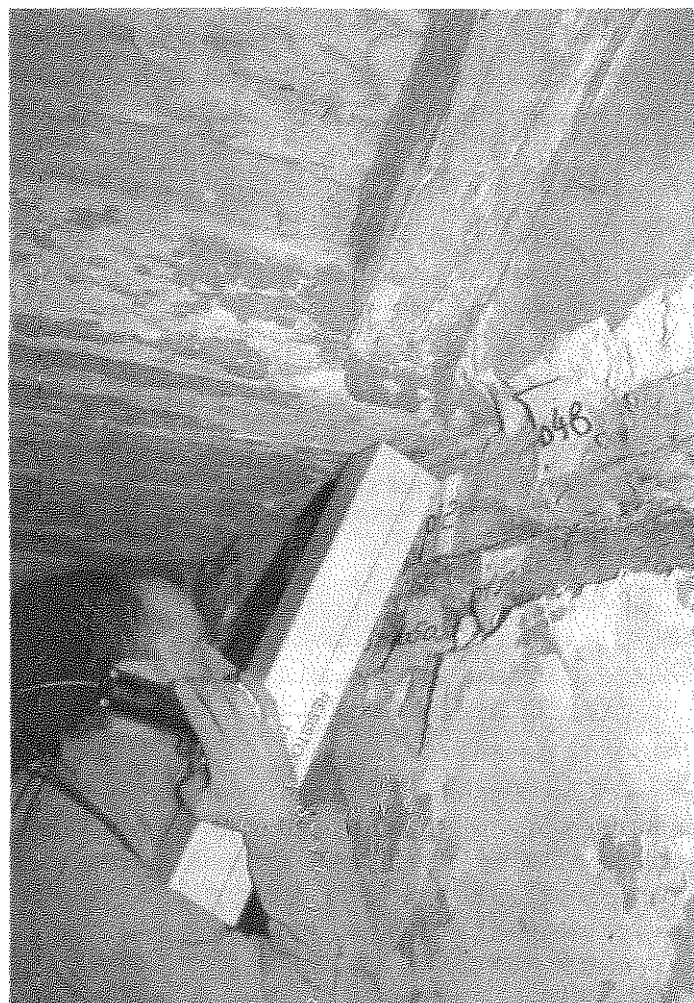


Fig.6.1. Resistograph; apparatus for measuring drilling resistance for testing old wood structures. (Photograph courtesy of F. Rinn)

also been used to check for decay in standing trees and wood in use such as transmission poles (Skutt et al. 1972). The electrical resistance of wood increases as moisture content decreases, and is affected by wood species, temperature, grain direction, and soundness (absence of deterioration). Resistance moisture meters are fitted with electrodes which differ for solid wood and for veneer. In the case of solid wood, the electrodes are driven into the wood or inserted into prebored holes. Provisions are made to allow for adjustments for species and temperature. Most portable moisture meters are comparable in size to the larger hand calculators. Håfors and Persson (1997)

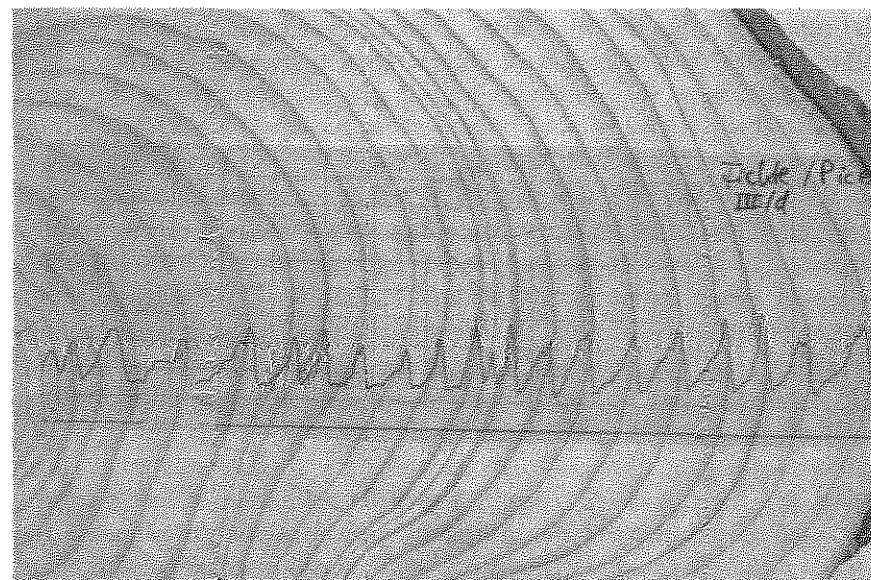


Fig.6.2. Dendrogram; density profile of a tree trunk with heart rot. (Photograph courtesy of F. Rinn)

determine the moisture content of the wood of the *Wasa* with a special electrical resistance meter.

The Shigometer (Shigo and Shigo 1974) and the Vitamat (Kučera 1986) are instruments which were developed to detect fungal decay in standing trees and in structural timber. They are based on the measurement of electrical conductivity, which increases in decayed wood owing to increased cation concentration. Since measured values are highly dependent on moisture content, reliable decay diagnosis is not possible and instruments of this type have not found general acceptance.

Dielectric and microwave methods for determining moisture content (Niemz 1993) utilize distinct differences in the dielectric constants of water ($\epsilon = 80$) and dry wood ($\epsilon = 2-3$). Dielectric measurements are affected by the measurement frequency in the kHz and MHz range and by wood density. Microwave methods, which use frequencies of 1-10GHz, are based on the much greater absorption of the radiated energy by water molecules than by dry wood. Temperature and wood density effects must be considered in interpreting the results.

6.4

Optical Methods

The simplest method is a visual inspection and estimation of damage to wood in use by biological deterioration or corrosive media. Whether brown rot,

white rot, or soft rot is present, and what species of fungus caused it, can be determined from the developmental stages of the fungus (hyphae, mycelia, fruiting bodies) and the types of deterioration that result (discolorations, warping, cubical or shell-like decay; cf. Chap. 5). In those cases, the fungal attack is already at an advanced stage. If there are no visible signs of fungal development, or if they have been inadvertently removed and no clear-cut changes of the wood are visible, suitable test specimens such as increment cores (cf. Sect. 6.2) must be examined by light or electron microscopy for possible fungal invasion. The same applies to characterization of bacterial attack or chemical deterioration as may be found for instance in waterlogged wood. Changes in archeological wood by impregnation with consolidants can also be studied by scanning electron microscopy (SEM; Hatchfield and Koestler 1987). In many cases, staining of microtome sections is helpful in locating fungal attack under the light microscope.

Wood-destroying insects can be identified by their characteristic bore pattern and their frass (cf. Chap. 5). Exact determination of insect species most often requires a hand lens or light microscope. Good knowledge of the pattern of damage caused by the insects, and the species of wood which they prefer, makes it possible in certain instances to unmask forgeries of panel paintings, icons, or furniture (Cymorek 1984). Incisions in wood produced by spike rolls or bombardment of 'art objects' with shot to simulate bore holes and suggest a certain age can be readily distinguished from real insect attack. A similar situation occurs when the reproduction of antiques uses wood attacked by insects which are not found in the country of origin of the object. Remanufacture of wood with insect damage may also give away a forgery when bore holes which should be entirely in the interior are sliced open longitudinally in the process. However, the possibility that artists of earlier centuries already knowingly used panels with some insect damage cannot be totally excluded (Rinuy and Schweizer 1986).

Inspection of historic buildings for deterioration by fungi or insects by endoscope has been carried out successfully for years (Janotta 1984). Practically inaccessible spaces such as those above wood-framed ceilings can be inspected with an endoscope which has an external diameter of not much more than 1 mm, and their condition interpreted with the help of photographs (Arendt and Seele 1996). The required bore holes can then be suitably plugged.

Optoelectronic methods are being used in the wood industry to inspect for defects and for quality control. The use of holographic interferometry for the nondestructive inspection of cultural wood items for damage such as checks, splits, delaminations, and decay pockets has not yet progressed very far (Paoletti et al. 1987). Fromm et al. (1998) have studied high-voltage photography (1–40 kV) to detect moisture distribution in wood.

Infrared (IR), Fourier transform infrared (FTIR), and near-infrared (NIR) spectroscopy are specific, useful optical methods. They are based on the correlation between the absorption of light of specified wavelength and the chemical constituents of a given material. These methods have been

used to determine wood moisture content and to characterize weathering of wood surfaces and deterioration by decay fungi (Körner et al. 1992). They have been used further to estimate the condition of archeological wood (Kommert and Pecina 1985; Kim 1988; Kirillov and Mikolajchuk 1990). Wood specimens which were consolidated with synthetic resins and subsequently subjected to fungal decay were also investigated by IR spectroscopy (Paciorek 1993).

6.5

Acoustic Methods

Acoustic diagnosis of wood condition primarily utilizes the speed of sound in wood and acoustic emission. The speed of sound is strongly influenced by structural details in wood, making it possible to detect such characteristics as knots and density differences as well as damage by decay fungi and insects. In the simplest case, regions of internal decay and insect damage can be detected by sounds produced mechanically with an impact hammer. For example, Ross et al. (1999) located areas of degradation in wood members of the *USS Constitution* by stress-wave inspection. Other instruments use ultrasound in the range 20 kHz to 1 GHz in transmission, where the time of traversal through the wood is measured. Machine grading of wood for strength is possible on this basis (Steiger 1997). Sending and receiving transducers are attached to the end surfaces of the wood, as for instance with the sylvatest instrument (Fig. 6.3). Density and moisture content of the wood affect the measurements, especially in the presence of decay (Konarski and Ważny 1977). The use of ultrasound to determine the presence of decay in wood structures has been investigated by Arita et al. (1986), Wilcox (1988), Klingsch and Neum (1989), Prieto (1990), and Emerson et al. (1999). Kim et al. (1993) found satisfactory to good correlation between the bending strength of decayed wood and a combination of ultrasound and pilodyn measurements. Defects in wood can be located and documented with the aid of graphic ultrasound tests (Neuenschwander et al. 1997).

Wood under load emits sound in the humanly audible as well as the ultrasound regions, which are produced by the release of stored energy which takes place during deformation and destruction of wood through fiber fracture, friction of fracture surfaces, and the formation and growth of cracks. Ultrasound waves in the range of 50–150 kHz produced by microfractures can be useful indicators in the control of drying processes (Honeycutt et al. 1985) and the detection of decay in structural timber (Niemz 1989). According to Noguchi et al. (1986, 1992), acoustic emission analysis is a nondestructive method which can estimate very early stages of decay before these are detectable by traditional strength test methods.

Not only the wood, but also wood-destroying insects living inside it emit acoustic signals from their feeding and movements. In the past, attempts have been made to detect active infestations of wood-destroying insects

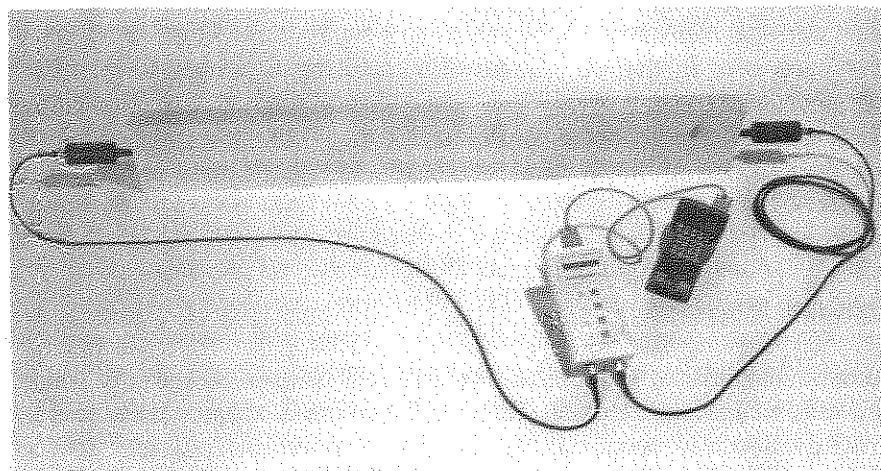


Fig. 6.3. Measuring speed of ultrasound with the sylvatest instrument. (Photograph courtesy of J.L. Sandoz)

with the aid of a stethoscope or a combination of microphone, amplifier and headphones. More accurate results are obtained with systems which record acoustic signals, as reported, for example, for the house longhorn beetle by Kerner et al. (1980), Pallaske (1988), Plinke (1991), Schmidt et al. (1995), and Hyvernaud et al. (1996). The vibrations or sound waves in the substrate caused by insect larvae or imagoes are measured nondestructively, the nature of their origin, whether from feeding or movement, is determined by computer analysis, and the results are compared with reference patterns. Termite infestations can also be detected in this manner at an early stage (Fujii et al. 1990; Lewis et al. 1991; Noguchi et al. 1991). Unlike the irregular feeding and movement noises of anobiid and house longhorn beetle larvae, the sounds produced by termites are continuous and can be more easily detected and interpreted. The development of equipment in this area (Scheffrahn et al. 1993) and its practical application for monitoring control measures (Fujii et al. 1999; Scheffrahn and Thoms 1999; cf. Chap. 10) is therefore more advanced.

6.6

Thermographic Methods

Every body at a temperature above absolute zero radiates heat in the infrared spectral range. Knots, splits, decay pockets, or insect bore holes in wood will disrupt heat conduction. If wood is heated from the outside, for instance with a heat lamp, and its temperature field is then measured with a pyrometer or a thermographic camera, any such defects become evident (Niemz 1993). This

method was used in attempts to detect void spaces (Miller 1978) and density and moisture content differences (Schwarz 1990) in panel paintings. Furthermore, location and condition of half-timbering and beam ends can be comprehensively determined (Cramer 1980; Zimmer et al. 1985). Estimation of damage in structural wood elements during loading is also possible by infrared thermography (Luong 1996). Cuany et al. (1989) used this method to determine the degree of insect damage in wood and the distribution of consolidants during impregnation into objects. However, their thermograms do show the general areas of insect damage, but they are not clearly defined. Insect galleries also did not show up clearly. The use of more modern instruments with better resolution makes it possible to detect growth rings and galleries. For wood-based materials with veneer faces, thermography is a contactless method to detect delaminations, joint gaps, and differing types of wood under the face veneer (Wu et al. 1997).

6.7

Radiographic Methods

The most common methods utilize X-rays or gamma rays, but charged particles or neutrons also find application in transmission through wood objects. As the radiation passes through wood, it is attenuated differentially by inhomogeneities before it reaches detectors at the opposite surface. In this respect there are similarities between speed of ultrasound measurements with separate senders and receivers and the radiographic methods, but the latter do produce highly informative images of density distribution within objects. X-ray microdensitometric analysis (Polge 1963) makes possible dendrochronological investigations (Schweingruber 1988) and studies of the kinetics of wood decomposition by fungi (Bucur et al. 1997).

Conventional X-ray radiography with stationary or mobile devices can elucidate the inner structure, including presence of decay or insect damage, of art objects and other cultural property. Damage by decay fungi can be detected by conventional X-ray methods only in its advanced stages. For this reason, Grattan et al. (1987) and Grattan and Bokman (1988) combined X-ray radiography with mechanical tests using the pilodyn in their study of totem poles damaged by decay.

When testing wood preservatives, X-rays are used for the determination of activity by insect larvae before and after treatment. Conventional X-ray radiography is now a standard method for the examination of art objects and other cultural property partially or entirely made of wood (Mairinger 1977; Hellwig 1982; Graham and Eddie 1985; Beck 1990). The internal condition of wood objects and their present status with respect to biological deterioration are thereby of primary interest. Applications range from panel paintings (Mairinger 1977), wood-wind instruments (Hellwig 1983), and sculptures (Vitali et al. 1986) to religious relics (Keene 1987).

A significant advance in the nondestructive interpretation of the internal structure of wood objects has been the development of X-ray or gamma ray computer tomography (CT), where the coefficient of absorption of the radiation is determined by location, layer by layer. The spatial distribution of the absorption coefficient is calculated by computer and presented graphically. The absorption coefficient depends on wood density and moisture content. Decay and insect damage effect a decrease in density which decreases the absorption of the radiation. Mobile computer tomographs have been developed for standing trees (Habermehl and Ridder 1992, 1993); in principle, they could also be used for works of art (Fig. 6.4), but a higher level of resolution would be necessary. CT, also referred to as CAT (computerized axial tomography), is also useful for determining density and moisture content of wood with or without protective coatings (Lindgren 1987; Ekstedt et al. 1992; Lindgren et al. 1992) and for studying diffusion of water through acrylic latex paints with differing particle sizes (Lindberg et al. 1996).

CT offers excellent opportunities for nondestructively determining the internal condition and structure of movable art objects made of wood (Jakob et al. 1986; Unger and Perleberg 1987), and is especially useful for investigating wood sculptures (Taguchi et al. 1984; Essers 1987). When wood is combined with other materials, as in the case of a small portrait head of an ancient Egyptian queen, later changes can be clearly shown by 3-D reconstruction of CT imagery (Illerhaus 1995). CT studies have also been made of panel paintings (Rinuy and Schweizer 1986), picture frames (Unger and Perleberg 1987; Fig. 6.5), coffins from the Middle Ages (Grupe et al. 1985), and musical instruments such as violins, structural wood elements, and archeological objects (Unger et al. 1988).

In principle, CT could also be used for dendrochronological investigations (Starling 1987; Reimers et al. 1989; Beck 1990), but the resolution of instruments designed for medical applications is too low to be effective for woods with very narrow growth rings. A significant step up in resolution can be obtained with X-ray microtomography (CMT; Davis et al. 1991). Whereas medical instruments cannot resolve areas $<1\text{ mm}^2$, the resolution with CMT using synchrotron radiation is in the range of $1\text{--}6\text{ }\mu\text{m}^2$. For example, using CMT, the extent of decay damage in wood can be determined by means of a 3-D reconstruction (Illman and Dowd 1997). CT is also a valuable tool for investigating the stabilization of air-dry wood objects (Planitzer et al. 1987; Paciorek 1993; Kučerová and Lisý 1999; Fig. 6.6) and of waterlogged wood finds (Cott and Unger 1991; Potthast 1996).

Furthermore, it is possible to use CT images of insect-damaged and sound wood to prepare calibration curves which represent the relationship between the quantity of absorbed radiation and certain physical properties of wood such as density or compression strength (Unger and Perleberg 1987; Lindgren 1991). On the basis of such calibration curves for particular species of wood such as linden or poplar, CT images could then be used to estimate

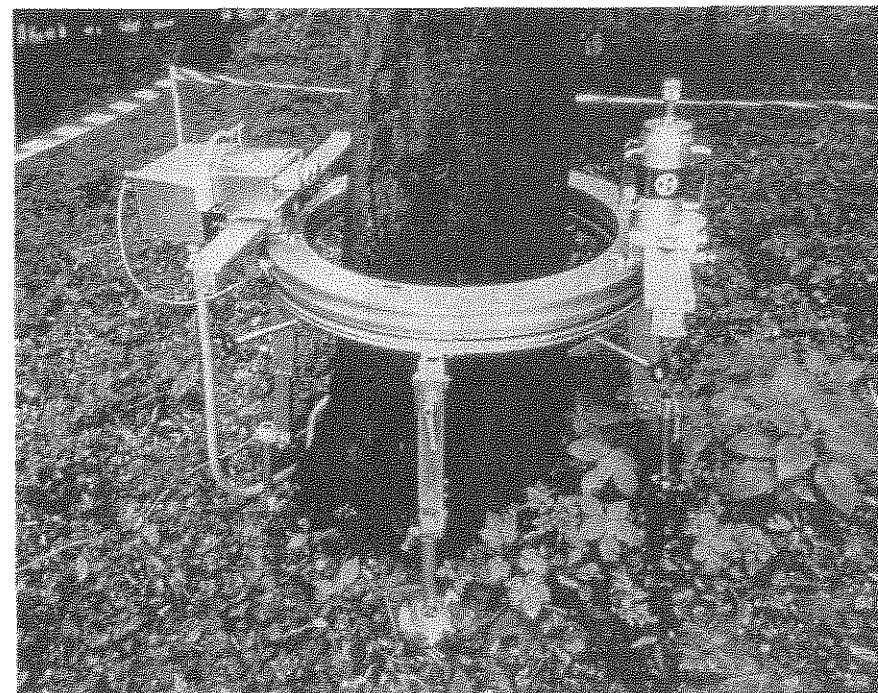


Fig. 6.4. Mobile computer tomograph. (Photograph courtesy of H.-W. Ridder)

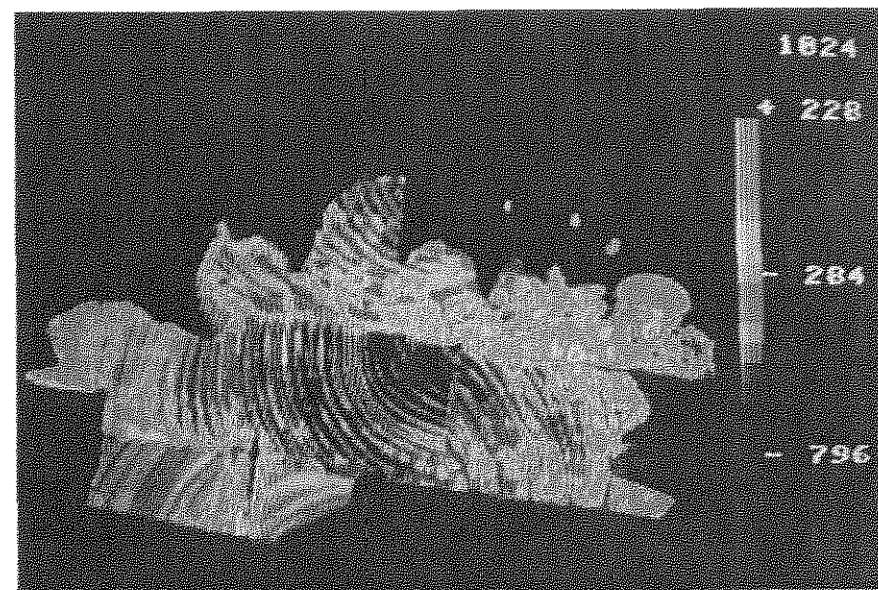
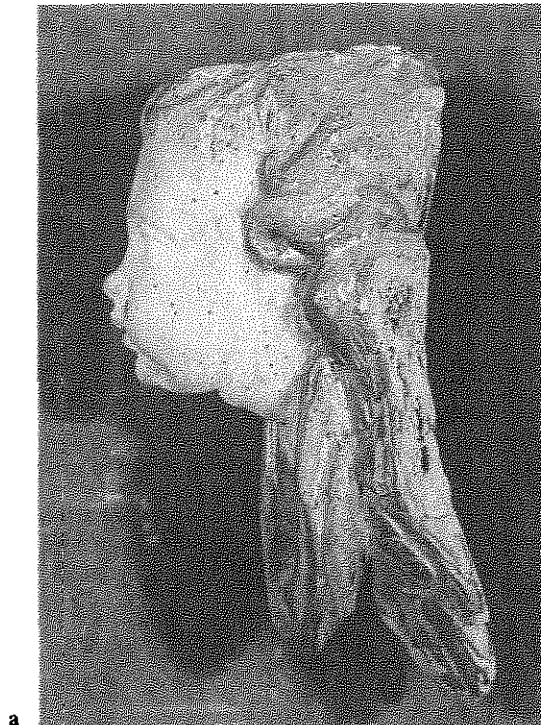
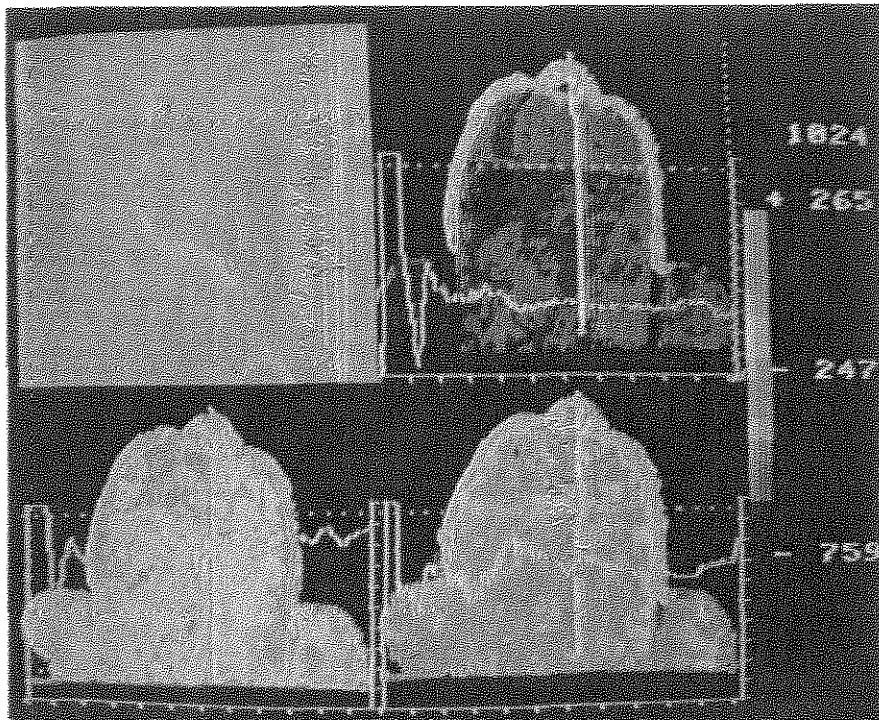


Fig. 6.5. CT image of a carved frame damaged by Anobiidae



a



b

Fig.6.6. CT documentation of the consolidation of a putto. a Putto. b Sectional CT images

nondestructively the reduction in density and strength of insect-damaged art objects such as sculptures. The results may then be used to calculate how much consolidant would need to be impregnated into the damaged wood in order to restore it to something approaching its original strength.

In some cases electroradiography (xeroradiography) affords better elucidation of detail than conventional X-rays when an object is composed of materials differing greatly in density (Keene 1987; Magliano and Boesmi 1988). Larvae of wood-destroying insects can also be detected with this technology.

Gamma-ray densitometers, which operate with beams of focused photons, can be used to determine moisture content of wood during the drying process (Davis et al. 1993), as well as the diminished density of old structural timbers with fungal decay, such as those affected by *Serpula lacrymans* (Madsen and Adelhøj 1989).

Neutron radiography is based on the principle that neutrons are attenuated more by the hydrogen atoms in water than the other elements contained in wood. The number of neutrons which are attenuated is a measure of moisture content, but measurements are strongly affected by wood density (Niemz 1993).

6.8

Nuclear Magnetic Methods

In contrast to X-ray and gamma-ray radiography, nuclear magnetic resonance tomography (NMRT) does not utilize ionizing radiation, but images are derived from magnetic moments of atomic nuclei with an odd number of protons. The simplest nucleus of this type is the nucleus of the hydrogen atom, the proton. Many chemical compounds contain hydrogen, among them water which is present in all living things. With the aid of NMRT, it is possible to draw conclusions from the obtained signal distributions about the condition of hydrogen-containing materials such as water (Hailey et al. 1985; Araujo et al. 1992). According to Hall et al. (1986a,b), growth rings, knots, and regions of deteriorated wood become clearly demarcated on fresh cross-sectional discs of aspen because of the uneven distribution of water. Similar results have been obtained for cherry wood (Wang and Chang 1986). Kučera (1986) used NMRT to characterize the state of health of spruce and fir trees, where early stages of damage can be recognized from uneven moisture content distribution in heartwood and sapwood. The condition and water distribution of archaeological waterlogged wood (Fig. 6.7) can be determined in this manner nondestructively (Unger et al. 1988; Cole-Hamilton et al. 1990) and the progress of conservation treatments can be followed (Cott and Unger 1991; Cole-Hamilton et al. 1995). In contrast to stationary NMRT equipment, a portable NMR inspection system provides nondestructive information on moisture content and distribution, as well as porosity and density distribution in wood (Anonymous 1999; Tran et al. 1999). Paramagnetic salts of

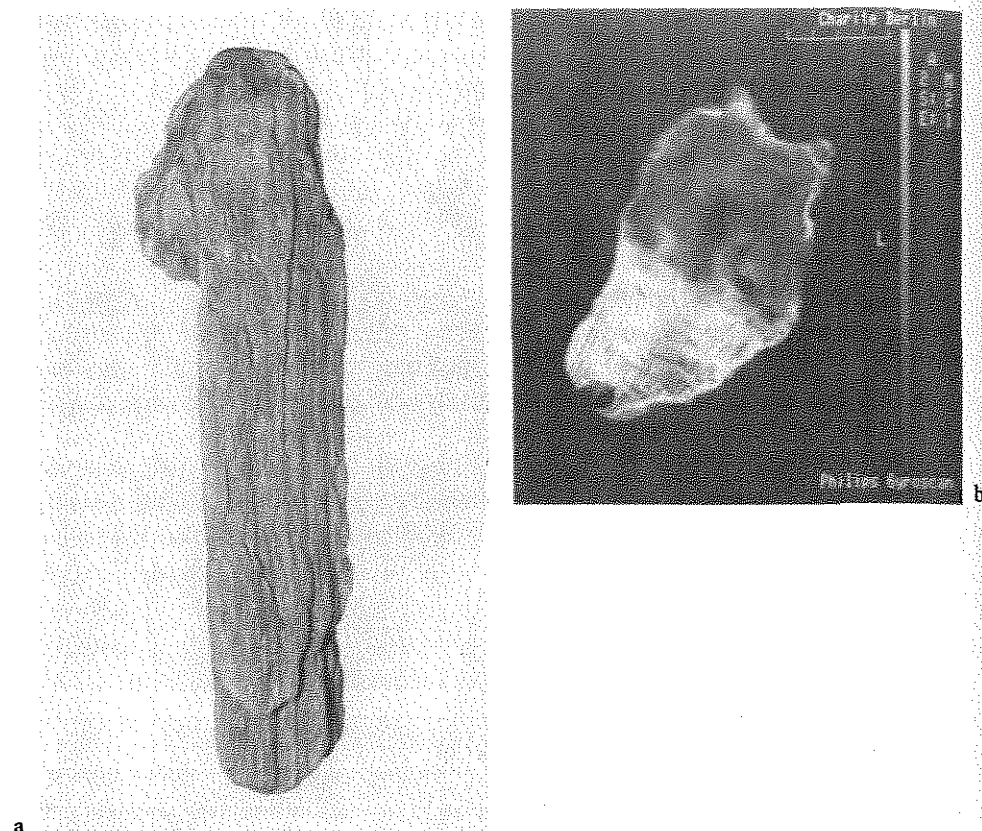


Fig.6.7. Nuclear magnetic resonance tomography (NMRT) of a waterlogged wood find. a Wooden idol. b Distribution of moisture in the head area

iron(II) and iron(III), which are often present in waterlogged archaeological oak wood, lead to poorer images, necessitating prior removal of the iron ions. The deposition of polymeric substances within the wood matrix cannot be determined directly, but requires a deuterium exchange (Cole-Hamilton et al. 1995).

6.9

Chemical and Biological Procedures

Most of the procedures mentioned in this section depend on the removal of test material and thus contain an element of mechanical methodology. The most important efforts are directed toward the detection of attack by decay fungi in general, and the identification of the fungal species (i.e., *Serpula*

lacrymans) causing the damage of wood in use. Peek et al. (1980) carried out extensive work on early detection of fungal decay in wood by means of color indicators (cf. Chap. 5). Recently, increased efforts have been directed toward the development of methods to detect brown rot, especially *Serpula lacrymans* (Koch 1990). Specifically, the emission of carbon dioxide has been measured (Toft 1995). Furthermore, molecular biological investigations by means of polyacrylamide gel electrophoresis of the intracellular proteins (Schmidt and Moreth-Kebernik 1989; Moreth and Schmidt 1996), immunological techniques (Jellison and Goodell 1988; Palfreyman et al. 1989; Glancy and Palfreyman 1993), and genetic studies such as DNA analyses with polymerase chain reaction (Jasalavich et al. 1998; Schmidt and Moreth 1998a,b) have been used. The use of dogs to detect active decay in buildings has also found application (Koch 1990). Nilsson (1996) has tested electronic noses for the detection of volatile organic compounds (VOC) emitted from wood colonized and decayed by fungi.

The presence of wood-destroying insects, such as termites, in museum objects can be determined by measuring carbon dioxide respiration with FTIR spectroscopy (cf. Sect.6.4) before and after eradication measures (Koestler 1993).

References

- Anonymous (1999) Leaflet NMR-INSPECT-nuclear magnetic resonance surface technique. Fraunhofer-Institut für Zerstörungsfreie Prüfverfahren (IZPV), Saarbrücken, Germany
- Araujo CD, MacKay AL, Hailey JRT, Whittall KP, Le H (1992) Proton magnetic resonance techniques for characterization of water in wood: application to white spruce. *Wood Sci Technol* 26:101–113
- Arendt C, Seele J (1996) Meßgeräte für Voruntersuchungen im Altbaubereich, Teil 1. *Bautenschutz Bausanierung* 19(2):8–10
- Arita K, Mitsutani S, Sakai H, Tomikawa Y (1986) Detection of decay in the interior of a wood post by ultrasonic method. *Mokuzai Kogyo* 41(8):370–375
- Beck A (1990) Original – Fälschung? Bildgebende Verfahren in der Diagnostik von Kunstwerken. Schnetztor, Konstanz
- Brandt M, Rinn F (1989) Eine Übersicht über Verfahren zur Stammfäule-diagnose. *Holz-Zentralblatt* 115(80):1268–1270
- Bucur V, Garros S, Navarrete A, de Troya MT, Guyonnet R (1997) Kinetics of wood degradation by fungi with x-ray microdensitometric technique. *Wood Sci Technol* 31:383–389
- Chagneau F, Levasseur M (1989) Diagrammes xylochronologiques par dynamostratigraphie. *Rev For Fr* 41:211–216
- Clarke RW, Squirrell JP (1985) The pilodyn – an instrument for assessing the condition of waterlogged wooden objects. *Stud Conserv* 30:177–183
- Cole-Hamilton DJ, Chudek JA, Hunter G, Martin CJM (1990) NMR imaging of water in wood, including waterlogged archaeological artefacts. *J Inst Wood Sci* 12:111–113
- Cole-Hamilton DJ, Kaye B, Chudek JA, Hunter G (1995) Nuclear magnetic resonance imaging of waterlogged wood. *Stud Conserv* 40:41–50
- Cott J, Unger A (1991) Resultate einer Naßholzkonservierung mit Zucker. *Restaur* 97:392–397
- Cramer J (1980) Untersuchung von Fachwerkbauten auf thermographischer Basis. *Bauen Holz* 82:59–62

- Cuany F, Schaible V, Schießl U (1989) Studien zur Festigung biologisch geschwächten Nadelholzes: Eindringvermögen, Stabilitätssteigerung, feuchtephysikalisches Verhalten. *Kunsttechnol Konserv* 3:249–292
- Cymorek S (1984) Schadinsekten in Kunstwerken und Antiquitäten aus Holz in Europa. Teil 1: Allgemeine Einordnung der Schadinsekten, Übersicht und Beziehungen zur Holzbeschaffenheit. *Holz-Zentralblatt* 110(42):638–641
- Davis JR, Ilic J, Wells P (1993) Moisture content in drying wood using direct scanning gamma-ray densitometry. *Wood Fiber Sci* 25:153–162
- Davis JR, Lerdin A, Wells P, Ilic J (1991) X-ray microtomography of wood. *J Inst Wood Sci* 12(4):259–261
- Ekstedt J, Lindgren O, Grundberg S (1992) Moisture distribution in coated wooden panels. Studies of moisture dynamics by computerized axial tomography. IRG/WP/2413
- Emerson RN, Pollock DG, McLean DI, Fridley KJ, Ross RJ, Pellerin RF (1999) Nondestructive testing of large bridge timbers. Proceedings of the 11th International Symposium on Non-destructive testing of wood, 9–11 Sept 1998, Madison, Wisconsin. Forest Products Society, Madison, Wisconsin, pp 175–184
- Essers G (1987) Computertomographische Untersuchungen von Bildwerken. Symposium Zerstörungsfreie Prüfung von Kunstwerken, Berlin, 19/20 Nov 1987, DGZfP, Berichtsband 13:61–68
- Fromm J, Sühlfleisch M, Schumacher P (1998) High-voltage photography: a new method for optical detection of moisture distribution in wood and wood-based panel products. *Holz Roh Werkst* 56:437–444
- Fujii Y, Noguchi M, Imamura Y, Tokoro M (1990) Using acoustic emission monitoring to detect termite activity in wood. *For Prod J* 40(1):34–36
- Fujii Y, Yanase Y, Yoshimura T, Imamura Y, Okumura S, Kozaki M (1999) Detection of acoustic emission (AE) generated by termite attack in a wooden house. IRG/WP/99-20166
- Glancy H, Palfreyman JW (1993) Production of monoclonal antibodies to *Serpula lacrymans* and their application in immunodetection systems. IRG/WP/93-10004
- Görlacher R (1987) Zerstörungsfreie Prüfung von Holz: Ein "in situ"-Verfahren zur Bestimmung der Rohdichte. *Holz Roh Werkst* 45:273–278
- Graham MD, Eddie TH (1985) X-ray techniques in art galleries and museums. Hilger, Bristol
- Grattan DW, Bokman W (1988) Poster session 2: examination of totem poles for the Canadian Museum of Civilization. Symposium 86. In: Barclay R, Gilberg M, McCawley JC, Stone T (eds) The care and preservation of ethnological materials: proceedings. Canadian Conservation Institute, Ottawa, pp 264–266
- Grattan DW, Bokman W, Cook CM (1987) Scientific examination of totem poles at Ninstints World Heritage Site. *J Int Inst Conserv Can Group* 12:43–57
- Grupe G, Herrmann B, Lüdtke H, Vogel V (1985) Computertomographische Untersuchung mittelalterlicher Särge aus Schleswig. *Archäolog Korrespondenzbl* 15:119–121
- Habermehl A, Ridder H-W (1992) Methodik der Computer-Tomographie zur zerstörungsfreien Untersuchung des Holzkörpers von stehenden Bäumen. *Holz Roh Werkst* 50:465–474
- Habermehl A, Ridder H-W (1993) Anwendungen der mobilen Computer-Tomographie zur zerstörungsfreien Untersuchung des Holzkörpers von stehenden Bäumen. *Holz Roh Werkst* 51:1–6
- Häfors B, Persson U (1997) Monitoring changes in water content of the Vasa wood with a resistance meter. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 35–46
- Hailey JRT, Menon RS, MacKay A, Burgess AE, Swanson JS (1985) Nuclear magnetic resonance scanning for wood characterization. Proceedings of 5th Symposium on Non-destructive testing of wood. Pullman, Washington, DC, 9–11 Sept 1985
- Hailey JR, Morris PI (1987) Application of scanning and imaging techniques to assess decay and wood quality in logs and standing trees. Forintek Canada Corp, Project 1432–43, 48 pp

- Hall LD, Rajanayagam V, Stewart WA, Steiner PRR (1986a) Magnetic resonance imaging of wood. *Can J For Res* 16:423–426
- Hall LD, Rajanayagam V, Stewart WA, Steiner PRR, Chow S (1986b) Detection of hidden morphology of wood by magnetic resonance imaging. *Can J For Res* 16:684–687
- Hamm EA (1995) Development of a rapid wood density evaluation instrument. *For Prod J* 45(4):75–82
- Hatchfield PB, Koestler RJ (1987) Scanning electron microscopic examination of archaeological wood microstructure altered by consolidation treatments. *Scanning Microscopy* 1(3):1059–1069
- Hellwig F (1982) Geschichte durchleuchten: Röntgentechnik im Museum. *Electromedica* 50(4):133–136
- Hellwig F (1983) Geschichte durchleuchten: alte Musikinstrumente im Röntgenbild. *Electromedica* 51(4):159–163
- Honeycutt RM, Skaar C, Simpson WT (1985) Use of acoustic emissions to control drying rate of red oak. *For Prod J* 35(1):48–50
- Hyvernaud M, Wiest F, Serment MM, Angulo M, Winkel O (1996) Make ready of a detection system for insect attack by acoustical method. IRG/WP/96-10183
- Illerhaus B (1995) Fortschritte in der Computertomographie. *Restaurio* 101(5):344–349
- Illman BL, Dowd BA (1997) Imaging fungal deterioration of wood using X-ray microtomography. IRG/WP 97-10240
- Jakob G, Ehlich V, Unger A, Perleberg J (1986) Anwendungsmöglichkeiten der Röntgen-Computertomographie auf dem Holz- und Kunstsektor. *Holztechnologie* 27:85–86
- Janotta O (1984) Die bautechnische Endoskopie, ein modernes Verfahren zur Untersuchung von Holzdecken. *Int Holzmarkt* 75(1/2):3–4
- Jasalavich C, Ostrofsky A, Jellison J (1998) Detection of wood decay fungi in wood using a PCR-based analysis. IRG/WP/98-10279
- Jellison J, Goodell B (1988) Immunological detection of decay in wood. *Wood Sci Technol* 22:293–297
- Keene S (1987) The Winchester Reliquary: conservation and elucidation. Recent advances in the conservation and analysis of artifacts. Jubilee conservation conference, Institute of Archaeology, University of London, pp 25–31
- Kerner G, Thiele H, Unger W (1980) Gesicherte und zerstörungsfreie Ortung der Larven holzzerstörender Insekten im Holz. *Holztechnologie* 21:131–137
- Kim GH, Barnes HM, Lyon DE (1993) Estimation of the residual strength of decayed wood. *Wood Protect* 2(2):47–55
- Kim YS (1988) Application of infrared spectroscopical techniques for investigation of archaeological woods. *Wood Sci Technol* 16:3–9
- Kirillov AL, Mikolajchuk EA (1990) Quantitative estimation of archaeological wood degradation degree by infrared Fourier transform spectroscopy. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden 26–31 Aug 1990, vol I, pp 239–240
- Klingsch W, Neum U (1989) Zerstörungsfreie Lokalisierung äußerlich nicht sichtbarer Holzschädigungen mittels Ultraschall. *Bauen Holz* 91(6):421–423
- Koch AP (1990) Dry rot – new methods of detection and treatment. BWPDA Record of Convention, The British Wood Preserving and Damp-proofing Association, London, 13 pp
- Koestler RJ (1993) Insect eradication using controlled atmospheres and FTIR measurement for insect activity. ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 22–27 Aug 1993, preprints, vol II, pp 882–886
- Körner I, Faix O, Wienhaus O (1992) Versuche zur Bestimmung des Braunfäule-Abbaus von Kiefernholz mit Hilfe der FTIR-Spektroskopie. *Holz Roh Werkst* 50:363–367
- Kommert R, Pecina P (1985) Die Anwendung der Infrarotspektroskopie zur Untersuchung von Holzfunden – Möglichkeiten und Beispiele. *Z Archäol* 19:115–126
- Konarski B, Ważny J (1977) Zusammenhang zwischen der Ultraschallgeschwindigkeit und den mechanischen Eigenschaften pilzbefallenen Holzes. *Holz Roh Werkst* 35:341–345

- Kothe E (1986) Moderne zerstörungsarme Prüfmethode zur Beurteilung verbauten Holzes. *Bauzeitung* 40:543-545
- Kučera LJ (1986) Kernspintomographie und elektrische Widerstandsmessung als Diagnosemethoden der Vitalität erkrankter Bäume. *Schweiz Z Forstwes* 137(8):673-690
- Kučerová I, Lisý J (1999) Sledování průniku impregnační látky do dřeva metodou počítačové tomografie (Study of the penetration ability of consolidating agent into wood using X-ray computer tomography). In: Reinprecht L (ed) *Rekonštrukcia a konzervácia historického dreva 1999*, 2nd International Symposium, 15-17 June 1999, Zvolen, pp 167-170
- Lewis VR, Lemaster RL, Beall FC, Wood DL (1991) Using AE monitoring for detecting economically important species of termites in California. *IRG/WP/2375*
- Lindberg H, Grahn J, Lindgren O, Hellgren A-C (1996) Water diffusion through acrylate latex paint films measured by computed tomography. *Proceedings of 10th international symposium on nondestructive testing of wood*, Lausanne, Switzerland, 26-28 Aug, p 408
- Lindgren O (1987) Computerized axial tomography - a non-destructive method for three-dimensional wood density/moisture content measurements. *IRG/WP/2285*
- Lindgren O (1991) Medical CAT-scanning: X-ray absorption coefficients, CT-numbers, and their relation to wood density. *Wood Sci Technol* 25:341-349
- Lindgren O, Davis J, Wells P, Shadboldt P (1992) Non-destructive wood density distribution measurements using computed tomography. *Holz Roh Werkst* 50:295-299
- Luong MP (1996) Infrared thermography of damage in wood. *Proceedings of 10th international symposium on nondestructive testing of wood*, Lausanne, Switzerland, 26-28 Aug, pp 175-185
- Madsen B, Adelhøj J (1989) Testing of wooden constructions in buildings. 7th international symposium on nondestructive testing of wood, Washington, Sept, 9 pp
- Magliano P, Boesmi B (1988) Xeroradiography for paintings on canvas and wood. *Stud Conserv* 33:41-47
- Mairinger F (1977) Untersuchungen von Kunstwerken mit sichtbaren und unsichtbaren Strahlen. Institut für Farbenlehre und Farbenchemie an der Akademie der Bildenden Künste, Wien
- Miller BF (1978) Thermographic detection of voids in panel paintings. Preprints of the contributions to the Oxford Congress on Conservation of wood in paintings and the decorative arts. The International Institute for Conservation (IIC), London, pp 145-147
- Moreth U, Schmidt O (1996) Molekularbiologische Untersuchungen an Hausfäulepilzen. *Holz-Zentralblatt* 122:2461,2464
- Mouzouras R, Jones AM, Jones EBG, Rule MH (1990) Non-destructive evaluation of hull and stored timbers from the Tudor ship *Mary Rose*. *Stud Conserv* 35:173-188
- Neuenschwander J, Niemz P, Kučera LJ (1997) Orientierende Untersuchungen zur Anwendung der bildgebenden Ultraschallprüfung zur Fehlererkennung in Holz. *Holz Roh Werkst* 55:339-340
- Niemz P (1989) Zur Anwendung der Schallemissionsanalyse in der Holzforschung. *Holz-Zentralblatt* 115:1704
- Niemz P (1993) Physik des Holzes und der Holzwerkstoffe. DRW, Leinfelden-Echterdingen
- Niemz P (1995) Entwicklungen in der zerstörungsfreien Werkstoffprüfung. Ihre Bedeutung bei Untersuchungen von Holz und Holzwerkstoffen. *Holz-Zentralblatt Teil I* 121:1181, 1182, 1184, *Teil II* 121:1242, 1244
- Nilsson K (1996) Electronic noses for detection of rot in wood. *IRG/WP/96-20098*
- Noguchi M, Ishii R, Fujii Y, Imamura Y (1992) Acoustic emission monitoring during partial compression to detect early stages of decay. *Wood Sci Technol* 26:279-287
- Noguchi M, Fujii Y, Owada M, Imamura Y, Tokoro M, Tooya R (1991) AE monitoring to detect termite attack on wood of commercial dimension and posts. *For Prod J* 41(9):32-36
- Noguchi M, Nishimoto K, Imamura Y, Fujii Y, Okumura S, Miyauchi T (1986) Detection of very early stages of decay in western hemlock wood using acoustic emissions. *For Prod J* 36(4):35-36

- Paciorek M (1993) Badania wybranych tworzyw termoplastycznych stosowanych do impregnacji drewna (A study of some thermoplastic resins used for wood impregnation). *Studia i Materiały*, Tom III, Akademia Sztuk Pięknych Kraków, Poland
- Palfreyman JW, Button D, Glancy H, King B, Nicoll G, Smith GM, Vigrow A (1989) The detection and destruction of basidiomycetes in the timber of artefacts of historical or archaeological interest. In: Baer NS, Sabbioni C, Sors AI (eds) *Science, technology and European cultural heritage. Proceedings of the European Symposium*, Bologna, Italy, 13-16 June 1989, pp 642-645
- Pallaske M (1988) Non-destructive detection of the presence and of behavior patterns of wood-destroying insects. *IRG/WP/2302*
- Panter I, Spriggs J (1997) Condition assessments and conservation strategies for waterlogged wood assemblages. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp 185-201
- Paoletti D, Schirripa Spagnola G, Volpe R, D'Altorio A (1987) Non-destructive method for analysing the ligneous samples. In: Hackens T, Munaut AV, Till C (eds) *Wood and archaeology: acts of the European Symposium held at Louvain-la-Neuve*, October. *PACT* (1988) 22: 319-338
- Peek R-D, Willeitner M, Harm U (1980) Farbindikatoren zur Bestimmung von Pilzbefall im Holz. *Holz Roh Werkst* 38:225-229
- Planitzer J, Unger A, Perleberg J (1987) Kontrolle der Konservierung von Kulturgut mittels Computertomographie. *Neue Museumskd* 30:161-163
- Plinke B (1991) Erkennung von Insektenbefall in Fachwerk. *Holz Roh Werkst* 49:404
- Polge H (1963) Une nouvelle méthode de détermination de la texture du bois: l'analyse densitométrique de clichés radiographiques. *Ann Sci For* 20(4):531-581
- Potthast I (1996) Untersuchungen an zuckerkonserviertem Naßholz. Diplomarbeit, Institut für Technologie der Malerei, Staatliche Akademie der Bildenden Künste, Stuttgart. *Kunsttechnol Konserv* 10(1):173
- Prieto G (1990) Detection and estimation of *Hylotrupes bajulus* L. wood damage by ultrasonic. *IRG/WP/2350*
- Reimers P, Riederer J, Goebels J, Ketsch A (1989) Dendrochronology by means of X-ray computed tomography (CT). In: Maniatis Y (ed) *Archaeometry: Proceedings of the 25th International Symposium*, pp 121-125
- Rinuy A, Schweizer F (1986) A propos d'une peinture florentine du Trecento: une contribution à la définition de critères d'authenticité. *Geneva* 34:95-122
- Ross RJ, Soltis LA, Otton P (1999) Role of nondestructive evaluation in the inspection and repair of the *USS Constitution*. *Proceedings of the 11th International Symposium on Nondestructive testing of wood*, 9-11 Sept 1998, Madison, Wisconsin. *Forest Products Society Madison, Wisconsin* 1999, pp 145-152
- Scheffrahn RH, Thoms EM (1999) A novel, localized treatment using spinosad to control structural infestation of drywood termites (Isoptera: Kalotermitidae). In: Robinson WH, Rettich F, Rambo GW (eds) *Proceedings of the 3rd International Conference on Urban pests*, Prague, 19-22 July 1999, pp 385-390
- Scheffrahn RH, Robbins WP, Busey P, Su N-Y, Mueller RK (1993) Evaluation of a novel, handheld, acoustic emissions detector to monitor termites (Isoptera: Kalotermitidae, Rhinotermitidae) in wood. *J Econ Entomol* 86(6):1720-1729
- Schmidt O, Moreth U (1998a) Detection of the dry-rot fungus *Serpula lacrymans* by amplified ribosomal DNA restriction analysis. *IRG/WP/98-10245*
- Schmidt O, Moreth U (1998b) Genetic studies on house rot fungi and a rapid diagnosis. *Holz Roh Werkst* 56:421-425
- Schmidt O, Moreth-Kebernik U (1989) Abgrenzung des Hausschwammes *Serpula lacrymans* von anderen holzzerstörenden Pilzen durch Elektrophorese. *Holz Roh Werkst* 47:336
- Schmidt R, Göller ST, Hertel H (1995) Computerized detection of feeding sounds from wood boring beetle larvae. *Mat Org* 29:295-304

- Schwarz A (1990) Infrarot-thermographische Dichte- und Feuchtedifferenzmessungen an bemalten Holztafeln. *Holz Roh Werkst* 48:36
- Schweingruber FH (1988) Tree rings. Basics and applications of dendrochronology. Kluwer, Dordrecht
- Shigo AL, Shigo AL (1974) Detection of discoloration and decay in living trees and utility poles. USDA Forest Service Research Paper NE-294
- Skaar C (1988) Wood-water relations. Springer, Berlin Heidelberg New York
- Skutt HR, Shigo AL, Lessard RA (1972) Detection of discolored and decayed wood in living trees using a pulsed electric current. *Can J For Res* 2:54–56
- Starling K (1987) The conservation, reconstruction, and dendrochronology of a medieval waterfront revetment from London. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6–11 Sept 1987, preprints, vol I, pp 321–324
- Steck G, Görlacher R (1986) Methoden der zerstörungsfreien und zerstörungsarmen Prüfung von Bauholz – eine Literaturschau. *Jahrbuch des Sonderforschungsbereiches 315*, University of Karlsruhe. Ernst, Berlin, pp 191–210
- Steiger R (1997) Sortierung von Rund- und Schnittholz mittels Ultraschall. *Holzforsch Holzverwert* 49(2):28–29
- Taguchi E, Nagasawa I, Yabuuchi S, Taguchi M (1984) Investigation of a wooden sculpture using X-ray computed tomography. *Sci Papers Jpn Antiques Art Crafts* 29:43–50
- Tenisch W (1999) Zerstörungsfreie Werkstoffprüfung an Holz: Literaturrecherche. *Wiss Ber Holzwiss ETH, Zürich*, vol 2
- Toft L (1995) Respiration measurements of dry rot. IRG/WP/95-10095
- Tran K, Romanet A-S, Locatelli M (1999) Non-destructive testing of waterlogged archaeological wood by nuclear magnetic resonance. Proceedings of the 6th International Conference on "Non-destructive testing and microanalysis for the diagnostics and conservation of the cultural and environmental heritage", Rome, 17–20 May 1999, vol 2, pp 1659–1667
- Unger A, Perleberg J (1987) X-ray tomography (XCT) in wood conservation. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6–11 Sept 1987, preprints, vol I, pp 99–105
- Unger A, Unger W (1995) Detection methods for biological damage in wooden cultural property: a review. Biodeterioration of Cultural Property 3, Proceedings of the 3rd International Conference, 4–7 July, Bangkok, Thailand, pp 181–186
- Unger A, Planitzer J, Morgós A (1988) Röntgencomputer- und Magnetresonanztomographie zur Charakterisierung von archäologischem Naßholz. *Holztechnologie* 29:249–250
- Vermaas HF (1996) Wood-water interaction and methods of measuring wood moisture content, part I: definitional aspects to NMR. *Holzforsch Holzverwert* 48(2):30–34; part II: nuclear radiation to resistive cancelling methods. *Holzforsch Holzverwert* 48(3):47–51
- Vitali V, Darcovich J, Williams W (1986) Construction of a Fudo-Myoo sculpture: an X-radiographic study. *Stud Conserv* 31:185–189
- Wang PC, Chang SJ (1986) Nuclear magnetic resonance imaging of wood. *Wood Fiber Sci* 18:308–314
- Wilcox WW (1988) Detection of early stages of wood decay with ultrasonic pulse velocity. *For Prod J* 38(5):68–73
- Wu D, Sembach J, Salerno A, Hora G, Busse G (1997) Qualitätssicherung beschichteter Holzwerkstoffe mittels Lockin-Thermographie. *Holz-Zentralblatt* 123:775
- Zimmer KM, Kothe E, Hannemann J (1985) Zerstörungsarme Diagnoseverfahren für den Bauzustand von Holzkonstruktionen und deren Interpretation. *Bauzeitung* 39:129–131

7 Liquid Wood Preservatives

7.1

Introduction

Wood preservation encompasses all measures designed to permanently prevent the damage or destruction of wood and wood-based materials by insects, fungi, marine borers, or bacteria. These measures may be preventive or a control of an active attack. Preventive measures include regulation of environmental factors, construction details in buildings, and chemical treatments. Control measures include structural, physical, and chemical treatments. Among the measures relating to building technology are selection of resistant wood species and detailing to protect wood from moisture accumulation and the effects of the weather. Physical methods to preserve wood include the application of heat, cold, and electromagnetic waves such as microwaves and gamma rays. Chemical preservative methods entail the use of preservatives or fumigants.

Whereas in the past individual methods for the protection of wood against wood-destroying organisms were introduced, today a combination of different materials and procedures has come to the forefront (Fig. 7.1) in order to meet the economic and ecological demands of practical applications. Integrated methods of wood preservation are intended to safeguard the durability of wood with respect to its intended function and its esthetic appearance using measures that are compatible with environmental concerns.

Wood preservatives may be biocides or preparations containing biocides which are designed to prevent attacks by wood-destroying or wood-discoloring organisms or to control such an attack. Decorative exterior coatings may or may not contain biocides (e.g., in Germany); a distinction is also made between water repellents (without biocides) and water-repellent preservatives (with biocides).

Wood preservatives consist of the biocide or biocide combination and a vehicle (water, solvent, or solvent combination), and may also contain surfactants, pigments, dyes, binders or fixatives. Based on the vehicle, preservatives are divided into waterborne and solvent-borne types. Waterborne preservatives predominantly involve treating wood with inorganic biocides (salts and salt-like compounds) which are impregnated in aqueous solution. They are particularly suitable for partially dried wood (moisture content 20–30%) and

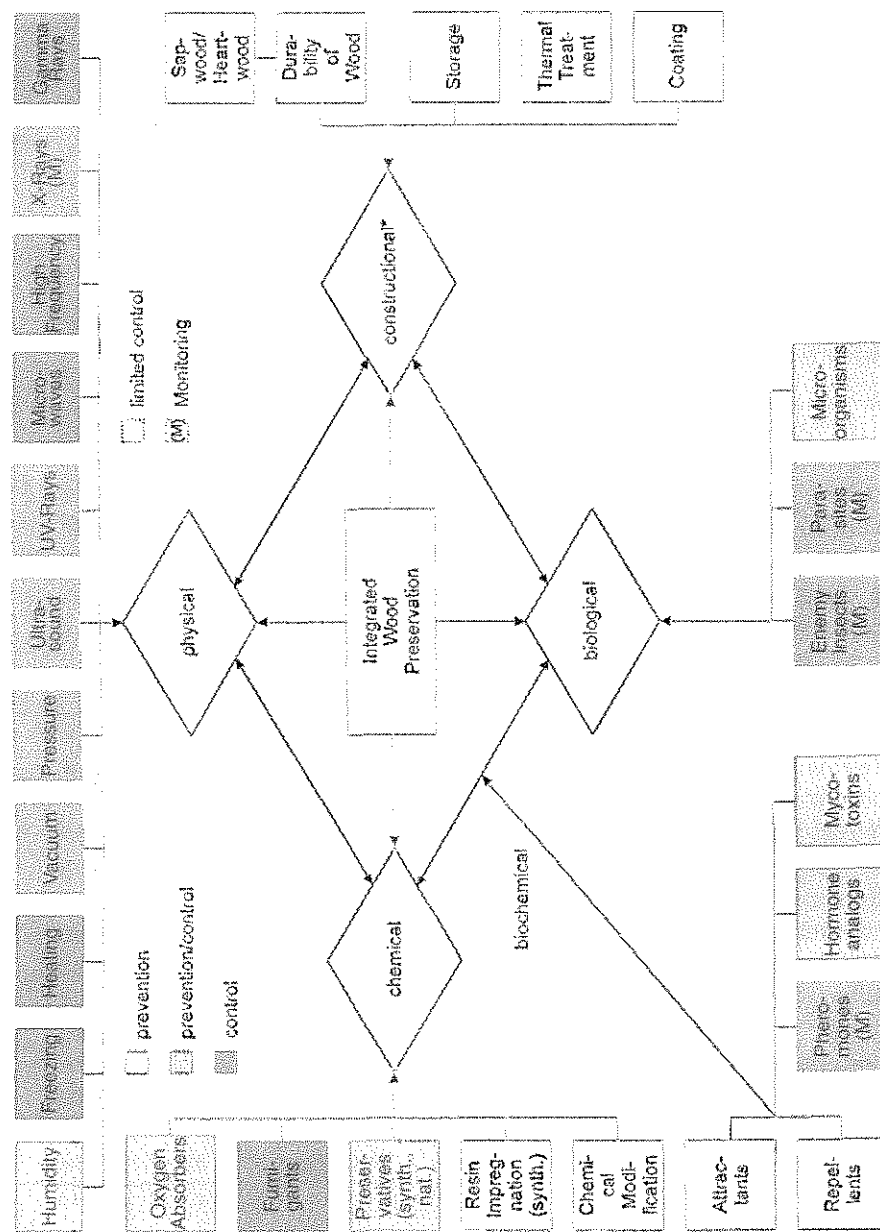


Fig. 7.1. Selection of materials and methods for integrated wood preservation. ("Constructional" refers to material selection and steps other than traditional wood preservation treatments to make wood less susceptible to pests.)

damp wood (moisture content >30%), but can also be used for dry wood (moisture content <20%). The preservative salts can be divided into substances which undergo fixation reaction with the wood, such as chromated salts, and those that remain soluble and leachable, such as boron or fluorine compounds.

Solvent-borne (also known as oil-borne) preservatives generally consist of organic biocides (Perkow and Ploss 1999) which are at least partially dissolved in organic solvents. They are sold ready to use without further adjustment, and are especially suitable for treating dry or semi-dry wood in the form of undercoatings, decorative preservative coatings, and for impregnation. The solvents will evaporate after treatment, while the biocides ideally remain in the wood and cannot be leached with water. Because of the relatively high vapor pressure of some organic biocides and their insufficient fixation in the wood, poor past choices of applications can lead to significant air pollution in interior spaces. Preservative emulsions are often sold as concentrates which must be diluted to application strength, as for instance for preservative foams. Liquid preservatives used for control of active pests also will serve a preventive function as they remain in the wood, but wood preventively treated with preservative, once infested, will have no further control capabilities.

Liquid preservatives applied by brushing will not penetrate wood completely, and in most cases only surface layers will be treated. Waterborne preservatives are largely odorless, but will swell the wood. Without emulsifiers they will generally penetrate wood less well than solvent-borne preservatives. Waterborne preservatives are suitable for unpainted structural timber used in architectural conservation, but not for valuable works of art and cultural property. Solvent-borne preservatives are now much less malodorous than they were in the past. They penetrate wood well and, depending on the type of solvent, will swell wood less than waterborne preservatives.

When cultural property is to be treated with liquid wood preservatives, it is important to know whether they are compatible with other, associated materials, such as pigments, dyes, binders, metallic attachments, or plaster, but such data are often lacking.

Various countries have defined risk levels for the use of preventive wood preservatives. In Germany, five hazard classes, GK 0–GK 4, are recognized (DIN 68800–3 1990), where interior living spaces are GK 0 and do not require any preventive treatment. Similarly, in Europe the wood-destroying organisms have been divided into five classes from GK 1–GK 5 (EN 335–1 1992), where GK 5 contains the marine borers.

Liquid preservatives can be applied by a variety of methods, which can be divided into pressureless, pressure, and special methods. Pressureless methods include brushing and soaking, pressure methods include treatment in pressure vessels and vacuum impregnation, whereas specialty methods are used for treating localized areas at risk. Depending on wood dimensions and species, even treatments at elevated pressure will often fail to penetrate wood completely.

Inorganic biocides will be presented in Section 7.2 and organic biocides in Section 7.3. Not all of the biocides discussed in these sections are used for the formulation of wood preservatives. Some biocides are used for the storage of waterlogged wood or for the prevention of microbial growth in solutions of conservation materials.

7.2

Inorganic Biocides

7.2.1

Alkali Chlorides

7.2.1.1

Sodium Chloride

Trade name:	Table salt
Formula:	NaCl
Properties:	Colorless, transparent cubes, not hygroscopic, m.p. 801 °C, very soluble in water
Toxicology:	No information
Biological effects:	Weakly insecticidal (food poison) and fungicidal
Application:	Usually as concentrated salt solution
Analysis:	Generally by X-ray diffraction for the compound; for chlorine with silver (I) nitrate/nitric acid solution after extraction from wood with water or by X-ray fluorescence spectroscopy (XFS)

Use with Dry Wood

Historical

Antiquity/middle ages Wood preservation by soaking in the ocean or in salt solution (cf. Appendix Table 1).
 Seventeenth/eighteenth centuries Table salt is added as preservative to guilders' glue (Schiessl 1984).
 1852 A. Stifter uses salt as a preservative against insects for the Kefermarkt altar in Austria (Aberle and Koller 1968).
 Up to 1900 Table salt was used to impregnate works of art to prevent insect and fungal attack (Schiessl 1984).

Table salt was also used to clean footwear infected with fungi and as a general disinfectant in a mixture with thymol crystals.

Present Day

Table salt is not used for wood preservation owing to its leachability and corrosiveness. In special cases it might be used to control relative humidity in microclimate chambers for paintings.

Use with Waterlogged Wood

Concentrated salt solutions could be exchanged with the contained water to achieve some dimensional stabilization of the wood.

Advantages/Disadvantages

In regard to both dry and waterlogged wood, the preventive and control efficacy of table salt against wood-destroying fungi and insects is insufficient, the salt has no resistance to leaching, it is corrosive, tends to bloom, and will shrink and swell with humidity changes.

7.2.2

Copper Compounds

7.2.2.1

Copper(II) Sulfate and Other Copper Salts

Trade names:	Blue vitriol (for $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$), and in wood preservatives, Aczol or Viczol (Germany) for ammoniacal copper and zinc salt solutions with phenol, Chemonite (USA) for ammoniacal copper arsenite (ACA) or ammoniacal copper-zinc arsenite (ACZA), Celcure N (Netherlands, Sweden, USA) for acid copper chromate (ACC), Ascu (India/Great Britain) and Celcure A and Tanalith C (Great Britain, USA) for chromated copper arsenate (CCA), Celcure CB (Great Britain) for chromated copper boron (CCB)
Formula:	CuSO_4 or $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$
Properties:	CuSO_4 crystals are colorless, $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ crystals are large, blue, and transparent, very soluble in water, soluble in methanol and glycerol
Toxicology:	Poisonous for warm-blooded animals only in its soluble form. Chronic health problems are not known, but can lead to water pollution
Biological effects:	Copper(II) sulfate alone is effective against soft rot, but has little effect on other fungus pests, especially species of <i>Poria</i> , because the fungi are able to detoxify the compound

by formation of oxalate. Cu^{2+} ions cause unspecific denaturing of proteins and enzymes

Application: One to 20% Cu in wood preservative concentrates; 0.1–2% Cu in treating solutions. Against soft rot a 1% aqueous solution

Analysis: Generally by X-ray diffraction for compounds; in wood by color reaction with Chrome Azurol S or rubeanic acid (pretest); by atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or XFS for copper (American Wood-Preservers' Association, AWP Standards 1999, Schoknecht et al. 1998)

Use with Dry Wood

Historical

- 1718 "Holtz-Balsam" of Hiarné based on blue vitriol (Schiesl 1984).
- 1791 English privilege patent: soaking of wood in blue vitriol solution (Anonymous 1935).
- 1837 Margary process for treating wood with dilute copper sulfate solutions (Richardson 1993).
- 1838 Boucherie patent: sap displacement process for green wood using copper(II) sulfate (Broese van Groenou et al. 1952).
- 1881 Copper(II) sulfate treatment against wood borers of a Gothic winged altar (Aberle and Koller 1968).
- 1907 Introduction of Aczol (Richardson 1993).
- ca. 1925 Gordon proposes the use of Paris green, copper aceto-arsenite, as a wood preservative (Richardson 1993).
- 1933/1934 Development of the first preservative (Ascu) based on chromated copper arsenite (CCA) by Kamesan in India (Richardson 1993).

Present Day

Copper(II) sulfate is not commonly used in its pure form because of its poor resistance to leaching. Therefore it is used in combination with other biocidal and fixing compounds in wood preservatives effective against insects and fungi for treating load-bearing timbers in both interior and exterior exposures. The salt solutions are usually applied by pressure treatment. Copper is one of the most effective components of inorganic wood preservatives.

Use with Waterlogged Wood

Historical

- 1982 According to Dawson, copper(II) sulfate has potential as a biocide for the conservation of waterlogged wood.

- 1993 The salt does not prevent microbial growth in 4 g/l sugar solutions (Hoffmann et al. 1994). The mortality of termites in wood treated with a 50% sugar solution with the addition of copper(II) sulfate was greater than in air-dry wood (Noldt 1994).

- 1996 Sakai et al. (1997) test copper(II) sulfate for waterlogged wood storage.

Present Day

Practically no use in the conservation of waterlogged wood.

Advantages/Disadvantages

In regard to dry wood: copper(II) sulfate is not effective against all fungi, has low resistance to leaching because of weak fixation, is very corrosive to iron and steel. Because of these disadvantages it is used together with more effective components, including improvements in fixation (CCA and CCB salts). The use of copper-based wood preservatives for cultural property is to be avoided because of discoloration and swelling of the wood. In regard to waterlogged wood: copper(II) sulfate does not sufficiently prevent growth of microorganisms in storage containers for waterlogged wood nor microbial growth in sugar solutions.

7.2.3

Mercury Compounds

7.2.3.1

Mercury(II) Chloride

Trade name:	Sublimate
Formula:	HgCl_2
Properties:	Sparkling white or colorless rhombic crystals, m.p. 276 °C, b.p. 302 °C, soluble in water, ethanol, ether, acetone, and benzene
Toxicology:	Very poisonous, causes visual and motor impairment, nerve inflammation, impairs kidney function; it is corrosive
Biological effects:	Particularly effective against fungi and bacteria, but also against insects. Reacts with cell proteins and other cell components, and inhibits glycolysis
Application:	Preventive against fungi and insects at a concentration of 0.66% (kyanizing); even a 0.1% aqueous solution deters bacteria and fungi
Analysis:	Generally by X-ray diffraction for the compound; in wood by color reaction with 1,5-diphenylcarbonohydrazide

or diphenylcarbazone for cation (pretest), by AAS (Schoknecht et al. 1998), ICP-AES or XFS for mercury

Use with Dry Wood

Historical

- Ca. 1500 Leonardo da Vinci impregnates backs of panel paintings and frames (Schiessl 1984).
 1705 The French physician Homberg uses sublimate solution to control wood borers in parquet flooring (Moll 1916).
 1832 Kyan patents soaking treatment of wood with sublimate solution (Broese van Groenou et al. 1952).
 1863 Last large-scale use of sublimate in Great Britain (cf. Appendix Table 1).
 1867 Treatment of Holbein's Solothurn Madonna with sublimate in alcohol against Anobiidae (Brachert 1972).
 1911 Disinfection of altars with sublimate in alcohol (Aberle and Koller 1968).
 1935 Sublimate outlawed as wood preservative in Germany (Richardson 1993).

In spite of the toxicity of sublimate it was still used in Europe in the 1940s and 1950s for the conservation of cultural property, and in other countries, e.g. India, in the early 1960s.

Present Day

Inorganic and organic mercury compounds are used in wood preservation only rarely because of their toxicity and danger to the environment.

Use with Waterlogged Wood

Historical

- 1924 Rathgen recommends storage of objects in water with some sublimate.
 1964 Ypey places a wooden spoon into water with sublimate added.

Present Day

No longer used.

Advantages/Disadvantages

Sublimate is an effective preventive against fungi and insects, but for control of insects ineffective because penetration is poor owing to rapid fixation. It is very corrosive, so that tanks must be made of wood, stone, or concrete. Its toxicity to humans and the environment is very high.

7.2.4

Zinc Compounds

7.2.4.1

Zinc(II) Chloride and Other Zinc Salts

- Trade name: In wood preservatives: Antorgan (Germany) for zinc salts other than zinc hexafluorosilicate
- Formula: ZnCl_2
- Properties: Very hygroscopic white powder, m.p. 283°C. Readily soluble in water, soluble in ethanol, ether, acetone, glycerol and pyridine
- Toxicology: Strongly caustic to mucous membranes and the respiratory system, and causes skin damage
- Biological effects: Acts as fungicide by unspecific action on cell components
- Application: One to 20% Zn in wood preservative concentrates; 0.1–2% Zn in treating solutions. At equal concentration less effective than copper(II) sulfate
- Analysis: Generally by X-ray diffraction for compounds; in wood by color reaction with dithizone, by AAS, ICP-AES or XFS for zinc (AWPA Standards 1999, Schoknecht et al. 1998)

Use with Dry Wood

Historical

- 1815 Zinc(II) chloride recommended as wood preservative (Clausnitzer 1990).
 1838 British patent by Burnett for pressure treatment of lumber with zinc(II) chloride (Richardson 1993).
 Up to 1921 Use of the salt as a wood preservative in the USA (Richardson 1993).
 1956 Plenderleith cites a 4% aqueous solution of zinc(II) chloride for control of wood-destroying insects in works of art.
 1963 Straub mentions the low effectiveness of the salt against insects.

Present Day

Zinc(II) chloride and other zinc salts are used as components in wood preservatives only to a limited extent (see under fluorosilicate).

Use with Waterlogged Wood

See under fluorosilicate.

Advantages/Disadvantages

In regard to dry wood: penetrates wood well but has poor resistance to leaching. It is less of a fungicide than copper(II) sulfate, and its effectiveness against insects is insufficient. Corrosion of wood and metals possible by traces of hydrochloric acid in the salt.

Other zinc (organic) compounds: zinc octoate and zinc naphthenate.

7.2.5

Arsenic Compounds

7.2.5.1

Arsenic Trioxide and Arsenic Salts

Trade name:	White arsenic; in wood preservatives: Boliden BIS (Sweden) for arsenites and arsenates of sodium, copper, zinc, and chromium, and Boliden S (Sweden) for a paste made by mixing zinc oxide and chromium trioxide into an arsenic pentoxide solution
Formula:	As_2O_3
Properties:	White to yellowish powder; sublimates at 321 °C. Poorly soluble in water, accompanied by formation of arsenous acid (H_3AsO_3)
Toxicology:	Skin damage; hair loss; inflammation of the mucous membranes; diseases of the stomach, intestines, liver, and kidneys; carcinogenic. Water pollutant
Biological effects:	Good insecticidal, termiticidal, and fungicidal effectiveness. Inhibits enzymatic processes and influences phosphorylation in fungal cells. It also inhibits respiration of insects
Application:	Not used in its pure form, as concentration ranges from 5–40% As in wood preservative concentrates, and from 0.1–2% As in treating solutions
Analysis:	Generally by X-ray diffraction for compounds; in wood for As(III) by color reaction with iodine-starch reagent and for As(V) by color reaction with ammonium molybdate-benzidine-hydrochloric acid reagent (pretest); by AAS, ICP-AES or XFS for arsenic (AWPA Standards 1999, Schoknecht et al. 1998)

Use with Dry Wood

Historical

- ca. 1500 Leonardo da Vinci knows the preservative effect of arsenic for wood (Schiessl 1984).
- 1540 Franciscan monks in San Domingo control termites with arsenic compounds (Lohwag 1967).
- 1730 Baster uses arsenic to impregnate lumber (Richardson 1993).
- 1768 Wood is coated with pulverized, dampened arsenopyrite (FeAsS) (Clausnitzer 1990).
- 1873 Leech obtains British patent 2567 for a preparation on an arsenite/arsenate basis (Clausnitzer 1990).
- 1976 The gate of the Nezu shrine (Japan) is treated with a 2% solution of chromated copper arsenate (CCA) against wood-destroying fungi and termites (Ishikawa et al.).

Present Day

Arsenic compounds are an important ingredient of wood preservatives for pressure impregnation. The impregnated wood is very resistant to leaching and can be used for exterior exposure. Interior uses are prohibited.

Use with Waterlogged Wood

No data available.

Advantages/Disadvantages

In regard to dry wood: arsenic is a strong biocide. Some decay fungi tolerate arsenic and can form volatile arsenic compounds (arsines). This is also possible with wallpaper containing Schweinfurth green, a copper(II) acetate-arsenate. Fixation of chromated copper arsenate (CCA) in wood is good to very good. Acute and chronic toxicity is high and arsenic pollutes the environment. When wood containing arsenic is burned, the element can be liberated or concentrated in the ash.

7.2.6

Fluorine Compounds

7.2.6.1

Sodium Fluoride and Other Fluorides

Trade name:	In wood preservatives: Wolman salts for fluor-chrome-arsenate-phenol (FCAP) preservatives in USA and fluorine-chromium-arsenic (FCA) in Europe, Basilit U (Germany) for alkalifluoride, dichromate, Basilit ULL
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(Germany) for fluoride and dichromate, Basilit UAS and Kulbasal ULL (Germany) for fluoride, arsenate and dichromate, Basilit UB (Germany) for hydrogen fluoride, boric acid and dichromate, and Basilit BF and TS (Germany) for hydrogen fluoride

Formula:	NaF
Properties:	Colorless, cubic crystals, m.p. 988°C, moderately soluble in water (4.2g/100ml) and poorly soluble in ethanol. Aqueous solutions are alkaline
Toxicology:	Highly caustic, high risk of damage to skin, eyes, the respiratory tract, liver and kidneys; very deleterious to plants
Biological effects:	NaF is a strong fungicide but less effective as an insecticide and limited to certain species. Reacts with enzymes containing metals of fungus cells and blocks them. KHF_2 and $(\text{NH}_4)\text{HF}_2$ are effective as fungicides and as insecticides
Application:	Five to 45% F in wood preservative concentrates; 0.2–10% F in treating solutions. NaF is used at approximately 4% in aqueous solution
Analysis:	Generally by X-ray diffraction for compounds; in wood by color reaction with zirconium alizarin reagent for fluorine (pretest, penetration), and by use of ion-selective electrode or photometry for fluorine (Schoknecht et al. 1998)

Use with Dry Wood

Historical

- 1861 In Great Britain fluorides or fluorosilicates are proposed as wood preservatives (Richardson 1993).
- 1901 Malenkovic investigates the suitability of zinc fluoride for wood preservation, and an Austrian patent is issued in 1903 (Broese van Groenou et al. 1952).
- 1907 Wolman obtains a patent for alkali fluorides as preservatives for mine timbers (Broese van Groenou et al. 1952).
- 1909 Wood preservative "Bellit" (since 1914 Basilit) on the basis of sodium fluoride and dinitrophenol aniline (Richardson 1993).
- 1926 Mixture of sodium fluoride and sodium fluorosilicate as wood preservative (Richardson 1993).
- 1944 B. Schulze uses hydrogen fluoride to control old house borers (Broese van Groenou et al. 1952).

- 1956 Plenderleith recommends sodium fluoride as a preventive against wood-destroying fungi (85–170g sodium fluoride in 4.5l water) for wood in contact with the soil. An aqueous solution of about 4% is listed for the control of wood-destroying insects in thin wood items.
- 1970 Mihailov (1970b) treats wood columns of Renaissance houses in Bulgaria with a solution of 3 parts sodium fluoride and 1 part sodium hexafluorosilicate in 4 parts water as a preventive against wood decay fungi (introduced via bore holes).
- 1977 Preservation of carved, boatlike grave monuments in Hungary by boring to the core and inserting a cartridge containing water glass, sodium fluoride, sodium dichromate and 4,6-dinitro-*o*-cresol (DNOC; Wirth).

Present Day

Sodium fluoride in its pure form is no longer used as a wood preservative but is found in combination with other agents in some preservatives. Hydrogen fluorides like potassium hydrogen difluoride and ammonium hydrogen difluoride are sometimes used in Europe to control or prevent wood-destroying insects, especially *Hylotrupes bajulus*, and for the control of fungi.

Use with Waterlogged Wood

Historical

- 1983–1985 Parrent adds 1% sodium fluoride and coumarin to sugar solution for conservation treatment (Morgós et al. 1994).

Advantages/Disadvantages

In regard to dry wood: sodium fluoride is a highly effective fungicide. It is not very soluble in water but has poor resistance to leaching. Reportedly, it is not corrosive (Richardson 1993), but a release of hydrogen fluoride is thought possible. Therefore sodium fluoride is not suitable for valuable works of art. Potassium hydrogen difluoride and ammonium hydrogen difluoride are effective fungicides and insecticides. They are very soluble, capable of deep penetration, but have poor resistance to leaching requiring their use together with fixatives. Strong emission of hydrogen fluoride can lead to glass etching, making them unsuitable for works of art. In regard to waterlogged wood: sodium fluoride is an insufficiently effective biocide for adding to sugar solutions.

7.2.6.2

Fluorosilicates (Silicofluorides)

Trade name: In wood preservatives: Fluorex S (USA) and Sikkuid (Germany) for magnesium hexafluorosilicate, Fluralsil

(Germany) for disodium hexafluorosilicate and zinc(II) chloride, Basilit BS, NT, SF, SP, UHL (Germany) for silicofluoride (SFsalts) and dichromate, Basilit CFK (Germany) for copper hexafluorosilicate, ammonium dichromate, and some diammonium hydrogenphosphate

Formula:	Disodium hexafluorosilicate – $\text{Na}_2[\text{SiF}_6]$ copper hexafluorosilicate – $\text{Cu}[\text{SiF}_6] \cdot 6 \text{H}_2\text{O}$ magnesium hexafluorosilicate – $\text{Mg}[\text{SiF}_6] \cdot 6 \text{H}_2\text{O}$ zinc hexafluorosilicate – $\text{Zn}[\text{SiF}_6] \cdot 6 \text{H}_2\text{O}$
Properties:	Hexafluorosilicates with Na, Mg, and Zn are colorless. $\text{Na}_2[\text{SiF}_6]$ solubility in water is poor, $\text{Cu}[\text{SiF}_6] \cdot 6 \text{H}_2\text{O}$ is readily soluble in water, and $\text{Mg}[\text{SiF}_6] \cdot 6 \text{H}_2\text{O}$ and $\text{Zn}[\text{SiF}_6] \cdot 6 \text{H}_2\text{O}$ are soluble in water
Toxicology:	Fluorosilicates are poisonous, and are caustic to skin, mucous membranes, and eyes
Biological effects:	Fluorosilicates are fungicides effective against basidiomycetes such as <i>Serpula lacrymans</i>
Application:	Zinc hexafluorosilicate is used at about 30% aqueous solution
Analysis:	See under sodium fluoride

Use with Dry Wood

Historical

- 1892 Bradley is awarded French patent 219,104 for silicofluorides (Broese van Groenou et al. 1952).
 1909/1910 Production of Fluralsil by combining disodium hexafluorosilicate and zinc(II) fluoride to eradicate house fungus from masonry (Richardson 1993).
 1931 Danish patent for Fluralsil with zinc hexafluorosilicate as the biocide (Clausnitzer 1990).
 1973 Mühlethaler mentions impregnation with fluorosilicates, followed by preservatives containing creosote or Carbolineum to protect wooden objects placed outdoors.

Present Day

Magnesium, copper, or zinc fluorosilicates are used either alone or in mixture with other compounds to eradicate decay fungi from masonry, or used as preventive treatment for structural timber which is not subject to leaching.

Use with Waterlogged Wood

Historical

- 1965 In Germany, parts of the *Bremen Cog* are brushed with a 1% Fluralsil solution (Weber).
 1977 A 1–2% Basilit NT solution is used as an additive to control bacteria and fungi in wet wood storage tanks (Zimmermann).
 1990 A 0.5–2.5% solution of zinc hexafluorosilicate is used with the conservation treatment with sugar (Wróblewska et al.).

Present Day

Practically no use in the conservation of waterlogged wood.

Advantages/Disadvantages

In regard to dry and waterlogged wood: the fungicidal effect is less than with fluorides. They corrode metals and glass and because of their poor resistance to leaching can only be used in interior locations. Fluorosilicates are not suitable for valuable cultural property.

7.2.7

Boron Compounds

7.2.7.1

Boric Acid (Orthoboric Acid)

Trade name: In wood preservatives: in Germany, Adolit Holzbau B, Difusit M, and Kulbasal M with boric acid and borax; Basilit B with sodium polyborate; Kulbasal B with boric acid and alkaliborate (Polybor); Basilit UB with hydrogenfluoride, boric acid, and dichromate; copper-chromium-boron formulations (CCB); Basilit CCO and Wolmanit CB with copper(II) oxide, boric acid, and chromium trioxide.

In Great Britain, Tim-bor with disodium octaborate-tetrahydrate; and Celcure CB with copper(II) oxide, copper(II) sulfate and boric acid.

In Sweden, Modolog antiqua with poly(ethylene glycol) (PEG), boric acid, borax, and methylpolysiloxane

Formula: $\text{B}(\text{OH})_3$

Properties: Boric acid can be translucent, flaky crystals or white powder. When heated to 100–130°C metaboric acid is formed. It is poorly soluble in cold water, but solubility rises rapidly with increasing temperature. It is also soluble

to a considerable extent in solvents with hydroxyl groups, such as ethanol and glycerol

- Toxicology:** The toxic effect on warm-blooded animals is extremely low; the toxicity is similar to that of table salt. Under leaching conditions it could become concentrated in the soil. Boric acid is poisonous to fish and their food animals. Environmental effects have not been investigated sufficiently. Recent research indicates that boric acid and borates can damage animal testicles and inhibit the formation of spermatocytes. Teratogenic effects have also been observed
- Biological effects:** Boric acid is effective as a preventive fungicide and insecticide. Boric acid and borates form stable complexes with cell components of fungi and insects, inhibits the function of enzymes and influences transport mechanisms from cell to cell
- Application:** At 0.5–15% B in wood preservative concentrates; 0.1–5% B in treating solutions. Used as 12–15% aqueous solution of boric acid/borate to eradicate house fungus from masonry
- Analysis:** Generally by X-ray diffraction for the compound; in wood by color reaction with tincture of tumeric (pretest, penetration), by ICP-AES, XFS, titration, photometry for boron (AWPA Standards 1999, Schoknecht et al. 1998)

7.2.7.2

Borax (Sodium Tetraborate-Decahydrate)

- Trade name:** Borax, in wood preservatives see under boric acid
- Formula:** $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$
- Properties:** Colorless crystals which weather on exposure to air. Upon rapid heating borax melts at 75°C and liberates eight molecules of water, and further heating to 320°C produces the water-free tetraborate. Borax is moderately soluble in cold water but solubility increases rapidly with increasing temperature. It is also soluble in glycerol but insoluble in ethanol
- Toxicology:** See under boric acid
- Biological effects:** See under boric acid
- Application:** See under boric acid
- Analysis:** See under boric acid

7.2.7.3

Polybor (Disodium Octaborate-Tetrahydrate)

- Trade name:** Tim-bor in wood preservatives
- Formula:** $\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4 \text{H}_2\text{O}$
- Properties:** Solubility is greater than that of boric acid or borax
- Preparation:** A solution of 1 part boric acid and 1.54 parts borax is dried by evaporation
- Toxicology:** See under boric acid
- Biological effects:** See under boric acid
- Application:** See under boric acid
- Analysis:** See under boric acid

Use with Dry Wood

Historical

- 1851 Boron salts as flame retardant substances (Bub-Bodmar and Tilger 1922).
- 1877 Zerener obtains a patent for a mixture of water-glass, sodium chloride, boric acid, and diatomite for impregnation of wood against attack by *Serpula lacrymans* (Bub-Bodmar and Tilger 1922).
- 1913 Wolman develops a chromium boron preservative (Richardson 1993).
- 1933 British patent for boric acid and borax as fire retardant and wood preservative (Celcure mixtures; Broese van Groenou et al. 1952).
- 1939 Cummins and Wilson use boric acid as a preservative against sapwood beetle attack in Australia
- 1939–1945 Kamesan in India develops copper-chromium-boron salts (CCB salts) as wood preservatives (Richardson 1993).
- 1960/1961 Wolmanit, a CCB salt, comes on the market in Germany (Richardson 1993).
- 1983 Creffield et al. show that *Lyctus* beetle attack in eucalyptus lumber can be controlled with 19 g boron/m²
- 1989 The steamer *Wapama* is treated by spraying with Tim-bor solution to control fungal decay (Birkholz Jr.).
- 1996 Control of fungi in ship timbers with steam (maximum 80°C) followed by a preventive treatment of spraying with saturated Tim-bor solution at 60°C (Dickinson and Murphy).
- 1998 Detailed report by Graf et al. on the control of wood-destroying insects with boron compounds.

Present Day

Boric acid, borax and Polybor are used in waterborne wood preservatives for preventive treatments against fungus and insect pests for structural timber protected from the weather. Boric acid and borax are also used to eradicate house fungus from masonry. These compounds are contained in delayed release control treatments against insect pests. Boron preparations are not suitable for wood components which might come into contact with food or animal feed. If boron compounds are to be used where wood is subject to leaching, fixation by chromium compounds (CCB salts, FCB salts) is necessary. Such preparations are not suitable for large areas in interior spaces unless the treated parts are covered. After hot air treatments against house borers a preventive treatment with boron salts is often applied (not harmful to bats).

Use with Waterlogged Wood

Historical

- 1962 Conservation of the Swedish warship *Wasa* using PEG with boron compounds added. Individual parts are placed in tanks with water, to which a 2% solution of boric acid and borax (7:3) and PEG are added. The hull is sprayed with a 15% aqueous solution of PEG 1500 with 4% boric acid and borax (7:3) added (Barkman 1965, 1969).
- 1965 Noack recommends the addition of boron compounds to PEG 1000 for the stabilization of the wood of the German ship *Bremen Cog*.
- 1970 Brorson Christensen describes soaking oak parts of the viking ships from the Roskilde-Fjord, Denmark, with PEG 4000 and 1% boric acid and borax (4:7) added.
- 1973 According to Mühlethaler, waterlogged wood should be placed into a 12% PEG solution with 2% boric acid and 2% borax.
- 1974 Plans are made to treat a freight boat from the Carolingian age with PEG 1000–1500 with Basilit B added (Pirling and Buchwald).
- 1978 Wooden objects from the *Mombasa* shipwreck in Kenya are stored in a 2% solution boric acid and borax (7:3; Turner; cf. Chap. 11); development of the Thessaloniki process with sodium borate (Borgin; cf. Chap. 11).
- 1979 Conservation of wooden objects with PEG 400 and 1% boric acid and borax (7:3) added, followed by freeze drying by Hug.
- 1981 Grosso treats waterlogged wood with sugar solution and 1% borax added.
- 1990 Boric acid and borax (7:3) are added to the sugar solution at 2.5–5% (Wróblewska et al.).
- 1996 Experiments by Sakai et al. (1997) to determine the suitability of 1% boric acid, 1% borax, or 3% borax and boric acid (3:7) as fungicides in waterlogged wood storage tanks. The compounds did not effectively prevent growth of microorganisms.

Present Day

Boron compounds are used in some cases.

Advantages/Disadvantages

In regard to dry wood: boron compounds are effective as preventives against fungal and insect pests, and they can be used to eradicate house fungi in masonry, but do not have sufficient effectiveness against mold fungi. Boron preparations can also serve as slow-acting poisons to control insect pest infestations (*Anobium*, *Lyctus*, *Hylotrupes*). They have low toxicity to humans and the environment. Leaching resistance is very low; therefore used only in interior exposure. Polybor is used increasingly because it has much better solubility than boric acid or borax. Boron compounds diffuse well even in woods with low permeability, but excessive concentration leads to blooming. Plaster adhesion may be impaired after masonry has been treated with borates. In regard to waterlogged wood: biocidal effects for waterlogged wood storage and conservation with sugar solutions is insufficient, but boron preparations diffuse more readily than sodium pentachlorophenolate.

7.2.8

Chromium Compounds

7.2.8.1

Sodium Dichromate (Sodium Bichromate)

Trade name:	In wood preservatives: see under copper(II) sulfate, sodium fluoride, fluorosilicate, and boric acid
Formula:	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$
Properties:	Orange-red, columnar crystals, water free at 100°C, m.p. 357°C (without water), readily soluble in water, soluble in ethanol
Toxicology:	Especially the sexivalent chromium compounds such as dichromate, chromate, chromium acid and chromium(VI) oxide are extremely poisonous. They cause far-reaching chronic caustic damage to mucous membranes and skin ("chromium eczema"), trigger allergies, and are carcinogenic. They are also highly harmful as water pollutants
Biological effects:	Chromium compounds are neither fungicides nor insecticides, but serve as fixatives
Application:	Five to 25% Cr(VI) in wood preservative concentrates; 0.2–3% Cr(VI) in treating solutions. The chromium content in salt-like wood preservative formulations can range from 30–60%

Analysis: Generally by X-ray diffraction for compounds; in wood, for Cr(VI) by color reaction with 1,5-diphenylcarbonohydrazide or chromotropic acid, and for Cr(III) by color reaction with lead(II) acetate and eriochromcyanine (pretest), by AAS, ICP-AES or XFS for chromium (AWPA Standards 1999, Schoknecht et al. 1998)

7.2.8.2

Potassium Dichromate (Potassium Bichromate)

Trade name: See under sodium dichromate
Formula: $K_2Cr_2O_7$
Properties: Orange-red crystals, m.p. 398°C, moderately soluble in cold water, very soluble in hot water, insoluble in ethanol
Toxicology: See under sodium dichromate
Biological effects: See under sodium dichromate
Application: See under sodium dichromate
Analysis: See under sodium dichromate

7.2.8.3

Chromium(VI) Oxide (Chromic Anhydride, Chromium Trioxide)

Trade name: In wood preservatives see under boric acid
Formula: CrO_3
Properties: Long, dark red needle crystals, m.p. 196°C, readily soluble in water. Should be kept apart from combustible materials because of fire danger
Toxicology: See under sodium dichromate
Biological effects: See under sodium dichromate
Application: See under sodium dichromate
Analysis: See under sodium dichromate

Use with Dry Wood

Historical

- 1912 British patent 2972 to Brüning to reduce the leachability of toxic salts with the aid of chromium compounds (Broese van Groenou et al. 1952).
 1915 German patent to reduce iron corrosion of wood preservatives by means of chromium salts (Broese van Groenou et al. 1952).

- 1924 Rathgen cites potassium dichromate as an adhesive hardener.
 ca. 1930 Increased dichromate content in Wolman salts, and use of the suffix U (Richardson 1993).
 1980 Efforts to develop chromium-free preservatives are begun in Germany.
 1988 Accelerated fixation of wood preservatives containing chromates by steam treatment.

Present Day

Chromium compounds serve as fixatives in the formulation of wood preservatives rather than as biocides, thereby imparting leach resistance to biocide components. The fixation in acid media occurs via reduction of chromium(VI) salts (orange color) by the lignin components of the wood to chromium(III) compounds (green). Copper, fluorine, and arsenic salts form compounds of very low solubility with the trivalent chromium. Because of their toxicity the use of chromium compounds will decrease in the future in favor of chromium-free preparations such as AAC, Cu-HDO and Betaine (cf. Sect. 7.3).

Use with Waterlogged Wood

See Chapter 11.

Advantages/Disadvantages

In regard to dry wood: the presence of chromium compounds as fixatives makes possible a long-lasting, preventive treatment of wood used in exterior exposures. However, in spite of the fixation, the leaching of preservative components is still relatively high, which leads to environmental pollution. The problem of safe methods of disposal of waste wood containing chromium is not completely solved. Chromium compounds are not suitable for the preservation of museum objects.

7.3

Organic Biocides

7.3.1

Tars, Tar Oils, and Kerosene

7.3.1.1

Wood Tar

Trade name: Stockholm tar, wood-tar creosote (tar oil fraction of wood tar)
Composition: Acetic acid, wood spirit, light and heavy oils, wood tar pitch, water, cresols, phenols, xylenols, guajacol, phenol-

	ether. Wood tar creosote contains mainly guajacol and cresol
Properties:	Dark brown to black, viscous, oily mass, with characteristic sharp odor. Soluble in organic solvents
Toxicology:	Excessive contact with the skin can cause damage. Certain tars, such as beech tar, are used in veterinary medicine to treat eczema
Biological effects:	Weak insecticide and fungicide; the oily components attack cell membranes
Application:	Undiluted or diluted with solvents
Analysis:	Generally by gas chromatography (GC) and mass spectroscopy (MS) for qualitative and quantitative analysis. In wood discoloration by tar (pretest), by gas chromatography/mass spectroscopy after extraction

Use with Dry Wood

Historical

- ca. 4000 B.C. Tar and pitch from wood were used in building Noah's ark (Lohwag 1967).
- ca. 1000 B.C. The Greeks reportedly used wood tar to coat ship bottoms and also to protect wooden roofs (Clausnitzer 1990).
- ca. 600 B.C. The Romans reportedly used wood tar for ship parts and wooden roofs (Clausnitzer 1990).
- 1613 Holland privilege of Sare Roman: coating wood with tar (Anonymous 1935).
- 1648–1658 Dry distillation of wood and anthracite by Glauber (Anonymous 1935; Clausnitzer 1990).
- 1835 Introduction of the term "Kreosot" by Moll (Anonymous 1935).
- 1857 British patent for wood tar (Lohwag 1967).

Present Day

This product no longer has much importance, but is used occasionally on boats or wooden houses.

Use with Waterlogged Wood

In early waterlogged wood conservation it was sometimes used, but not now.

Advantages/Disadvantages

In regard to dry and waterlogged wood: wood tar is a preventive for fungi and insects, but is sufficiently effective only at higher concentrations which would

require pressure treatment. The wood becomes discolored and oily. Water-soluble components are subject to leaching. The tar, and especially its oily substances, may migrate and discolor adjacent materials. It is not suitable for interior spaces.

7.3.1.2 Coal Tar Oil

Trade name:	Creosote for coal tar distillate, Creolin for heavy coal tar oils and resin soaps, Carbolineum for tar oil distillate with a large proportion of high boiling point fractions, Carbolineum Avenarius for chlorinated Carbolineum, Barol for Carbolineum containing copper salts
Composition:	Phenol, xylene, cresol, pyridine, chinoline, acridine, naphthalene, pyrene, fluorene, anthracene, and phenanthrene
Properties:	A dark liquid, b.p. 200–400 °C, soluble in organic solvents
Toxicology:	Direct contact with the skin very harmful; carcinogenic, among other components because of benzo[a]pyrene. Strong water polluter
Biological effects:	Effective against fungus pests including soft rot, termites and marine borers, by bursting cell membranes and other effects
Application:	Coal tar oil is used without dilution in industrial pressure treating equipment
Analysis:	Generally by GC and MS for qualitative and quantitative determinations; in wood qualitatively by odor and discoloration (pretest); by high performance liquid chromatography (HPLC) or GC/MS after extraction

Use with Dry Wood

Historical

- 1838 British patent to Bethell for pressure impregnation of timber with heavy tar oil (Lohwag 1967).
- 1888 Patent to Avenarius for treating tar oil with chlorine (Richardson 1993); trade name Carbolineum (from carbon and oleum) Avenarius.
- ca. 1900 Nördlinger develops Barol, a Carbolineum containing copper salts (Richardson 1993).
- 1956 Plenderleith cites a preservative treatment against termites with creosote and metal naphthenates

- 1973 Mühlethaler mentions conservation treatment of wooden objects placed outdoors with preservatives containing creosote or with Carbolineum after fluorosilicate impregnation (cf. under fluorosilicates).
- 1991 Tar oil legislation in Germany, limiting the use of tar oil because of pollution by polycyclic aromatic hydrocarbons, and limiting the content of benzo[a]pyrene to <50 ppm.

Present Day

Tar oils are used in closed systems for the pressure impregnation of railroad ties, utility poles, and timbers for marine structures. The treated wood can be used in exterior exposure with or without contact with the soil. In Germany wood so treated is not permitted in children's playgrounds.

Use with Waterlogged Wood

Historical

- 1904 Parts of the *Oseberg* ship (Norway) are brushed with creosote and linseed oil at the location of unearthing. The impregnation is later continued until the wood is saturated. The results are good for oak but unsatisfactory for pine (Rosenqvist 1959).
- 1941 Unearthed wooden remains of the Prague castle are coated with Carbolineum and kerosene (Borkovský).
- 1958 Garczynski uses a mixture of 75% turpentine and 25% linseed oil with additions including about 5% of a 30% solution of Carbolineum.

Present Day

No longer used for waterlogged wood conservation.

Advantages/Disadvantages

In regard to dry and waterlogged wood: coal tar oil has good fungicidal and insecticidal effects, but wood becomes discolored and oily, the oil tends to bloom, metal parts become iridescent, and there is a persistent odor. It is toxic to humans and to the environment, it cannot be used for interior spaces, and it is unsuitable for cultural property.

7.3.1.3

Kerosene

Trade name:	Lamp kerosene, Steinöl (Germany)
Composition:	Intermediate fraction of petroleum, consisting of saturated hydrocarbons with 10–18 carbon atoms
Properties:	Colorless, somewhat oily liquid, b.p. 150–280°C, immiscible with water and ethanol, but miscible with ether,

	carbon disulfide, linseed oil and turpentine oil; it is lighter than water
Toxicology:	Concentrated vapor and the liquid have a slight narcotic effect. Prolonged contact with the skin withdraws its oils and leads to inflammation. Kerosene is a water pollutant
Biological effects:	It is hardly effective as insecticide, but can extract fats from cell membranes
Application:	Undiluted
Analysis:	Generally by GC and MS for qualitative and quantitative determinations, in wood by GC/MS after extraction

Use with Dry Wood

Historical

- 1802 Kerosene is mentioned under the name "Steinöl" as a preparation against insect pests (Schiessl 1984).
- 1873 Hochberger uses brushing treatment of kerosene against the house fungus (Clausnitzer 1990).
- Ca. 1900 Kerosene is a popular substance for the control of pests in wood, but Rathgen warns against its use (Schiessl 1984).
- 1916/1918 Bolle treats the Kefermarkt altar (Austria) using kerosene with hexachloroethane added (Aberle and Koller 1968).
- 1953 A mixture of equal parts kerosene and gasoline for treating works of art is still termed a "well tried" method (Aberle and Koller 1968).
- 1961 Oily substances from prior conservation treatments are removed from wood sculptures with pastes of magnesium carbonate (Wehlte; cf. Sect. 7.6).
- 1963 Straub cites a paste of magnesium silicate and tetrachloromethane for removing oily substances from panel painting supports (cf. Sect. 7.6).

Present Day

No longer used for cultural property.

Use with Waterlogged Wood

Historical

- 1883 Krause describes the slow drying of prehistoric and antiquity finds wrapped in straw and subsequent repeated applications of a mixture of equal parts varnish and kerosene to the end surfaces.
- 1924 Rathgen cites in his book the procedure of Reid in which objects are soaked in kerosene for prolonged periods to displace the water.

Subsequently the kerosene is exchanged with benzene and the object is dried

- 1925 Impregnation of a viking boat with varnish/kerosene by Conwentz.
- 1939 Von Stokar treats wood from bogs with varnish/kerosene under vacuum (50–100 g linseed oil varnish in 100 g kerosene).
- 1940 Conservation of a dug-out with "Aczol" (cf. copper(II) sulfate) and linseed oil varnish/kerosene (Dolenz).
- 1941 Brushing of historic structural timbers with kerosene (cf. coal tar oil).

Present Day

Kerosene is no longer used.

Advantages/Disadvantages

In regard to dry wood: kerosene is a good solvent for organic biocides but is only minimally effective by itself. Therefore attempts were made in the past to add effective substances such as trichloroethane, tetrachloroethane, hexachloroethane, lindane, or pentachlorophenol. It penetrates well but the objects become oily and the kerosene tends to migrate. It causes color changes in natural wood and polychrome coatings, has a penetrating odor, and poses a fire danger to treated objects. In regard to waterlogged wood: water exchange is not good and dimensional stabilization is unsatisfactory. See also under dry wood.

7.3.2

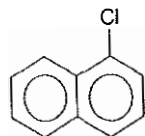
Chlorinated Hydrocarbons

7.3.2.1

Chloronaphthalenes

Trade name: In wood preservatives: Halowax for trichloronaphthalene, Anabol (later Wykamol; Great Britain) for chloronaphthalene wax and *o*-dichlorobenzene, Xylamon, e.g., Xylamon-Hell (Germany) and Olimith C 20, Ridsol (Netherlands) for mono- and dichloronaphthalenes

Formula:



1-Chloronaphthalene

Properties:

Mono- and dichloronaphthalenes are liquid; tri- and tetrachloronaphthalenes are wax-like. 1-Chloronaphthalene is a colorless, oily liquid with a characteristic odor. b.p. 259°C, insoluble in water and soluble in ethanol and ether. It is a solvent for DDT, oils, and fats

- Toxicology: 1-Chloronaphthalene damages eyes, skin, stomach and the intestinal tract. Higher chlorinated naphthalenes cause chlorine acne upon skin contact
- Biological effects: Chloronaphthalenes are fungicides and insecticides. The addition of stearic or palmitic acid improves their effectiveness
- Application: Chloronaphthalene waxes are very effective against termites at up to 10% in organic solvents
- Analysis: In wood by Beilstein test (pretest), by thin layer chromatography (TLC) after extraction from wood, or by GC/MS

Use with Dry Wood

Historical

- 1921 German patent for chloronaphthalenes as wood preservatives (Clausnitzer 1990).
- 1923 Vereinigte Alkaliwerke Westeregeln (Germany) begin marketing Xylamon (Broese van Groenou et al. 1952).
- 1934 Introduction of Anabol in Great Britain.
- 1956 Spraying insecticides which contain 1-chloronaphthalene into the exit holes of wood-destroying insects (Plenderleith).
- 1963 According to Straub, chloronaphthalene preparations have only limited uses, because it will swell old oil paints.
- 1968 Chloronaphthalenes and Xylamons are cited by Aberle and Koller as the most effective preservatives at that time.

Present Day

Because of their strong olfactory pollution and environmental toxicity, chloronaphthalenes are practically no longer used. After their discontinuation, wood preservatives sold under the name "Xylamon" contained such biocides as lindane and or permethrin. Modern Xylamon preparations for the control of insect pests contain substances which retard chitin synthesis (see under flufenoxuron).

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: effectiveness against insects and fungi is good, but it has high vapor pressure and mono and dichloronaphthalene emit an intense odor.

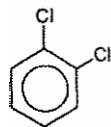
7.3.2.2

Dichlorobenzenes

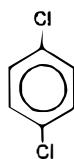
Abbreviated names: ODB for *o*-dichlorobenzene; PDB or Paradi for *p*-dichlorobenzene

Trade name: Paracide, Paradow (USA), in wood preservatives: Rentokil (Great Britain) for *o*-dichlorobenzene, and Anabol (later Wykamol, Great Britain) for chloronaphthalene wax and *o*-dichlorobenzene

Formulas:



1,2-Dichlorobenzene
(*o*-Dichlorobenzene)



1,4-Dichlorobenzene
(*p*-Dichlorobenzene)

Properties: 1,2-Dichlorobenzene is a colorless liquid, b.p. 180.5°C, vapor pressure 133 Pa (20°C), insoluble in water, readily soluble in ethanol, ether and benzene. 1,4-dichlorobenzene is a colorless, fluid mass with a strong odor, m.p. 53°C, b.p. 174°C, vapor pressure 200 Pa (20°C), also reported as 170 Pa, solubility as for 1,2-dichlorobenzene

Toxicology: Vapors have anesthetic effects and strongly irritate the eyes, the respiratory tract and the skin; if swallowed there is danger of damage to liver and kidneys

Biological effects: These are insecticides which impair oxidative phosphorylation and prevent the adenosine 5'-triphosphate (ATP) synthesis. Attacks insect respiration

Application: Treatments by vaporization of PDB are insecticidal only at the high concentration of about 1 kg/m³

Analysis: In wood by Beilstein test (pretest), by TLC after extraction from wood, or by GC/MS

Use with Dry Wood

Historical

1915 Druckett describes the preservative effect of PDB (Broese van Groenou et al. 1952).

1934 Introduction of the wood preservative Anabol (Richardson 1993).

1939 ODB in Wykamol is replaced by Rotenon (extract from the derris root; Richardson 1993).

1963 Straub lists solutions of 250 g PDB in 1 l xylene or white spirit as preventive and control media against wood-destroying insects.

1970 Mihailov (1970 b) sprays the wooden interior millwork of Renaissance houses against insects and fungi with a 20–25% solution of PDB in xylene.

1971 Insect control in small objects by vapor treatment with PDB in closed containers (Schmidt).

1974 After fumigation of objects attacked by insects with bromomethane they are injected or brushed with PDB in benzene (Mihailov).

1978 Mori and Arai report the use of PDB for the control of insect pests in small objects.

1987 Child and Pinniger evaluate the suitability of PDB for the control of insects in museums.

1990 Treatment of a bullock cart with 2% PDB in ethanol, followed by a 1% solution of pentachlorophenol (PCP; Rama Rao and Pandit Rao).

Present Day

Because of their long-term persistent toxicity (Linnie 1990), the use of these substances has either decreased significantly or has been prohibited in many countries.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: 1,4-dichlorobenzene is generally not corrosive but could possibly damage bronze surfaces (Child and Pinniger 1987). It softens binders and plastics, discolors paper, pigments, feathers and leather, and it does not have sufficient long-term effectiveness.

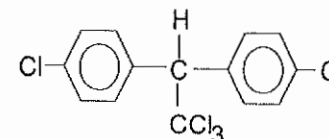
7.3.2.3

DDT [Dichlorodiphenyltrichloroethane,
1,1,1-Trichloro-2,2-bis(4-chlorophenyl)-ethane]

Short designation: DDT

Trade name: Gesarol, Dicophane. In wood preservatives: Arbezol-Spezial for DDT and diazinon, in the former German Democratic Republic Hylotox 59 for 3.5% DDT (technical) and 0.5% lindane, and Hylotox IP for 3% DDT and 5% PCP

Formula:



- Properties:** Colorless, crystalline when pure, wax-like in technical grades, characteristic odor, combustible, m.p. 109°C, b.p. 260°C, vapor pressure 2.5×10^{-5} Pa (20°C); other reports give 4.5×10^{-5} Pa and 1.7×10^{-5} Pa (20°C). DDT is insoluble in water (5.5 µg/l at 20°C), poorly soluble in methanol, ethanol and white spirit, soluble in 1,3-dioxolane; in the following the solubility in 100ml solvent at 27°C is 100 g in dioxane and cyclohexanone, 77 g in benzene, 68 g in ethyl acetate, 50 g in acetone, 47 g in tetrachloromethane, and 41 g in toluene
- Toxicology:** DDT is soluble in lipids and is accumulated in fat tissue. It is excreted slowly with urine accompanied by formation of metabolites. It irritates skin, eyes, and mucous membranes. Ingestion causes sweating, headaches, nausea, and nerve damage. Carcinogenic potential is suspected. Enzymatic splitting off of HCl and formation of 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethene (DDE) and 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethane (DDD) can occur. DDT is persistent and accumulates in water supplies and food stuffs, but exposure to UV radiation results in rapid decomposition into CO₂ and HCl. Pollution by dust containing DDT is markedly higher than room air pollution
- Biological effects:** DDT is a broad-band insecticide with neurotoxic effects. It attacks the peripheral regions of the central nervous system, blocks information transfer by the nerve cells, and triggers hyperactivity
- Application:** Depending on the content of 4,4'-DDT, insecticidal effectiveness is good but requires a high concentration of 2–3.5% in wood preservatives. In preparations against termites the concentration is as high as 5%
- Analysis:** In wood by Beilstein test (pretest); for crystalline bloom on the surface of treated objects by melting point determination, fluorescence microscopy and Fourier transform infrared (FTIR) spectroscopy; by GC with flame ionization detector (FID) (Glastrup 1987), electron capture detector (ECD) or MS after extraction from wood

Use with Dry Wood

Historical

- 1874 Synthesis of DDT by O. Zeidler in the laboratory of A.v. Baeyer (Römp 1995).
- 1939 Discovery of the insecticidal effect by P. Müller (Clausnitzer 1990).

- 1948 Nobel prize for medicine for P. Müller (Römp 1995).
- 1956 Control of wood-destroying insects in works of art with preparations containing DDT (Plenderleith).
- 1959/1960 Hylotox 59 comes on the market in the German Democratic Republic. Wood preservatives with DDT as the biocide are used, especially in eastern Europe.
- 1961 Csillag recommends gasoline with 1% DDT and 0.3–0.6% HCH as residueless treatment against wood pests.
- 1962 The book "Silent Spring" by R. Carson is published (Römp 1995). Historic objects are impregnated with wax, using a mixture of wax, turpentine, and white spirit with the addition of DDT (Lehmann).
- 1963 Straub lists a solution of 100 g DDT in 1 l of white spirit for the control of insect pests in carved wooden objects and polychromed wood sculptures.
- 1968 Aberle and Koller mention Arbezol-Spezial for the control of insects in cultural property made of wood.
- 1972 Control of insect pests other than termites with DDT in kerosene (Majewski). DDT is outlawed in the Federal Republic of Germany.
- 1987 Production of Hylotox 59 is halted in the German Democratic Republic; remaining supplies were permitted to be used until 1990/1991
- 1996 First attempts in Germany to decontaminate cultural property that had been treated with Hylotox 59 (Lefèvre and Unger; cf. Sect. 7.5).

Present Day

DDT is no longer used as biocide in wood preservatives in industrialized countries.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

DDT has neurotoxic effects on humans, is very persistent, and somewhat corrosive to iron and aluminum. In many art objects which had been treated with oil-borne wood preservatives containing DDT the biocide blooms to the surface as time passes and threatens the environment.

7.3.2.4

Lindane (γ -1,2,3,4,5,6-Hexachlorocyclohexane)

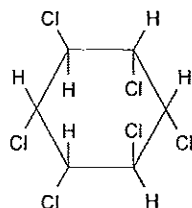
Short designation: γ -HCH, γ -BHC

Trade name: Gammexan

In wood preservatives: Hylotox 59 (see under DDT), Xylamon Holzwurm-Tod (Germany) with 0.9% lindane (1984), and Xylophen SC (see under PCP)

In combined wood preservatives and consolidants in Germany: Xylamon LX Härtend with 0.9% lindane (1983), and Basileum LX Härtend with 0.9% lindane (1984)

Formula:



Properties:

Colorless, incombustible crystals, with characteristic musty odor; m.p. 112.5–113.5°C; b.p. 176°C at 1.3 kPa; vapor pressure 1.2×10^{-3} Pa (20°C); other reports give 9.4×10^{-4} Pa (20°C). Lindane is hardly soluble in water (9–10 mg/l at 20°C); solubility in 100 ml of solvent at 27°C is 43.5 g in acetone, 36.7 g in cyclohexanone, 35.7 g in ethyl acetate, 31.4 g in dioxane, 27.6 g in toluene, 6.4 g in ethanol, and 2.9 g in petroleum ether (80–100°C)

Toxicology:

Lindane is a strong nerve poison, accumulates in fat tissue and mother's milk, damages the blood, and causes chronic damage in the form of hypersensitivity, changes in the blood, and neurological disease. In mice it forms liver tumors, it is a serious water pollutant, but less persistent than other chlorinated hydrocarbons, as it is decomposed by sunlight and microorganisms

Biological effects: Lindane is a broad-band insecticide with neurotoxic effects; it inhibits the transmission of stimuli along the nerve strands. It penetrates rapidly into the cuticula of insects

Application: In solvent-based pest control preparations for wood it is used at a concentration of 0.3–0.9%

Analysis: In wood by Beilstein test (pretest), by TLC after extraction from wood, or by GC (Lorenz et al. 1985, Petrowitz 1986)

Use with Dry Wood

Historical

- 1825 Discovery of HCH by Faraday (Römpf 1995).
1912 Van der Linden (source of the name) separates the mixture of isomers (Römpf 1995).

1933 Bender recognizes the insecticidal effect (Roth 1996a).

1942 It is discovered at ICI that the insecticidal effect is due to γ -HCH (Roth 1996a).

1945 Lindane is substituted for Rotenon in Great Britain (Richardson 1993).

1945–1947 Manufacture of technical grade HCH begins in Germany (Römpf 1995).

1956 Lindane for controlling wood-destroying insects in works of art (Plenderleith).

1968 Lindane and Xylophen SC are recommended as well-suited for control of insects in works of art (Aberle and Koller).

1970 Inaccessible wood members in Renaissance houses are treated by Mihailov (1970b) by vaporizing 1–2 g lindane/m³ in the air space.

1971 The use of lindane in wood preservation is outlawed in Switzerland (Leiß 1992).

Since 1985 Synthetic pyrethroids are substituted for lindane in wood preservatives in Germany.

Present Day

Use is much decreased and finds almost no application in wood preservatives.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: lindane is an effective insecticide. It is long-acting because of good penetration, but its high vapor pressure causes it to lose strength slowly over time. It is very toxic to humans and the environment, and has some corrosive effect on metals which can be magnified in the presence of condensation because of its relatively high solubility. The high danger of water and soil pollution is also due to the high solubility of lindane in water.

7.3.3 Cyclodiene Insecticides

7.3.3.1

Aldrin (HHDN), Dieldrin (HEOD), and Heptachlor (Chlordane)

These substances are used to control termite pests in countries where termites occur, but their use is decreasing because of their great persistence and noticeable toxicity. They have had almost no importance for the conservation of cultural property.

7.3.4

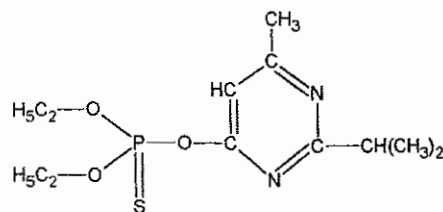
Organophosphates

7.3.4.1

Diazinon [O,O-Diethyl-O-(2-isopropyl-6-methylpyrimidine-4-yl)-monothiophosphate]

Trade name: Basudin (Switzerland); in wood preservatives: Arbezol-Spezial (Switzerland) and Lignal-Spezial (Austria), both containing diazinon and DDT

Formula:



Properties: Colorless oil in its pure form; the technical grade (95%) is yellow; b.p. 83–84°C at 3×10^{-2} Pa and 125°C at 1.3×10^2 Pa; vapor pressure 1.8×10^{-2} Pa (20°C); other reports give 9.7×10^{-3} Pa (20°C). It is almost insoluble in water and readily soluble in organic solvents such as ethanol, ether, acetone, hexane, cyclohexane, benzene, toluene, and petroleum ether

Toxicology: Diazinon inhibits cholinesterase, blocks synaptic stimulus transfer, and disrupts behavior. It causes weak eye irritation and is a water pollutant

Biological effects: Diazinon is an insecticide which inhibits the activity of acetylcholinesterase by reacting with it and thus prevents stimulus transfer

Application: In wood preservatives based on organic solvents it is used at 0.5–1% concentration

Analysis: By GC/MS after extraction from wood

Use with Dry Wood

Historical

1952 The Geigy company introduces diazinon as an insecticide (Römpf 1995).

1968 According to Aberle and Koller, Arbezol-Spezial or Lignal-Spezial should be suitable for the treatment of works of art. The degree

of discoloration of the wood can be reduced by diluting the preservative.

1989 Caputi Jambrenghi treats the wind-chest of an organ with Arbezol.

Present Day

Of no importance as insecticide for wood preservation.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: precise information for evaluating the suitability of this insecticide for use on cultural property is not available.

Other organophosphates: dichlorvos (DDVP), parathion, and phoxim.

7.3.5

Carbamates

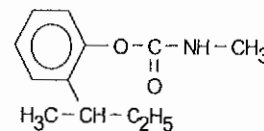
7.3.5.1

Bassa (2-Isobutylphenyl-N-methyl-carbamate)

Short designation: BPMC

Trade name: Baycarb (Germany); in wood preservatives: Basileum (Germany) for bassa, fumeccyclo, propoxur, and dichlofluamide

Formula:



Properties: The pure form is crystalline, and the technical grade a viscous liquid; m.p. 32°C; b.p. 112–113°C (30 Pa) and vapor pressure is 2.1×10^{-2} Pa (20°C). Bassa can be dispersed in water

Toxicology: Bassa inhibits cholinesterase and blocks nerve paths. Acute poisoning causes cramps, rapid breathing and rapid heart beat, and damage to liver and kidneys

Biological effects: The insecticidal effect is caused by blockage of synaptic stimulus transfer owing to inhibition of acetylcholinesterase

Application: As a dispersion of about 2% concentration
 Analysis: By TLC or GC/MS after extraction from wood

Use with Dry Wood

Historical

1975–1980 Use as biocide in wood preservatives.

Present Day

No longer used in wood preservatives.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

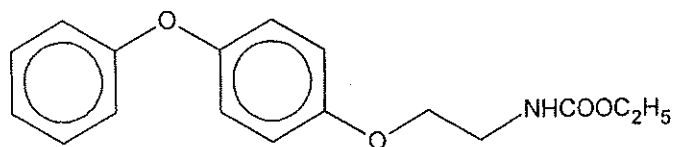
In regard to dry wood: the substance outgases because of its high vapor pressure and therefore has little persistence; it is also readily decomposed in alkaline environments.

7.3.5.2

Fenoxycarb – Ethyl[2-(4-phenoxyphenoxy)ethyl]carbamate

Trade name: Insegar (for fruit-growing)

Formula:



Properties: Fenoxycarb is white and crystalline; m.p. 53–54 °C; vapor pressure 1.7×10^{-5} Pa; solubility is 0.6mg/100g in water and >25g/100g in organic solvents (except *n*-hexane) at 20 °C

Toxicology: In animal experiments no skin irritation or sensitization could be observed, except for minimal eye irritation in rabbits. It is harmless to bees, but is a water pollutant

Biological effects: Fenoxycarb is not neurotoxic, but a juvenile hormone analog which acts as an insect growth regulator. It disrupts or prevents the transition from egg to larva (ovicide) and influences pupation

Application: This substance has not been completely tested as a biocide for wood preservatives. Minimum concentration is presumed to be 0.04%

Analysis: By TLC or GC/MS after extraction from wood

Use with Dry Wood

Historical

Since 1990 Investigations at the Swiss Federal Laboratories for Materials Testing and Research (EMPA) on the suitability of fenoxycarb as a preventive biocide against *Hylotrupes bajulus* (Pallaske 1997). First wood preservative based on juvenile-hormone analogs such as fenoxycarb (cf. juvenile hormones).

1998 Pallaske (1998,1999) describes the preventive effectiveness of fenoxycarb against *A. punctatum*, *H. bajulus*, and *L. brunneus*.

Present Day

Fenoxycarb is not yet widely used in the formulation of wood preservatives although its effectiveness as an adverse growth regulator against *Hylotrupes bajulus* has been proven.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: fenoxycarb has only the characteristics of a preventive substance. It is not corrosive to metals and because of its selective effects poses no significant danger to humans or the environment. Its compatibility with works of art has not yet been tested.

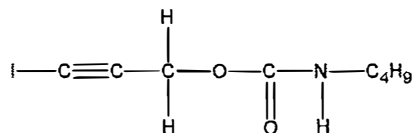
7.3.5.3

3-Iodo-2-propynyl-butyl-carbamate

Short designation: IPBC

Trade name: Troysan Polyphase (USA); in wood preservatives: Resistol 2629 (Great Britain) for propiconazole, tebuconazole, IPBC, and permethrin (1997); Adolit SM and Serpalit 2000 (Germany) for 17.0% IPBC (1999); Basiment Holzschutzlasur wäßrig U 4942 and Xyladecor plus U 4052 (Germany) for 0.60% and 0.45% IPBC (2000)

Formula:



Properties: Crystalline, white powder, m.p. 64–66°C, vapor pressure 2.6×10^{-3} Pa (26°C); insoluble in water and soluble in polar and aromatic solvents

Toxicology: IPBC irritates the eyes and possibly also the skin. It does not inhibit cholinesterase, and interference with the central nervous system are possible. It is a water pollutant

Biological effects: IPBC is a fungicide effective against decay fungi, blue stain fungi, molds and algae

Application: At 0.1–3% in aqueous or solvent systems.

Analysis: By pyrolysis-GC/MS after extraction from wood (Horn and Marutzky 1994), and in treating solutions by HPLC (AWPA Standards 1999)

Use with Dry Wood

Historical

1981 The effectiveness of IPBC against blue stain fungi is discovered (Plackett).

1984 Hansen (1984a,b) promotes IPBC as a new fungicide in wood preservation.

Present Day

IPBC is used in wood preservatives against blue stain fungi and molds, as a biocide in barrier treatments for house fungus control in masonry, and as a fungicide in paints and varnishes.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: IPBC has good effectiveness against wood decay and stain fungi. Its leachability is very low, but owing to its high vapor pressure it may be fugitive. So far there is no information on the compatibility of IPBC and preservatives based on it with cultural property.

Other carbamates: propoxur.

7.3.6

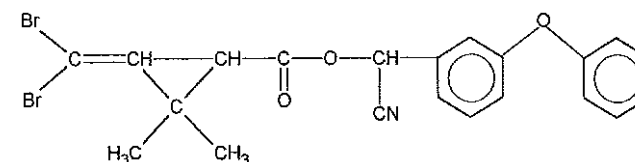
Synthetic Pyrethroids

7.3.6.1

Deltamethrin [(S)- α -Cyano-3-phenoxybenzyl-(1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylate]

Trade name: Decis (Roussel Uclaf); in wood preservatives: Aidol Anti-Insekt and Avenarol Holzwurmfrei (Germany) for 0.02% deltamethrin (2000)

Formula:



Properties: Solid, colorless and odorless crystals; m.p. 98–101 °C; b.p. 270°C (exothermal decomposition); vapor pressure 2×10^{-6} Pa (25°C); solubility in 100g solvent is 1 µg in water, 90 g in cyclohexanone, 50 g in acetone, 35 g in ethyl acetate, 1.5 g in ethanol and 25 g in xylene

Toxicology: Deltamethrin is poisonous with irreversible effects as a neurotoxin. It irritates eyes and skin, and causes abnormal skin sensitivity, excessive salivation, writhing motions of torso and limbs, and cramps [choreoathetose salivation (CS) syndrome]. It is a strong water pollutant and is poisonous to bees and fish

Biological effects: Deltamethrin is an insecticide of high selectivity which affects the central nervous system of insects. Impulses are conducted in nerve cells by way of potential differences of Na^+ and K^+ ions, and by disrupting the migration of Na^+ ions the stimulus transfer becomes hyperactive or blocked

Application: At 0.02–0.5% in solvent systems

Analysis: By TLC (Petrowitz and Wagner 1987), or by pyrolysis-GC/MS (Horn and Marutzky 1994) after extraction from wood

Use with Dry Wood

Historical

1973 Discovery of the insecticidal effect of synthetic pyrethroids by Elliot et al. (Rothamsted Experimental Station, UK).

- 1976 First positive results from tests of this substance against wood insect pests at Princes Risborough Laboratory, Aylesbury, UK (Berry).
 1980 Comprehensive report on the effectiveness of synthetic pyrethroids against wood-destroying insects and their use characteristics by Baker and Berry. Discontinuation of chlorinated hydrocarbons and phosphoric acid esters is begun
 Since 1993 Limitations on the use of wood preservatives containing pyrethroids in interior applications in Germany (Wegen 1996).
 1995/1996 Discontinuation of synthetic pyrethroids in wood preservatives is begun in Germany because of their potential neurotoxic effects.

Present Day

No information.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

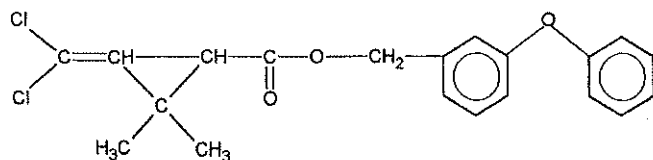
In regard to dry wood: deltamethrin is an effective insecticide which requires a lower concentration than permethrin, has lower toxicity to mammals than lindane, and there is no bioaccumulation.

7.3.6.2

Permethrin [3-Phenoxybenzyl(1-*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylate]

Trade name: Ambush (Great Britain); in wood preservatives: Permetar (Italy); in Germany: Xylamon Holzwurm-Tod and Basileum Holzwurm BV U 155 for 0.25% permethrin (1985/1986), Xylamon Holzwurm-Tod U 103 for 0.1% permethrin (1997), Delttox IT and Wolmanol-Holzwurmfrei for 0.25% permethrin (2000), and KULBANOL HB-PM for 0.6% tebuconazole and 0.25% permethrin (2000)

Formula:



Properties: Viscous, yellow to light brown liquid; m.p. ca. 35°C; b.p. 210–220°C at 101.3 kPa; vapor pressure 1×10^{-4} Pa (20°C); other reports 3.4×10^{-5} Pa; solubility in 100 g of solvent at

20°C: 0.2 ppm in water, >45 g in acetone, >45 g in chloroform, >45 g in hexane, and >31 g in methanol

Toxicology: Permethrin causes tremors of the limbs, exhaustion, hyperexcitability, muscle cramps [tremor (T) syndrome], and disruption in the immune system. The Ames test shows it as carcinogenic, and it is a strong water pollutant (Roth 1996b)

Biological effects: For its insecticidal action see under deltamethrin

Application: At 0.01–2.5% in solvent systems

Analysis: By GC/FID, GC/ECD, GC/MS or pyrolysis-GC/MS (Horn and Marutzky 1994) after extraction from wood

Use with Dry Wood

Historical (see also under deltamethrin)

- 1982 Control of *Xestobium rufovillosum* by vaporization of permethrin with a laboratory generator (Read).
 1985 Becker publishes an overview of the properties and effectiveness of synthetic pyrethroids against wood-destroying insects.
 1987 Child and Pinniger mention permethrin as insecticide for vaporization in museums.
 1989 Tests of the compatibility of the permethrin containing preservative Delttox IT with cultural property by Unger et al.
 1990 Treatment of retables with sculptures by use of wood preservatives with permethrin (Gerard, also Serck-Dewaide). Linnie reports on the use of permethrin in museums and evaluates health dangers associated with it.

Present Day

Permethrin is still a component in most wood preservatives for the prevention and control of insects and also in preparations for the combined prevention of insect and fungal attacks (as of 1997). However, its replacement by chitin synthesis inhibitors (see flufenoxuron) appears to be on the horizon.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: the penetration of the biocide is often only 1–2 mm, but compared with natural pyrethroids it is more persistent and of greater long-term effectiveness. There has been no acute or chronic poisoning by permethrin-containing wood preservatives (Kulzer 1985). The biocide decom-

poses in the soil, and a cumulative effect has not been found so far. It causes very weak corrosion of steel, galvanized steel, copper and aluminum. The use of permethrin is controversial because of its potential for neurotoxic effects in humans and is under active discussion.

Other synthetic pyrethroids: cyfluthrin, cypermethrin, and fenvalerate.

7.3.7

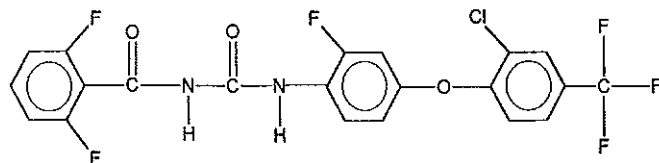
Benzoylurea Derivatives

7.3.7.1

Flufenoxuron (Flurox) – 1-[4-(2-Chloro- α,α,α -trifluoro-*p*-tolylloxy)-2-fluorophenyl]-3-(2,6-difluorobenzoyl)-urea

Trade name: Cascade; in wood preservatives: Aidol HWT, Basileum Holzwurm BV U 1551, and Xylamon gegen Holzwürmer (Germany) for 0.02% flufenoxuron (2000)

Formula:



Properties: Colorless, odorless crystals; m.p. 169–172°C (decomposes); vapor pressure 4.6×10^{-12} Pa (20°C); other reports 6.52×10^{-12} Pa (20°C); solubility in 1 l solvent at 25°C is 4.0 µg in water, 6 g in xylene, 24 g in dichloromethane, 82 g in acetone, and 3.5 g in methanol at 15°C

Toxicology: Flurox has only minor acute toxicity. Skin and eye irritation has not been reported, but it is classified as a skin irritant in Germany. It has no sensitizing effect, and there are no indications of mutagenic, carcinogenic, or teratogenic effects. It is a water pollutant but is less poisonous to fish and fish food animals than synthetic pyrethroids

Biological effects: Flurox attacks the external skeleton of insects, which consists of chitin, by disruption of chitin synthesis, and it inhibits skin sloughing by larvae. The biocide is taken up with food and accumulates in chitin-forming tissues. The effect only initiates at the time of skin sloughing, and the growth of the insects is delayed and eventually prevented (insect growth regulator, chitin synthesis inhibitor)

Application: At 0.02–0.1% in aqueous and solvent systems. Flurox is effective in a concentration of about 0.02%, at a rate of application of 300–350 ml/m²

Analysis: By HPLC or GC/MS after extraction from wood

Use with Dry Wood

Historical

- 1973 First investigations of the effect of benzoylurea derivatives as skin sloughing inhibitors by Post and Vincent.
- 1980 Use of benzoylurea compounds (Dimilin®) against larvae of wood-destroying insects (Doppelreiter).
- 1982 Cymorek and Pospischil discuss the effectiveness of hormone mimics and chitin synthesis inhibitors as biological preservatives.
- 1993 Synthetic pyrethroids can be replaced by flufenoxuron if effectiveness against termites is not required (Pallaske et al.).
- 1995/1997 Further publications on the application characteristics of skin sloughing inhibitors (Pallaske and Wegen 1995; Valcke and Pallaske 1995; Wegen 1996; Wegen et al. 1996; Pallaske 1997).
- 1998/1999 Further reports by Pallaske on the effectiveness of benzoylurea derivatives and the principle it is based on.

Present Day

Flufenoxuron is used to control the larvae of wood-destroying insects and also has preventive effectiveness against attack.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: flufenoxuron has very good long-term persistence and resistance to aging, which can be explained by its low solubility in water and its extremely low vapor pressure. The selective effect of the substance reduces the danger to humans and the environment. So far, there is no information on the compatibility of flufenoxuron and preservatives based on it with cultural property.

Other benzoylurea derivatives: diflubenzuron (dimilin), triflumuron (alsystin), hexaflumuron (against *Coptotermes formosanus*, Su et al. 2000).

7.3.8

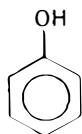
Phenols

7.3.8.1

Phenol (Hydroxybenzene)

Trade name: Carboic acid (5% aqueous solution of phenol); in wood preservatives: TC oil (Great Britain)

Formula:



Properties:

Colorless needles of characteristic odor, which turn reddish on exposure to air. M.p. 40.8 °C; b.p. 182.2 °C; vapor pressure 20 Pa (20 °C); solubility: moderately soluble in water, readily soluble in ethanol and ether, not very soluble in aliphatic hydrocarbons

Toxicology:

Phenol is a strong protoplasmic poison. It is very corrosive to skin, and chronic poisoning leads to liver and kidney damage

Biological effects:

Phenol is a weak fungicide; it has an inhibiting effect on respiratory paths by disrupting phosphorylation

Application:

No information available, since it is not commonly used as a wood preservative

Analysis:

By GC or FTIR

Use with Dry Wood

Historical

1834 Runge discovers phenol in coal tar (Römpf 1995).

1858 Wohl coats wood with a mixture of carbolic acid and soda (Troschel 1916).

Present Day

Not used in wood preservatives.

Use with Waterlogged Wood

1924 Storage of archaeological finds in water with carbolic acid added to prevent decay (Rathgen).

1956 Plenderleith cites the storage of waterlogged wood in water with 2% phenol.

1985 Treatment against molds of water-saturated building timbers with an alcohol solution containing 0.5% phenol and 0.5% thymol (Schweizer et al.).

Present Day

Almost no use in storage tanks for waterlogged wood.

Advantages/Disadvantages

In regard to dry wood: can be an effective fungicide but is unsuitable for wood preservatives because it is readily leached and volatile. In regard to waterlogged wood: phenol has fungistatic effects but they are not always sufficient.

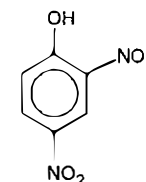
7.3.8.2

Dinitrophenols and Dinitrocresols

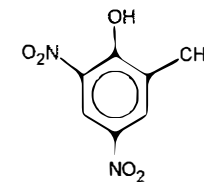
Trade name:

In wood preservatives: in Germany Basilit (Bellit) for sodium fluoride and dinitrophenol aniline, Schwamm-schutz Rütgers for sodium fluoride and dinitrophenol, Antinonin for potassium dinitro-*o*-cresolate, soft soap and water, Antingermin for dinitro-*o*-cresol and a copper compound, and Mykantin for sodium dinitro-phenate; in Austria Malenit for sodium fluoride, dinitrophenol, and antimonyfluoride double salt

Formulas:



2,4-Dinitrophenol



4,6-Dinitro-*o*-cresol
(2-Methyl-4,6-dinitrophenol)

Properties:

2,4-Dinitrophenol: light yellow needles, m.p. 114–115 °C; not very soluble in cold water, soluble in hot water, readily soluble in acetone, soluble in chloroform and benzene; in the dry form it is explosive. 4,6-dinitro-*o*-cresol: yellow, strongly dyeing prisms; m.p. 86.5–87.5 °C; not very soluble in water, soluble in ethanol, readily soluble in ether and acetone

Toxicology:

2,4-Dinitrophenol causes localized irritation of skin and eyes, and acts as a metabolic poison; 4,6-dinitro-*o*-cresol also irritates skin and eyes, is a blood poison, and kidney and liver damage is possible

Biological effects:

These substances are fungicides which prevent ATP synthesis

Application:

Effectiveness threshold is about 6 kg/m³ for sodium-dinitro-phenolate and 1 kg/m³ for sodium-dinitro-*o*-cresolate

Analysis: In wood by the yellow discoloration of the treated wood (pretest), by TLC after extraction from wood

Use with Dry Wood

Historical

1892 Antinonnin is patented (Broese van Groenou et al. 1952).

1909 Malenkovic applies for a patent for Bellit (later Basilit) (Richardson 1993).

Before 1912 Falck proposes Mykantin paste for impregnation of utility poles (Richardson 1993).

1913 "Schwammschutz Rütgers" is patented (Broese van Groenou et al. 1952). Chromates are used to lessen the corrosiveness of dinitrophenol

1923 Malenkovic develops Malenit (Broese van Groenou et al. 1952).

Present Day

Practically no longer used in the preservation of lumber.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: the wood is dyed yellow, and the color bleeds through mortar and plaster. The substances tend to explode, and are very corrosive.

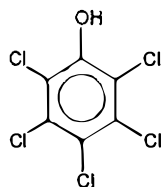
7.3.8.3

Pentachlorophenol (2,3,4,5,6-Pentachloro-phenol)

Short designation: PCP, Penta

Trade name: Dowicide 7 (USA), Preventol P (Germany), Xylophen SC (France) for HCH and PCP

Formula:



Properties: Odorless, white, needle crystals when pure and brownish flakes for the technical product; m.p. 190–191 °C; b.p. 300 °C (decomposes); vapor pressure 2.3×10^{-2} Pa (20 °C); other reports 1.5×10^{-2} Pa and 7×10^{-3} Pa; difficult to dis-

solve in water, soluble in ethanol, ether, acetone, and benzene

Toxicology: PCP is carcinogenic; the technical grade may have dioxin (Seveso poison) as an impurity. PCP can be taken in through the skin, by breathing, and through the alimentary canal and accumulates in the body as well as in the environment. Poisonous effects are nausea, loss of appetite, weakness, headaches, sleep disruption and loss of concentration

Biological effects: PCP is a fungicide with broad-band effectiveness. It causes unregulated ATP production leading to cell mortality

Application: In solvent-borne wood preservatives at a concentration of 4–6%

Analysis: In wood by Beilstein test (pretest) (Willeitner et al. 1988) and by color reaction with copper sulfate-sodium acetate-acetone reagent, by alkali phosphate-4-aminoantipyrine/potassium hexacyanoferrate(III) reagent; by 4,4'-bis-dimethylamino triphenylmethane (DMTM) or by a silver-copper complex (Pentacheck) (AWPA Standards 1999; penetration); by TLC, HPLC, GC/ECD, GC/MS and pyrolysis-GC/MS (Horn and Marutzky 1994) after extraction from wood and derivatization or by ion mobility spectroscopy (IMS) (Peylo 1998)

Use with Dry Wood

Historical

1841 Initial production of PCP by Erdmann (Broese van Groenou et al. 1952).

1936 PCP becomes known as a biocide for preserving windows and structural timber (Broese van Groenou et al. 1952).

1947–1949 Solutions with 5% PCP are used as standard wood preservatives against wood decay fungi (Broese van Groenou et al. 1952).

1956 Control of wood-destroying insects in cultural property by injecting a solution of PCP in kerosene distillate (Plenderleith).

1963 PCP in xylene is used for the conservation of carved objects and polychromed wood sculptures (Straub). Xylophen SC is only effective with good penetration.

1968 PCP and Xylophen SC are cited by Aberle and Koller as very effective treatments against wood-destroying insects and fungi.

1970 Mihailov (1970a) sometimes adds 0.5% PCP to Paraloid B72 when used to consolidate wood carvings.

1978 Consolidation of polychromed wood sculptures with Paraloid B72 with the addition of PCP (Serck-Dewaide).

Since 1980 Replacement of PCP as a biocide in Germany after the discovery of strong air pollution in the interiors of treated buildings such as churches and museum storage facilities

1989 PCP is outlawed in Germany.

Present Day

As a biocide in wood preservatives against decay fungi including soft rot fungi, but its use is decreasing worldwide because of its toxicity.

Use with Waterlogged Wood

Historical

1975 A mixture of 2 parts by mass of PEG, 2 parts of Paraloid B72, and 1 part PCP plus 95 volume parts of turpentine are used for the preservation and antistatic surface treatment of waterlogged wood (Mihailov).

Present Day

Because of its low water solubility and high toxicity PCP is not used.

Advantages/Disadvantages

In regard to dry and waterlogged wood: pentachlorophenol is a highly effective fungicide but has limited effects on insects. It has a minor corrosive effect on iron. PCP is not fixed permanently in the wood, and there is a slow but steady emission of the biocide because of its high vapor pressure. It tends to bloom and is dangerous to health and the environment, including water pollution. PCP is not suitable for individual works of art and for interior spaces.

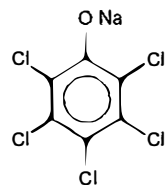
7.3.8.4

Sodium Pentachlorophenolate

Short designation: Na-PCP

Trade name: Dowicide G and Santobrite (USA), Cryptogil (France), and Preventol PN flüssig (Germany)

Formula:



Properties: Needles (from acetone and ligroin); m.p. ~373 °C; readily soluble in water (22.4g Na-PCP in 100ml water); insoluble in toluene, xylene and white spirit

Toxicology: With direct contact, irritation of skin and mucous membranes; see also under PCP

Biological effects: See under PCP. Na-PCP is also a fungicide against blue stain fungi

Application: Concentrations of 4–6% in aqueous solutions

Analysis: In wood by color reaction with copper(II) sulfate, by IMS (Peylo 1998); see also under PCP

Use with Dry Wood

Historical

1966 Molds on bark paintings by Australian aborigines are controlled with a solution of 2.5% Na-PCP in ethanol (Boustead).

1970 Mihailov (1970b) treats wood members of Renaissance houses by impregnation or spraying with a 6–8% Na-PCP solution with 1–2% sodium carbonate or borax added.

Present Day

In Germany Na-PCP is outlawed but in other countries it is still used to treat wood against blue stain.

Use with Waterlogged Wood

Historical

1961/1962 Na-PCP is added to PEG for the conservation of the *Wasa* (Sweden). It was later exchanged for boric acid/borax because of the formation of precipitates (Barkman 1965, 1969).

1963 Gaudel describes the addition of 1% Na-PCP to PEG 4000. The solution should have a pH >7.5; if it becomes less, a 10% solution of sodium carbonate must be added

1972 After cleaning waterlogged wood it is placed into a 10–12% aqueous solution of PEG with 1% Na-PCP (Ankner). Krchňavý recommends dipping waterlogged wood into a 2% Na-PCP solution and a 1% formaldehyde solution prior to stabilization treatment.

1973 Rosenqvist impregnates Runepinnen (wood with Rune inscriptions) with a 10% PEG 4000 solution containing 0.01% Na-PCP (Preventol), followed by freeze drying.

- 1975 One percent Na-PCP is added to 5–25% solutions of PEG 4000 in water and ethanol (2:1; Mihailov). Suthers uses a 10% solution of PEG 4000 with 1% Na-PCP for the conservation of the *Ferriby* boat (Great Britain).
- 1977 Parts of the Punic ship of *Marsala* (Italy) are stored in water with 0.01% Na-PCP (Alagna). De Jong cites Na-PCP and sodium carbonate as additives to PEG 4000.
- 1985 During controlled air-drying of building timber from the time of the Romans a 3% aqueous solution of Na-PCP is among the biocides used to control mold fungi (Schweizer et al.).
- 1990 Sanchez Ledesma et al. add Na-PCP as a biocide during the conservation of waterlogged wood with cane sugar.

Present Day

Na-PCP is now of only minor importance in the storage and conservation of waterlogged wood.

Advantages/Disadvantages

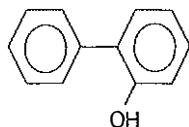
In regard to dry wood: very effective against blue stain fungi. Na-PCP is leach resistant but the weakly acidic nature of wood leads to conversion into PCP, and thereby reduces the depth of penetration. Better penetration can be obtained by buffering with alkali carbonates or borates. If objects previously treated with Na-PCP are fumigated with ethylene oxide, an exothermic reaction can take place (Kleitz 1987). Na-PCP is strongly toxic to humans and the environment. In regard to waterlogged wood: Na-PCP precipitates in PEG solutions.

7.3.8.5

o-Phenylphenol (2-Biphenylol)

Trade name: Dowicide 1 and Lysol (USA), and Preventol O extra and Preventol OF (Germany) for *o*-phenylphenol; Dowicide A (USA) and Preventol ON extra (Germany) for Na-*o*-phenylphenolate

Formula:



Properties: Colorless crystals; m.p. 58–60°C, b.p. 286°C; insoluble in water, soluble in ethanol, ether, and PEG 1500; the sodium salt is water soluble

Toxicology: *o*-Phenylphenol irritates eyes, the respiratory system, and the skin

Biological effects: The substance is a fungicide and a bactericide. It prevents the oxidation of the nicotinamid-adenin-dinucleotide (hydrated; NADH) by disrupting electron transport

Application: Solution of 0.1% *o*-phenylphenol in ethanol (Lysol)

Analysis: By GC or FTIR

Use with Dry Wood

Historical

- 1975 *o*-Phenylphenol and its sodium salt are effective against fungi at a concentration of 0.01–0.05% (Baynes-Cope).
- 1982 Paint layers infected with mold fungi were dipped into a solution of Preventol O extra; the binder turned brown (Hartlieb et al.).
- 1990 Fumigation of cultures of mold fungi with *o*-phenylphenol does not result in a kill (Gustafson et al.).
- 1993 The addition of *o*-phenylphenol affects 6 of 11 pigment systems tested. Cobalt blue is altered especially severely (Koestler et al.).

Present Day

The sodium salt is sometimes used as a biocide in preservatives against blue stain and for the control of fungi in masonry (Koch 1990).

Use with Waterlogged Wood

Historical

- 1975 Conservation treatment with PEG 1500 with 0.01% *o*-phenylphenol added (Baynes-Cope).
- 1983–1985 Parrent (1983a,b, 1985) controls bacterial growth in sugar solutions for the conservation of waterlogged wood by adding 1% Dowicide A.

Present Day

o-Phenylphenol is no longer used.

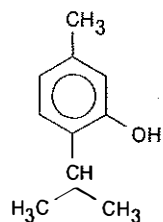
Advantages/Disadvantages

In regard to dry and waterlogged wood: Na-phenylphenolate is less effective against blue stain fungi than Na-PCP, which also applies to control of fungi in masonry. Na-phenylphenolate is less of an irritant than Na-PCP. A 10% solution of the sodium salt is alkaline with a pH of 10. It can be used to control fungal and bacterial attack in storage tanks for waterlogged wood. According to Parrent (1985), waterlogged wood treated with sugar and Na-phenylphenolate did not show any signs of mold after 3 months.

7.3.8.6

Thymol (Thyme camphor, 2-Isopropyl-5-methyl-phenol, *p*-Cymene-3-ol)

Formula:



Properties: Colorless crystals with thyme odor and a burning taste; m.p. 51°C; b.p. 233°C; slightly soluble in water and glycerol, and readily soluble in ethanol, ether, chloroform, and fatty oils

Toxicology: Affects the skin but does not cause any deeper corrosion

Biological effects: Thymol vapors are only fungistatic and have no fungicidal effects; it has a weak effect on insects

Application: Objects are exposed to thymol vapor, or a 5% solution in ethanol is used

Analysis: By GC

Use with Dry Wood

Historical

- ca. 1910 Wood is impregnated with glue containing decay-inhibiting substances, e.g. "hardening" of French glue with thymol crystals.
- 1982 Control of molds on paint layers by dipping into a thymol solution. Hartlieb et al. evaluate the fungicidal effect as good
- 1988 According to Baer and Ellis, thymol fumigation is only effective if the objects are dried in an environment of low humidity.
- 1989 Brokerhof discusses the biocidal effect of thymol.
- 1990 Thymol has no effect on books attacked by mold (Gustafson et al.).
- 1991 Arai et al. control molds on painted wooden surfaces by spraying with 5% thymol in ethanol.

Present Day

Thymol is used occasionally to treat objects attacked by molds or bacteria, but its biological effectiveness is controversial, and sensitive materials might be harmed (Baer and Ellis 1988).

Use with Waterlogged Wood

Historical

- 1985 Use of 0.5% phenol and 0.5% thymol in ethanol to control molds on wood surfaces (Schweizer et al.).
- 1987 De la Baume adds 1% thymol to a conservation sugar solution.
- 1990 Dumkov and Preuss also use 1% thymol in conservation treatment with sugar.
- 1991–1993 Koesling controls microbial growth in sugar solutions by adding 1% thymol.

Present Day

There is no continuing use of thymol as a microbicide.

Advantages/Disadvantages

In regard to dry wood: thymol is not suitable as a biocide in wood preservatives. It has a low capability for penetration, and can dissolve old printer's ink, paint pigments and wood finishes and can soften acrylics. In regard to waterlogged wood: microbial growth cannot be completely prevented over the long term.

7.3.9

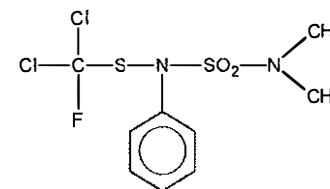
Sulfamide Derivatives

7.3.9.1

Dichlofluamid (*N*-Dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-phenylsulfamide)

Trade name: Euparen (50%) and Preventol A 4 (Germany); in wood preservatives: in Germany Aidol Imprägniergrund for Xyligen Al, deltamethrin and dichlofluamid (2000); and Xylamon Grundierung U 2012 for tebuconazole and dichlofluamid (1997); in Belgium WOCSEN "Grundierung" for propiconazole, permethrin, and dichlofluamid (1997)

Formula:



Properties: A colorless, crystalline substance; m.p. 105–106°C; b.p. cannot be determined as it is not distillable; vapor pres-

sure 1.4×10^{-5} Pa (20°C); solubility at 20°C: in water 2 mg/l, in dichloromethane and toluene 100–1000 g/l, in methanol 15 g/l, and in hexane 1–10 g/l

- Toxicology:** Light skin and moderate eye irritation, possible sensitization of skin areas. Poisonous effects greatly increase upon inhalation. Dichlofluanid is poisonous to fish but not to bees
- Biological effects:** Dichlofluanid is a fungicide especially against blue stain; it inhibits enzyme activity
- Application:** It is used at a concentration of 0.2–2% in solvent-based wood preservatives or in emulsions
- Analysis:** By HPLC or GC/ECD, GC/MS or pyrolysis-GC/MS (Schoknecht et al. 1998) after extraction from wood

Use with Dry Wood

Historical

- 1964 The Bayer company introduces the fungicide for plant protection (Römpf 1995).
- 1976 Use of dichlofluanid for the conservation of adhesives and paint dispersions (Wallhäußer and Fink).

Present Day

Used as a blue-stain-resistant fungicide in solvent-borne wood preservatives, especially undercoatings, for the preventive treatment of structural wood members. However, it is not suitable for living spaces or for wood that might come into contact with food or animal feed. It is used as a component in exterior varnish for nonload-bearing members without soil contact, and as a preservative in paint dispersions and waterborne paints and varnishes.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

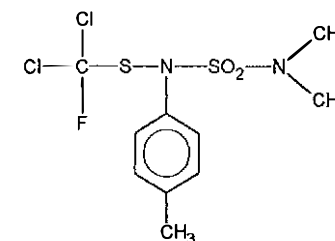
In regard to dry wood: dichlofluanid is effective against blue stain. It is more readily soluble in organic solvents than other fungicides. Its long-term effectiveness decreases slowly. Detailed investigations of the compatibility of dichlofluanid and wood preservatives containing it with works of art and other cultural property are not available.

7.3.9.2

Tolyfluanid (*N*-Dichlorofluoromethylthio-*N,N'*-dimethyl-*N*-4-tolylsulfamide)

- Trade name:** In Germany: Euparen M (50%) and Preventol A 5; in wood preservatives: Aidol Bläueschutz for tolyfluanid (2000), Xylamon Grundierung U 2013 for tebuconazole and tolyfluanid (1997), Xyladecor U 4015 for propiconazole, tolyfluanid, and permethrin (1997)

Formula:



- Properties:** Colorless, odorless, crystalline substance; m.p. 95–97°C; b.p. cannot be determined because it is not distillable; vapor pressure 1.6×10^{-4} Pa (20°C); other reports 2×10^{-5} Pa (20°C); solubility in 100 ml solvent at room temperature is 0.4 g in water, 4.6 g in methanol, 57.0 g in benzene, and 23 g in xylene
- Toxicology:** This compound has been classified the same as dichlofluanid, but according to more recent investigations tolyfluanid appears to be much more poisonous than previously assumed
- Biological effects:** It is a fungicide against blue stain, probably by inhibiting enzyme activity
- Application:** Effective concentration is 0.1–3% in solvent-borne wood preservatives or emulsions
- Analysis:** By HPLC or GC after extraction from wood

Use with Dry Wood

Historical

- 1973 The Bayer company brings tolyfluanid on the market as an agricultural fungicide (Römpf 1995).
- 1992 Buschhaus publishes data on the effectiveness of tolyfluanid against various blue-stain fungi.

Present Day

It is used as biocide against blue stain in wood preservatives, and in combination with triazoles and synthetic pyrethroids in exterior varnishes. Its use will probably decrease because of its toxicity.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: tolylfluand is similar in its effectiveness against blue stain, but is suspected of being more poisonous.

7.3.10

Benzimidazole Derivatives

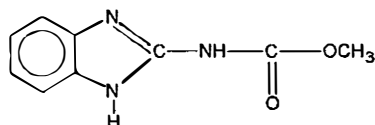
7.3.10.1

Carbendazim – 2-(Methoxy carbonylamino)-benzimidazole

Short designation: BCM, MBC

Trade name: In Germany: Derosal and Mergal BCM; in preservative wood coatings: Consolan Holzschutz (Wetterschutz)-Farbe for carbendazim (1984)

Formula:



Properties: Colorless to sand-colored, odorless, crystalline substance; m.p. 307–312°C, other reports 304°C (decomposition); vapor pressure 9.0×10^{-5} Pa (20°C); solubility in 100g solvent is 0.1 mg in water (other reports 0.8 mg), 0.03 g in acetone, 0.01 g in chloroform, 0.001 g in ether and <0.001 g in ethyl acetate

Toxicology: No irritation to skin or eyes or sensitization in rabbits; chronic application to rats caused liver damage; no carcinogenic or neurotoxic effects; possibly mutagenic

Biological effects: Carbendazim is an effective fungicide against blue stain. It interferes with the biosynthesis of deoxyribonucleic acids (DNA), ribonucleic acids (RNA) and protein, and with the phosphorylation of the fungal organism

Application: At 0.2–4.5% in aqueous and solvent systems. It is used in a concentration of 0.1–0.3% against blue stain

Analysis: By TLC (Petrowitz and Wagner 1992), HPLC or GC/FID, GC/ECD or pyrolysis-GC/MS (Schoknecht et al. 1998) after extraction from wood

Use with Dry Wood

Historical

Carbendazim was introduced by BASF, DuPont, and Hoechst for plant protection and seed treatment (Römpf 1995).

Present Day

Its use is decreasing because of suspected mutagenesis.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: the toxicity of carbendazim has not been investigated sufficiently; there is also evidence of resistance.

Other benzimidazole derivative (with fungicidal effect): thiabendazole [2-(thiazol-4-yl) benzimidazole].

7.3.11

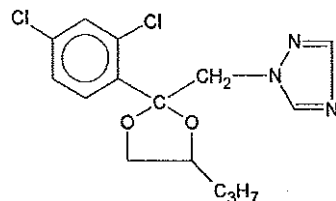
Triazole Derivatives

7.3.11.1

Propiconazole – (±)-1-[2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl-methyl]-1H-1,2,4-triazole

Trade name: WOCOSIN Technical (Belgium) for propiconazole (90–95% purity); in wood preservatives: AVENAROL HOLZSCHUTZGRUNDIERUNG, Priem Imprägniergrund AN 33/5, and Xylamon Holzschutz-Grundierung U 1051 (Germany) for 1% propiconazole (1997), WOCOSIN Holzschutzlasur (Belgium) for propiconazole, dichlofluand, permethrin (2000), and Basilit M-P (Germany) for 9.60% propiconazole (2000)

Formula:



- Properties:** Odorless, yellowish liquid; b.p. 180°C at 13 Pa; vapor pressure 1.3×10^{-4} Pa (20°C); other reports 5.6×10^{-5} Pa (25°C); solubility in water 100 mg/l (20°C), readily soluble in acetone, dichloromethane, 2-propanol, methanol and toluene
- Toxicology:** Does not irritate eyes or skin, not sensitizing, not dangerous to bees, but very poisonous for water organisms
- Biological effects:** Propiconazole is a fungicide; it inhibits the sterol biosynthesis which is important for the function of cell membranes
- Application:** Concentration in waterborne wood preservatives 1%, and for control of house fungus in masonry 10%
- Analysis:** By TLC, HPLC or GC after extraction from wood (AWPA Standards 1999, Petrowitz and Wagner 1992)

Use with Dry Wood

Historical

- Propiconazole is a fungicide discovered at Janssen Pharmaceutica and developed by Ciba-Geigy (Römpf 1995).
- 1981 Triazole derivatives are patented as fungicides for plant protection (Holmwood et al.).
- 1984 European patent for the use of triazoles in wood preservation (Van Dyk et al.).
- 1989 Valcke describes the suitability of propiconazole as a fungicide in wood preservation.
- 1993 Review by Wüstenhöfer et al. on the fungicidal effect of triazoles in wood preservatives.

Present Day

Propiconazole is used in waterborne wood preservatives with fungicidal effects against basidiomycetes and blue-stain fungi for the protection of wood in windows and exterior doors. It is also used to control house fungus in masonry.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

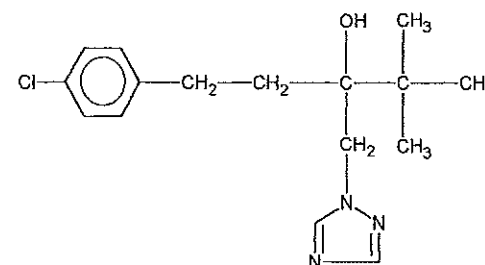
In regard to dry wood: propiconazole is a relatively new, effective fungicide which is not corrosive to metals. It is reported to prevent mold in protein glues. Technical studies of its use for cultural property are not yet available.

7.3.11.2

Tebuconazole [α -tert-Butyl- α -(4-chlorophenylethyl)-1H-1,2,4-triazole-1-ethanol]

- Trade name:** Preventol A 8 (Germany); in wood preservatives: in Great Britain, Resistol 2629 for propiconazole, tebuconazole, IPBC and permethrin (1997); in Germany, Basiment Tauchgrundierung U 4112 and Aidol Bläue- und Fäulnis-schutz for tebuconazole and tolylfluamid (1997); KULBA-Lasur for tebuconazole, dichlofluamid and permethrin (2000); and Aidol Multi GS for tebuconazole and deltamethrin (2000)

Formula:



- Properties:** Colorless and odorless crystals; m.p. 104.7°C; vapor pressure 7.2×10^{-7} Pa (20°C); other reports 1.3×10^{-6} Pa (20°C); solubility in 1 l of solvent (20°C) is 32 mg in water, <0.1 g in *n*-hexane, 50–100 g in toluene and 100–200 g in 2-propanol
- Toxicology:** Some effects on behavior, breathing, and mobility in animal experiments. In rabbits there was no irritation of skin or eyes. No danger to bees. Tebuconazole has the potential for damaging embryo and is a water pollutant
- Biological effects:** It is a fungicide with the same effects as propiconazole
- Application:** At 0.1–4% in aqueous and solvent systems
- Analysis:** By TLC, HPLC, GC/FID, and pyrolysis-GC/MS (Schoknecht et al. 1998)

Use with Dry Wood

Historical (See also under propiconazole)

- 1988 The Bayer company introduces tebuconazole for plant protection (Römpf 1995).
 1990 Wüstenhöfer et al. introduce the properties of tebuconazole as a wood preservative. Bayer publishes product information on the use of Preventol A8 in wood preservation (Anonymous).

Present Day

Tebuconazole is used as a fungicide in oil-borne wood preservatives against basidiomycetes.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: tebuconazole is an effective fungicide in solvent-borne wood preservatives, and is also effective against molds such as *Aspergillus niger*. The substance is almost unleachable, stable in exposure to light and heat, not volatile, and warrants long-term effectiveness (Anonymous 1990). The biocide is compatible with binders, pigments, siccatives, and other fungicides or insecticides in wood preservatives, e.g., permethrin. Investigations on the compatibility of tebuconazole and wood preservatives containing it with cultural property are not yet available.

7.3.12

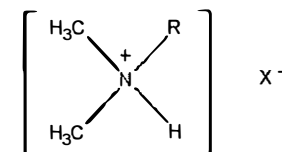
Quarternary Ammonium Compounds (Alkylammonium Compounds)

Short designation: AAC, QAC, quats

Trade name: In Germany: Dodigen 226 for alkyl benzyl dimethyl ammonium chloride (benzalkonium chloride), Lignosan for (coconut) alkyl benzyl dimethyl ammonium propionate, Sterogenol for cetylpyridinium bromide, Eurecid 9047 for quarternary ammonium salt and tributyltin oxide (5:1), Polymeric Betaine for oligomers [didecyl(2-hydroxy-ethyl-poly-2-oxidoethyl)-(poly-2-oxidoethyl)-(ω-hydroxy-poly-ethoxy)ammonium-O,O']borate, Tego 51 for dodecyl di-(aminoethyl) glycin, and Tego 51B for alkyl (aminoethyl) glycin hydrochloride; in Europe Gloquat C for benzalkyl trimethyl ammonium compounds, in USA Arquat 16-50 for alkyl trimethyl ammonium chloride, and in Switzerland Bardap-26 for *N,N*-didecyl-*N*-methyl-poly(oxethyl)-ammonium propionate

In wood preservatives: in Germany impra-MSK 10 for 99.5% didecyl-poly(oxethyl)-ammonium borate (Betaine) (2000), Basilit M for 33% dimethyl benzyl alkyl(DBA)-ammonium chloride (2000), and impralit-TTS for didecyl-poly(oxethyl)-ammonium borate (Betaine), copper carbonate and boric acid (1999).

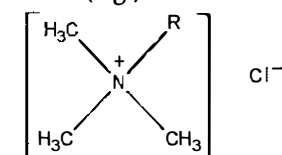
Formulas:



Type I: alkyl-dimethyl-ammonium salt

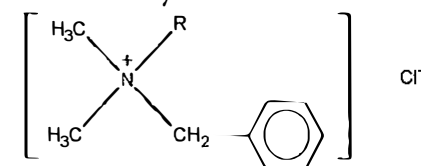
R = alkyl

X⁻ = (e.g.) Br



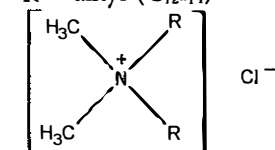
Type II: benzalkyl-trimethyl-ammonium chloride

R = benzalkyl



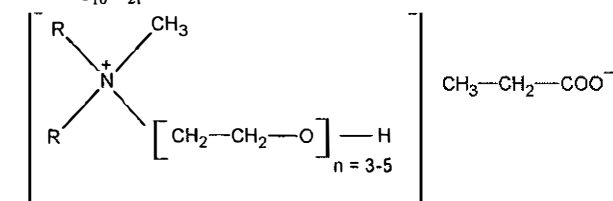
Type III: alkyl(C₁₂₋₁₄)-benzyl-dimethyl-ammonium chloride

R = alkyl (C₁₂₋₁₄)



Type IV: didecyl(C₁₀C₁₀)-dimethyl-ammonium chloride (DDAC)

R = C₁₀H₂₁



Type V: didecyl(C₁₀C₁₀)-methyl-poly(oxethyl)-ammonium propionate (Betaine-type)

R = C₁₀H₂₁

Properties:	These compounds are liquids with a weak but characteristic odor. They are soluble in water and miscible with alcohol
Toxicology:	The production of Type II compounds sometimes causes health hazards. Type III compounds are strong irritants to skin and mucous membranes, and are water pollutants. Type IV compounds are probably not carcinogenic and cause almost no skin irritation. Type V compounds are strong irritants to skin and eyes, and are poisonous to water organisms
Biological effects:	AACs are primarily fungicides, bactericides, and algicides, and sometimes are effective insecticides against termites. They can also prevent spore formation in the house fungus (Hegarty 1988). Didecyl-dimethyl-ammonium chloride (DDAC) is the most effective against brown-rot and white rot fungi (Preston and Nicholas 1982). Probable influences of AACs are on the semipermeable cell membrane, causing leakage, and on cell respiration
Application:	Depending on the type of AAC and the organisms to be controlled, concentrations can vary considerably. For benzalkonium chloride 5–75%, for didecyl-dimethyl-ammonium chloride 40%, and for didecyl-methyl-poly (oxethyl)-ammonium propionate 8–70% in water-soluble concentrates. To control house fungus in masonry, an aqueous solution of 33% DBA-ammonium chloride or of 10% didecyl-poly(oxyethyl)-ammonium borate is used
Analysis:	In wood by color reaction with (1) NaOH, HgI ₂ and KI, and (2) bromophenol blue, e.g., for Polymeric Betaine, by HPLC or titration (AWPA Standards 1999) after extraction from wood

Use with Dry Wood

Historical

- 1965 Oertel and also Thompson discover the properties of AACs for wood preservation.
- 1977/1978 Fundamental investigations of the suitability of AACs as wood preservatives by Butcher and Drysdale. They are used in New Zealand for the preservation of wood which is not in contact with the ground (Preston 1983).
- 1985 Butcher lists advantages and disadvantages of the use of AAC-treated wood in contact with the ground.

- 1989 Comprehensive discussion of AACs as biocides for wood preservatives by Becker (1989b).
- 1991 Jin and Preston investigate the pH dependence of adsorption of didecyl-dimethyl-ammonium chloride (DDAC) on the principal chemical constituents of wood.
- 1993 Polymeric Betaine as a new fungicidal and termiticidal biocide in wood preservation (Barth and Härtner).
- 1996 Copper-amine/Polymeric Betaine formulations exhibit increased fungicidal effectiveness (Härtner and Barth).

Present Day

AACs are used in combination with chromium-free copper preparations such as copper carbonate or copper hydroxide carbonate for pressure or soaking treatments of structural timber for interior and exterior applications, with and without contact with the soil. They are also used to control house fungus in masonry and as surfactants.

Use with Waterlogged Wood

Historical

- 1973 Addition of 1% Tego 51B to prevent decay of objects stored in water (Mühlethaler).
- 1975 Cetylpyridinium ammonium bromide and alkyl-trimethyl-ammonium bromide inhibit growth of algae in storage tanks for waterlogged wood (Baynes-Cope).
- 1977 Quarternary ammonium compounds such as a 1% solution of Dodigen to control fungi and bacteria in water storage of waterlogged wood (Zimmermann).
- 1990 Addition of 0.2% Eurecid 9047 to a sugar solution for the conservation of waterlogged wood (Hoffmann).
- 1991 Morgós uses Sterogenol as a biocide in a sugar solution.
- 1996 The addition of 0.1% benzalkonium chloride or 1% didecyl-dimethyl-ammonium chloride do not prevent microbial growth during wet wood storage (Sakai et al. 1997).

Present Day

AACs are not used extensively for wet wood storage or sugar conservation.

Advantages/Disadvantages

In regard to dry wood: AACs are well suited as general biocides because of their lack of specificity. They are inexpensive and their toxicity to mammals is low. In high concentrations they are suitable for controlling house fungus in masonry. The fungicidal effectiveness of AACs can be increased by combi-

nations with inorganic copper compounds (Tsunoda and Nishimoto 1987). Such preparations can be used to preserve softwoods with soil contact. Polymeric Betaine has good penetration, owing to its solubility in water, and is suitable for tank immersion treatments. It is leach-resistant and is not emitted into the air. Bardap 26 can be added to gesso to impart mildew resistance; it can still be sanded. Some fungi are resistant to certain AACs and can even decompose some, e.g., DDAC in wood (Richardson 1993, Dubois and Ruddick 1998). AACs with halogen ions can possibly be corrosive to metals. In regard to waterlogged wood: most of the AACs tested so far are not sufficiently effective in preventing microbial attack during waterlogged wood storage or in sugar conservation treatments.

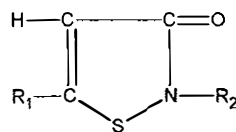
7.3.13

Isothiazolones

Short designation: ITA

Trade name: In the USA and Germany: Kathone CG, Kathone WT and Kathone WT 1.5% for 5-chloro-2-methyl-4-isothiazol-3-one (I) and 2-methyl-4-isothiazol-3-one (II); Microbizid DP III for (I), (II) and 2-*n*-octyl-4-isothiazol-3-one; in the USA: Skane M-8 (Kathone) for 2-*n*-octyl-4-isothiazol-3-one (45%) in propylene glycol

Formula:



$R_1 = \text{Cl or H}$

$R_2 = \text{CH}_3 \text{ or } n\text{-C}_8\text{H}_{17}$

Properties: The various types of Kathone are clear to cloudy, slightly yellowish liquids with a pH of about 3.5. They are miscible with water, lower alcohols, and glycols

Toxicology: In concentrated form, isothiazolones are strong eye and skin irritants, and can cause skin allergies. They are water pollutants and are poisonous to fish and their food animals

Biological effects: Isothiazolones have fungicidal, bactericidal and algicidal properties; they inhibit cell growth and respiration

Application: Kathone CG is used in a concentration of 0.02–0.1% (3–15 ppm of active ingredient) for drywood. For waterlogged wood the following initial concentrations are recom-

mended: for wood with little degradation, 3–15 ppm active ingredient (0.02–0.1% Kathone CG); for wood with moderate to extensive degradation, 15–60 ppm of active ingredient (0.1–0.4% Kathone CG); for very highly degraded wood up to 150 ppm (1% Kathone CG) may be necessary

Analysis: Generally by colorimetric determination with dithio-bis-(2-nitrobenzoic acid), HPLC and GC

Use with Dry Wood

Historical

- Ca.1975 Kathone CG comes on the market in Europe as a preservative for cosmetics.
- 1979 Hedley et al. discover excellent effectiveness of Skane M-8 against wood stain and decay fungi.
- 1984 4,5-Dichloro-2-*n*-octyl-4-isothiazol-3-one shows high effectiveness against brown-rot and white-rot fungi (Nicholas et al.).
- 1990 Wood impregnated with the same isothiazolone shows good preservative effects against termites and fungi after 5-year field tests (Leightley and Nicholas).
- 1997 Hegarty et al. describe the anti-fungal efficacy of isothiazolone microemulsions and their suitability as long-term wood preservatives.

Present Day

Isothiazolones are rarely used in wood preservatives, in spite of good fungicidal properties.

Use with Waterlogged Wood

Historical

- 1990 Use of isothiazolones in conservation with sugar begins in Germany.
- 1994 Morgós et al. describe the properties of various Kathone products and their suitability for the prevention of microbial sugar decomposition during conservation treatments.
- 1996 Isothiazolones in a concentration of 0.01–0.02% are most effective in the protection of waterlogged wood against decay (Sakai et al. 1997).

Present Day

Isothiazolones are used as microbicides in conservation treatments of waterlogged wood with sugar.

Advantages/Disadvantages

In regard to dry wood: isothiazolones have good biocidal properties. The concentration for use of Kathone CG is very low, and it has good solubility in water. At higher concentrations isothiazolones are strong irritants for skin and mucous membranes. Their use for controlling biological attack in cultural property has not been investigated in detail. In regard to waterlogged wood: isothiazolone is an effective microbicide for waterlogged wood treatment with sugar. It does not accumulate in the environment and is easily degraded. See also under dry wood.

7.3.14

Organoaluminum Compounds

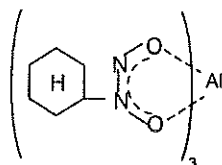
7.3.14.1

Xyligen Al [tris-(*N*-Cyclohexyldiazeniumdioxo)-aluminum]

Short designation: Al-HDO, NCH-Al

Trade name: In Germany Xylasan Al and Xyligen NCH; in wood preservatives: Aidol Imprägniergrund for Xyligen Al, deltamethrin and dichlofluanid (2000); and Wolmanol-Holzbau B and Kulbanol Holzbau 120 B for Xyligen Al, permethrin and dichlofluanid (2000)

Formula:



Properties: White powder with weak characteristic odor; m.p. 94 °C; vapor pressure 5.9×10^{-6} Pa; other reports: 8×10^{-6} Pa (20 °C); solubility in 100 g solvent at 20 °C is 10 µg in water, 40 g in benzene, 50.5 g in chloroform, 42.6 g in dichloromethane, 47.9 g in dimethylformamide, 44.5 g in dioxane, 31.5 g in ethyl acetate, 7.6 g in methanol, 28.3 g in Shellsol AB, and 33.9 g in toluene

Toxicology: On long-term exposure, Al-HDO is a strong irritant to skin and mucous membranes and can cause great damage to stomach and small intestines. Its chronic toxicity is largely unknown. In animal experiments long-term exposure was found to be carcinogenic; it is poisonous to fish and their food animals

Biological effects: Al-HDO is an effective fungicide against basidiomycetes

Application: It is used in concentrations of 2–5% in solvent-borne wood preservatives, generally at 3.5%

Analysis: By ICP-AES for Al, and colorimetric as azo dye after extraction from wood

Use with Dry Wood

Historical

- 1975 Dickinson and Coggins discover the fungicidal effect of Xyligen-NCH against wood-destroying fungi.
- 1977 Xyligen-NCH is considered to be a promising fungicide (Metzner et al.).
- 1978 Hädicke et al. describe the properties of Al-HDO.
- 1988 Xyligen Al in organic solvent is found to be the most suitable preservative for the conservation of polychromed wood in historic buildings (Lutomski et al.).

Present Day

Al-HDO is used as a fungicide in solvent-borne wood preservatives in combination with synthetic pyrethroids and sometimes dichlofluanid for the industrial production by pressure treatment or soaking of structural timbers, including exterior exposure.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: the concentration required against basidiomycetes is relatively high, but it has good long-term effectiveness. It is not suitable for spaces with human occupancy, and its suitability for cultural property has not been sufficiently investigated.

7.3.15

Organoboron Compounds

7.3.15.1

Trimethyl Borate (Boric Acid Trimethylester)

Short designation: TMB

Trade name: –

Formula: $(\text{CH}_3\text{O})_3\text{B}$

Properties: Colorless liquid which is sensitive to humidity and burns with a green flame; m.p. –29.3 °C, b.p. 68.7 °C; soluble in

	organic solvents; with water it is saponified to boric acid and methanol
Toxicology:	Irritates mucous membranes and the respiratory tract; in higher concentrations it has a narcotic effect. Continuous contact with the skin leads to loss of fat and eczema
Biological effects:	TMB is a fungicide but also effective as an insecticide by formation of complexes with important molecules of the cell. Organic boron compounds of a "complex" structure show reduced effectiveness
Application:	By gas phase and pressure treatments for wood impregnation
Analysis:	After hydrolysis as boric acid (cf. boric acid), by GC/MS

Use with Dry Wood

Historical

- 1985 Gas phase treatment of wood and wood panel products with TMB in New Zealand (Vinden et al.).
 1990/1991 Burton et al. and Vinden et al. describe in detail the use of TMB for pressure treatment of wood.

Present Day

Gas phase treatments with TMB are not yet used extensively, but appear to be promising for the future.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: compared to the customary diffusion treatments, the use of TMB in pressure treatments reduces the treatment time. Gas phase treatment alone does not result in sufficient loading of wood with boric acid, the active ingredient. For cultural property, especially painted objects, TMB is hardly suitable because of the formation of methanol and the swelling it will cause.

Other organoboron compounds: trihexylene glycol biborate (Becker 1983, Richardson 1993), and protein borates (Thevenon et al. 1997, 1998).

7.3.16

Organocopper Compounds

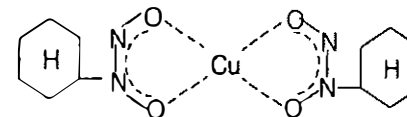
7.3.16.1

Copper-HDO [bis-(*N*-Cyclohexyldiazeniumdioxy)-copper]

Short designation: Cu-HDO

Trade name: Xyligen Cu; in wood preservatives: in Germany Adolit TA 50, impralit-CX4, impralit-CX12, Kulbasal KB, Wolmanit CX-10 and Wolmanit CX-S for Cu-HDO, copper hydroxide carbonate and boric acid (1999)

Formula:



Properties: Blue, crystalline powder; m.p. 157°C (decomposes); vapor pressure $< 1 \times 10^{-5}$ Pa (20°C); other reports: ca. 1×10^{-6} Pa (20°C); solubility in 100 g solvent at 20°C is 0.6–1 mg in water (practically insoluble), 0.12 g in petroleum, 4.3 g in toluene, 0.49 g in 2-propanol, 24.1 g in chloroform, 2.05 g in methanol and 10.5 g in dimethylformamide

Toxicology: Cu-HDO irritates mucous membranes, causes corrosion and eye damage, is not sensitizing, not mutagenic, not teratogenic, and not carcinogenic, but is a water pollutant

Biological effects: Cu-HDO is primarily a fungicide against brown rot, white rot, and soft rot, but is also effective against insects, e.g. termites. Probably brings on denaturing of proteins and enzymes, but also impairs the mitochondria

Application: At 0.6–6% in water-soluble concentrates

Analysis: In wood by color reaction with 4-(pyridyl-(2)-azo)-resorcinol (pretest); the HDO anion can be determined after digestion by ICP-AES [see copper(II) sulfate, Schoknecht et al. 1998], and by HPLC after extraction from wood (Wittenzellner et al. 1999)

Use with Dry Wood

Historical

- 1956 German patent No. 102,474 for the use of *N*-cyclohexyldiazeniumdioxy salts as fungicides in wood preservation (Götsche and Marx 1989).

- 1973–1976 First experiments in application technology by Dr. Wolman GmbH (Göttsche and Marx 1989).
 1979 Definitive elucidation of the structure of Cu-HDO by Hickmann et al. (Göttsche and Marx 1989).
 1988 Beginning of large-scale pressure impregnation (Göttsche and Marx 1989).
 1989 Göttsche and Marx, and also Becker (1989a) describe in detail the properties and suitability of Cu-HDO for wood preservation.

Present Day

Cu-HDO is used for preventive treatment, by pressure or soaking methods, against insects and fungi. Depending on the particular composition of the preservative, the treated wood may be used for exterior exposure or in contact with the soil. Cu-HDO is used as a substitute for preservatives containing chromium, usually in combination with inorganic copper salts and boric acid. Since Cu-HDO is practically insoluble in water, it is converted in alkaline solutions of pH 9–9.5 into a water-soluble form by means of complexing agents such as polyamines, and sold as a salt concentrate of blue color. After impregnation, the solution is neutralized by the wood components. Cu-HDO begins to flocculate at a pH below 7. Within 24h, 75% of the substance is fixed in the wood.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

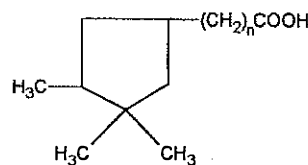
In regard to dry wood: Cu-HDO is effective against brown-rot and white-rot fungi, especially *Poria vaillantii* (*Antrodia vaillantii*). It has low vapor pressure, good leach resistance and long-term effectiveness. Treated wood takes on a light green coloration, and because of this and the aqueous formulation it is not suitable for works of art and other cultural property.

7.3.16.2

Copper Naphthenates

Trade name: In wood preservatives: Cuprinol in Denmark and Oborex Cu in the Netherlands for copper naphthenates

Formula:



The above is the structure of cyclopentane carbonic acid, a naphthenic acid, which is used to produce copper naphthenate (after Eaton and Hale 1993)

- Properties: Copper naphthenate products are viscous, green liquids with about 6 to 8% Cu content; solubility in water is poor, but they are soluble in organic solvents and mineral oils
- Toxicology: Copper naphthenate has a noxious odor, is poisonous, and persistent in the environment
- Biological effects: Copper naphthenate is a fungicide; for its effects see under copper(II) sulfate or Cu-HDO
- Application: Dosage is 6–8% Cu as copper naphthenate
- Analysis: By titration with potassium iodide and sodium thiosulfate (AWPA Standards 1999)

Use with Dry Wood

Historical

- 1889 In Russia, von Wolniewicz proposes the use of metal naphthenates as wood preservatives (Richardson 1993).
 1899 Charitschkow describes the preservative effect of copper naphthenates for wood (Broese van Groenou et al. 1952).
 1911 Industrial production of Cuprinol in Denmark (Richardson 1993).
 ca. 1920 Cuprinol is introduced into Sweden (Richardson 1993).
 1933 Cuprinol is used in England (Richardson 1993).
 1939/1945 Extensive use of copper naphthenate for the impregnation of wood and textiles (Richardson 1993).
 1962 Lehmann describes the Cuprinol treatment of ethnographic and archaeological objects of wood with fungal decay.
 1975 Stoia and Lambru in Romania obtain a patent for a wood preservative for works of art which contains copper naphthenate among other active ingredients.

Present Day

Copper naphthenate serves as a fungicide in wood preservatives and in protective wood varnishes, but its use is decreasing.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: copper naphthenate has good fungicidal effectiveness at high dosage, is leach resistant and has long-term effectiveness. It is better against fungi than zinc naphthenate, and weakly effective against termites and other wood-destroying insects. It does affect the environment because of its persistence.

7.3.17

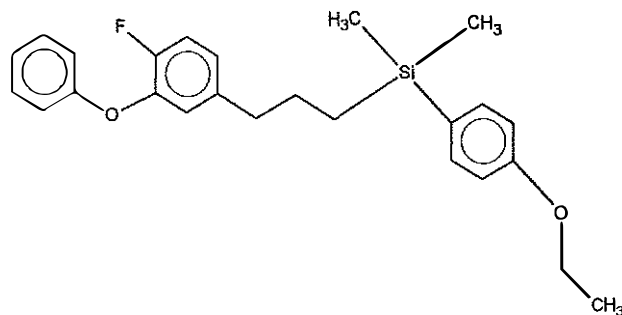
Organosilicon Compounds

7.3.17.1

Silafluofen – (4-Ethoxyphenyl) [3-(4-fluoro-3-phenoxyphenyl)-propyl]-(dimethyl)-silane

Trade name: In wood preservatives: in Germany, impralit-BKD 2 and impralit-TSK 17 for didecyl-poly(oxethyl)-ammonium borate and silafluofen (2000)

Formula:



Properties: Silafluofen is a colorless, odorless liquid; b.p. cannot be determined; vapor pressure 2.5×10^{-6} Pa (20°C); solubility in water is 1 µg/l at 20°C; soluble in most organic solvents

Toxicology: Silafluofen irritates eyes and skin, but is not neurotoxic, mutagenic, teratogenic or carcinogenic. It is dangerous to bees

Biological effects: Silafluofen is an insecticide taken up by ingestion and contact

Application: It is used at 0.1–0.5% in solvent-based formulations and water-soluble concentrates, and in combination with Betaine at a concentration of 0.375–0.5%

Analysis: By gas liquid chromatography (GLC) or HPLC

Use with Dry Wood

Silafluofen is a new insecticide against wood-destroying insects and termites used in preventive wood preservatives (Anonymous n.d.; Rustenburg and Klaver 1991; Adams et al. 1995).

Advantages/Disadvantages

So far intended only for soaking and pressure treatments.

7.3.18

Organotin Compounds

7.3.18.1

Tributyltin Oxide [bis-(Tri-*n*-butyl-tin)-oxide]

Short designation: TBTO

Trade name: In wood preservatives: in Scandinavia, BP Hylosan PT (Permapruf T) for TBTO and AACs; in Germany, Xylamon Braun for TBTO and lindane (1984), later TBTO and permethrin (1985/1986); in the former German Democratic Republic, Kombinal TO for TBTO (1984), later TBTO and thiram (1985)

Formula: $(n\text{-C}_4\text{H}_9)_3\text{Sn-O-Sn}(n\text{-C}_4\text{H}_9)_3$

Properties: Colorless to yellowish liquid with a tin content of $\geq 38.3\%$; b.p. 180°C at 2.66×10^2 Pa; vapor pressure 1.46×10^{-3} Pa (25°C); solubility in water 30 mg Sn/l, soluble in benzene and white spirit

Toxicology: Strong irritant to skin and mucous membranes, causes sneezing, tearing, and acute chronic toxicity which manifests itself in metabolic disorders, muscular weakness, paralyzing of the extremities, intestinal inflammation, and liver and kidney damage. TBTO is a heavy water pollutant and accumulates in clams and fish

Biological effects: TBTO is effective against brown-rot and soft rot, but of limited effectiveness against white-rot and blue-stain fungi. It also has insecticidal properties and is effective against marine borers. It blocks the formation of ATP

Application: Effective concentration for solvent-borne wood preservatives is 0.5–1%, up to a maximum of 2%. It is used for wooden windows, especially in Great Britain, and in antifouling paints, but TBTO use is declining rapidly

Analysis: In wood by color reaction with bromopyrogallol or pyrocatechol violet. The results are not always clear, particularly for dark woods or low tin concentrations. A spot test can be made with phenylfluorone indicator (Plackett 1984), by TLC, HPLC or GC/MS after extraction from wood; for tin by photometry with 4-hydroxy-3-nitrophenyl-arsonic acid after extraction from wood (AWPA Standards 1999), or by ICP-AES (Voss et al. 1999)

Use with Dry Wood

Historical

- 1949 Systematic investigations of the biocidal effect of organotin compounds begin in the Netherlands (Becker 1987/1988).
- 1954 The excellent biocidal effectiveness of TBTO is recognized (Becker 1987/1988).
- 1958/1959 Tests of the suitability of TBTO as a fungicide for wood preservation (Becker 1987/1988). TBTO comes on the market in the USA and Great Britain (Becker 1987/1988; Richardson 1993).
- 1962 Sculptures attacked by fungi of the genera *Aspergillus* and *Penicillium* were sprayed with TBTO in alcohol in Japan. The treatment was still effective after 10 years (Emoto 1972).
- 1969 First comprehensive publication on TBTO as a fungicide for wood preservatives (Hof).
- 1971 Treatment of decaying wood in historic buildings with TBTO (Matějková). It is also recommended to add the biocide to gypsum and cement
- 1984 TBTO is added as a biocide to poly(butyl methacrylate) used for consolidation of wardrobe parts (Michaelsen).
- 1987 Extensive overview report by Becker (1987/1988) on the fungicidal effectiveness of organotin compounds. Substitution of other organic tin-based biocides for TBTO. Treatment of historic structural timbers to eradicate house fungus with TBTO and furmecyclox (Xyligen B) as biocides in the wood preservative (Graf). Use of TBTO as a biocide in the restoration of wooden chests (Morgós).
- ca. 1990 Organotin compounds are being replaced in Germany because of their considerable toxicity to humans and the environment.

Present Day

TBTO and other organotin compounds no longer play more than a minor role as biocides in wood preservatives.

Use with Waterlogged Wood

Historical

- 1981 Organotin compounds are used to control marine borers (gribble) in timbers of marine structures (Mori and Arai).
- 1988 According to Gambetta et al. timbers of marine structures impregnated with TBTO were still resistant to fungi after 12 years, whereas shipworms attacked the wood after only 1 year.
- 1990 TBTO is used in sugar treatments (see under AACs).

Present Day

TBTO is not used in waterlogged wood conservation.

Advantages/Disadvantages

In regard to dry wood: TBTO is effective against brown rot and soft rot. Because of its low effectiveness against white rot and blue stain, and also to reduce its concentration, it is used in combination with furmecyclox (Xyligen B), AACs and dichlofluanid (against blue stain). Such combination with other fungicides has synergistic effects, extends the period of effectiveness and is less toxic to warm-blooded animals. In part TBTO also has good insecticidal effectiveness, e.g., against *Hylotrupes bajulus*, at higher concentrations, but it is most often used in combination with insecticides such as endosulfan or synthetic pyrethroids. TBTO does not have sufficient long-term stability, as it decomposes to less effective dibutyl and monobutyl compounds, and is not stable on exposure to UV radiation, heat, and ozone. It also loses effectiveness due to evaporation, and can possibly be detoxified by wood-destroying fungi. The use of TBTO in antifouling paints for boats and ships has been outlawed because it is a serious water pollutant.

Other organotin compounds: tributyltin benzoate (TBTB), tributyltin naphthenate (TBTN) and tributyltin phosphate.

7.3.19

Mixtures of Natural Products

Consumers have become uneasy about the use of synthetic biocides in wood preservatives because of the attendant human and environmental toxicity problems, and this has led in part to attitudes of disapproval. For this reason efforts are now under way to use more natural products or substances derived from them as wood preservatives. Although such products often have the actual advantage of better ecological compatibility, there are a number of problems which, so far, have not been solved. Many natural products do have biocidal effectiveness, but it is often insufficient to ensure long-term protection or to stop if not eradicate an existing attack. The content of effective substances in the plants and animals which are potential sources often varies

considerably, so that a desired, defined level of effectiveness cannot be guaranteed. Furthermore, many preparations or their constituent chemical compounds do not have sufficient shelf life. There may be precipitation, separation or decomposition of the ingredients so that the biocidal effect decreases rapidly or is lost entirely. Even after natural wood preservatives have been impregnated into the wood they may degrade rapidly under the influence of UV radiation, oxygen in the air, or bacteria, so that the necessary long-term effectiveness is no longer certain. Natural products consist of many chemical constituents, and it is difficult to judge how they might react with each other, with the material to be treated, or with the environment. The situation becomes especially critical if years later the use of a natural products turns out to be damaging to the material and methods for its decontamination have to be found. Surely a single, well-defined biocide will be easier to remove than a complex of different compounds.

7.3.19.1

Pyroligneous Acid (Wood Vinegar)

Production: Wood is heated under exclusion of air (destructive distillation) to obtain wood gas, wood vinegar, and wood tar

Composition: Raw wood vinegar contains 75% water, 12% acetic acid and homologs, 2% methanol, 1% acetone and methyl acetate, and 10% dissolved tar. Free acetic acid can be obtained by distillation

Formula (for acetic acid): CH_3COOH

Properties (for acetic acid): Colorless liquid with a pungent odor; m.p. 16.5°C , b.p. 118°C ; solubility: miscible with water, ethanol, ether, tetrachloromethane, chloroform and glycerol; immiscible with carbon disulfide

Toxicology: Vapors and aerosols are strong irritants, especially for the eyes; aqueous solutions of 1% or more corrode the mucous membranes, and of 10% or more, the skin

Biological effects: Wood vinegar is a weak insecticide and fungicide

Application: Should preferably not be used

Analysis: By HPLC or GC/MS after extraction from wood

Use with Dry Wood

Historical

1740 Reed: Preservation of wood with wood vinegar (Troschel 1916).

1837 Boucherie: Impregnation via the sap with such substances as lead acetate or ferric acetate obtained from wood vinegar (Clausnitzer 1990).

1844 Wood vinegar is expressly recommended as a preservative (Schiessl 1984).

1908 Warning against the use of acetic acid to control wood borers (Schiessl 1984).

1909 A warm mixture which is prepared by boiling 12.5 g garlic, 25 g onions, 11.5 g salt, 80 g wormwood leaves and 2.25 g powdered pepper in 1.5 l of vinegar is recommended for the impregnation of "worm eaten" wood (Aberle and Koller 1968).

1924 Rathgen rejects the spraying of acetic acid into "worm holes".

1982 Cymorek and Pospischil determine that the controlling or preventive effect of wood vinegar against *Anobium punctatum* larvae, and egg and large larvae of the house longhorn beetle is completely insufficient even if the wood is impregnated to saturation.

1996 Leiße classifies wood vinegar among the natural products unsuitable for wood preservation.

Present Day

Wood vinegar is not a recognized wood preservative. It is sold occasionally for maintaining and cleaning wood.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: the fungicidal and insecticidal effect of wood vinegar is insufficient. The acid could cause damage to the paint of polychromed art objects and discolorations by impurities such as wood tar are possible.

7.3.19.2

Essential Oils

Production: By steam distillation or extraction of comminuted plant parts

Composition: Complex mixtures of partially very volatile alcohols, aldehydes, ketones, esters, lactones, compounds containing sulfur or nitrogen, and hydrocarbons

Kinds: Camphor oil, cashew nut-shell oil, citrus oils, hiba oil (from *Thujaopsis dolabrata*), hop oil, garlic oil, lavender oil (from *Lavandula angustifolia* or *L. officinalis*), nard oil (e.g., from *Valeriana celtica*), neem-oil (from *Azadirachta indica*), clove oil, olive oil, spike oil (from *Lavandula latifolia* or *L. spica*), thuja oil (e.g., from *Thuja occidentalis*), thyme oil, tung oil (e.g., from *Aleuritis fortii* or *A. cordata*), cedar oil, and cinnamon oil

Properties:	Each oil has its characteristic odor; solubility in water is low, the oils are soluble in alcohol, petroleum ether, benzene, and partially in chloroform and glycerol
Toxicology:	In higher concentrations the oils can irritate skin and mucous membranes. The thujaplicines which are found in the heartwood of western red cedar (<i>Thuja plicata</i>) and in thuja oil are poisonous, causing nerve paralysis and cramps
Biological effects:	The oils act as insect repellents and have fungistatic effects
Application:	Usually in concentrated form or in organic solvents
Analysis:	By HPLC after extraction from wood, or by GC

Use with Dry Wood

Historical

- ? B.C. In China wood is impregnated with tung oil (Clausnitzer 1990).
 ca. 2900–600 B.C. Plinius reports that beams in an Egyptian labyrinth had been coated with oil (Clausnitzer 1990).
 ca. sixth century B.C. According to Plinius, the wooden statue of Diana in Ephesos had been soaked in pleasantly scented and presumably insect repellent nard oil (Schultze-Dewitz 1969).
 555–538 B.C. In Babylon oil is poured over building timber (Clausnitzer 1990).
 356–323 B.C. Alexander the Great has bridge timbers treated with olive oil (Broese van Groenou et al. 1952).
 Fourth century B.C.–fifth century A.D. The Romans adopted treating structural wood with oil (Broese van Groenou et al. 1952).
 1693 Beurs reports that the backs of panel paintings were coated repeatedly with “spikenard oil” to prevent an attack by wood borers (Clausnitzer 1990).
 1781 Krünitz reports that wood can be preserved by treatment with various oils such as lavender, juniper, turpentine, linseed and nut oil (Clausnitzer 1990).
 1802 Impregnation of wood with hop oil (Schiessl 1984).
 1909 Thyme oil is used to disinfect glue used for consolidation (Schiessl 1984).
 1995 Investigations on the use of essential oils against blue-stain fungi (Kunz et al.).

Present Day

At present there are no officially recognized wood preservatives based on essential oils. However, biocides contained in certain oils such as hiba, neem,

and thuja oil could possibly be used in the future for the formulation of wood preservatives. Some essential oils, e.g., cedar oil, serve as a moth repellent.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: hiba oil, neem oil, and thuja oil which contains the effective fungicide thujaplicine, have definite preventive properties against fungi and insects. The oils have a strong odor, are very volatile, are not very leach-resistant, and lack long-term effectiveness. The content of biocide varies, and their aging characteristics have not been elucidated. When applied directly to works of art and other cultural property there is danger of the object becoming oily and discolored.

7.3.19.3

Woad (*Isatis tinctoria*)

Distribution:	Europe, e.g., Germany, France, Turkey; Western Asia, and North Africa
Description:	Plant with yellow flowers, 50 to 120 cm tall
Constituents:	Isatan B (indigo precursor), tryptanthrin, indolyl-3-acetonitril, 4-coumaric acid methyl ester
Toxicology:	The constituents have not been investigated in detail
Biological effects:	The constituents tryptanthrin and indolyl-3-acetonitril exhibit preventive effects against the larvae of <i>Hylotrupes bajulus</i> . Tryptanthrin also inhibits feeding of termites and retards growth of <i>Coniophora puteana</i>
Application:	Woad is used in the form of aqueous extracts
Analysis:	By TLC, HPLC, and nuclear magnetic resonance (NMR) spectra after extraction and isolation of components from treated wood

Use with Dry Wood

Historical

Woad extracts have been used in antiquity and the Middle Ages to dye textiles and in painting.

1986/1988 Patent applications filed for the use of woad extracts as wood preservatives (Feige).

1994 Seifert and Unger investigate the biological effectiveness of woad constituents.

Present Day

Woad preparations are not among the officially recognized wood preservatives, but in Germany they are sold as wood preservative coatings.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

Woad extracts do not offer reliable protection because of variation in the content of effective biocides and insufficient shelf life. They can also discolor wood. Woad extracts can therefore not be recommended for cultural property.

7.3.19.4 Chitosan

Occurrence:	Found as chitin in insects, crustaceans, molluscs, and in the cell walls of algae and fungi
Production:	The insoluble chitin is treated with alkali to obtain the deacetylated and partially depolymerized chitosan
Properties:	A substance which can be crystallized, and which can form gels and films; soluble in aqueous methanol and glycerol, and in dilute acids except sulfuric acid
Toxicology:	Chitosan is used in wound-healing
Biological effects:	Chitosan is a fungicide which effects a clear reduction of wood breakdown by <i>Coniophora puteana</i> and <i>Gloeophyllum trabeum</i>
Application:	No information, as it is still under development
Analysis:	Generally by X-ray structure analysis

Use with Dry Wood

Historical

1996 Experiments in Japan on the use of chitosan in wood preservation as an alternative to synthetic chemicals. Its fungicidal effectiveness is tested with *Coniophora puteana*, *Gloeophyllum trabeum*, and *Tyromyces (Oligoporus) placenta* (Schmidt et al.).

Present Day

Investigations on the suitability of chitosan for wood preservation are still in the research and development stage.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: chitosan is not effective against *Tyromyces (Oligoporus) placenta*. Further testing is necessary.

7.3.19.5

Neem Tree (*Azadirachta indica*)

Occurrence:	Native to India and Myanmar (Burma); it is being cultivated in Africa, Australia, and Central and South America
Description:	Evergreen tree of medium height (12–15 m) with white flowers and yellow to pale reddish stone fruit usually with a single seed
Constituents:	Azadirachtins, limonoids and disulfides. Azadirachtin is a highly oxidized triterpene in the form of crystalline powder, m.p. 155–158 °C. The substance is obtained by extraction from the pits of the cherry-like fruit
Toxicology:	Neem extracts are not harmful to humans, warm-blooded animals or the environment
Biological effects:	Neem extracts are a systemic feeding deterrent for insects, and disrupts growth of larvae
Application:	Used as neem oil or extract
Analysis:	Generally by TLC, HPLC, and GC/MS

Use with Dry Wood

Historical

In antiquity and the Middle Ages neem oil was obtained from the seeds in India and used to make soap, personal hygiene products, and medicine. The insect repellent effect was also known, using neem wood for textile chests.

1980 First of the so-called Neem Conferences on the use of natural pesticides (Schmutterer et al. 1981).

1986 The structure of azadirachtine was completely clarified (Broughton et al.).

1996 Leiß describes tests of the preventive effect of neem extracts against egg larvae of *Hylotrupes bajulus*.

Present Day

There are no officially recognized wood preservatives based on biocides in neem extracts. In India leaves of the neem tree are placed in books and manuscripts to protect them from cockroaches and silverfish.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: neem oil is more effective against insects than the pure azadirachtin. Products obtained from neem trees are harmless to humans and the environment. Work is in progress to investigate the suitability and practicality of neem-tree isolates as biological wood preservatives.

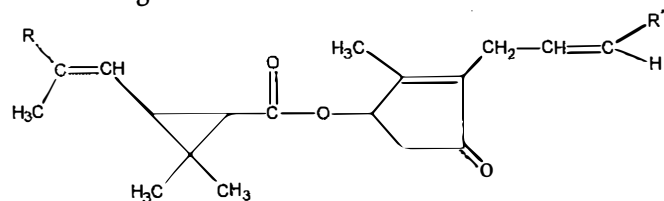
7.3.19.6

Pyrethrum

Occurrence: Dalmatian pyrethrum, *Chrysanthemum cinerariifolium*, is cultivated, especially in Kenya and Tanzania

Constituents: Pyrethrins: cinerin I and II, jasmolin I and II, and pyrethrin I and II. Pyrethrum is obtained by pulverizing the dried flowers or by extraction. The biocide content of the flowers varies from 0.3 to 2%

Formula: Scheme of general structure



	R	R'
Pyrethrin I	-CH ₃	-CH=CH ₂
Jasmolin I	-CH ₃	-CH ₂ -CH ₃
Cinerin I	-CH ₃	-CH ₃
Pyrethrin II	-COOCH ₃	-CH=CH ₂
Jasmolin II	-COOCH ₃	-CH ₂ -CH ₃
Cinerin II	-COOCH ₃	-CH ₃

Properties: Pyrethrum is a viscous oil with about 25% biocide in its concentrated form; the raw extract is dark brown; m.p. of

pyrethrin I is 170°C and of pyrethrin II is 200°C, both at 13 Pa (with decomposition); vapor pressure is very low; pyrethrum is insoluble in water, readily soluble in alcohols, chlorinated hydrocarbons, and petroleum ether. Stability is not good because it is easily oxidized, and its activity is rapidly lost on exposure to light, air, and alkali. Synergic substances such as piperonyl butoxide serve as stabilizers and increase effectiveness.

Toxicology: Irritation of skin, eyes and mucous membranes. Inhaling of dust or spray fog can lead to headaches, nausea, and later to tremors and loss of coordination. Pyrethrum triggers allergic dermatitis. Toxicity to warm-blooded animals is low. Pyrethrum degrades rapidly in nature and in organisms. It is harmful to bees and highly poisonous to fish

Biological effects: Insecticides which act as contact poisons; pyrethrin I is especially effective. The substances rapidly enter the nervous system, causing hyperactivity, loss of coordination, paralysis, and death. The initial effect is rapid (knock-down effect), but in the case of pure pyrethrum formulations the insects can sometimes recover. For this reason pyrethrum is used in combination with other active ingredients

Application: Pyrethrum is hardly used for wood preservation because of its lack of long-term effectiveness. It is usually applied as a fog to control insects in stored materials and in showcases

Analysis: Generally by GC/MS

Use with Dry Wood

Historical

1577 Hyronimus Book describes in his book of herbs a powder derived from chrysanthemums "against all manner of vermin" (Roth 1996b).

ca. 1800 The use of pyrethrum as an insecticide is already generally known (Clausnitzer 1990).

1828 The production of pyrethrum begins in Europe (Clausnitzer 1990).

1880/1981 Cultivation of *Chrysanthemum cinerariifolium* in California and Japan. Pyrethrum is used against grasshoppers (Clausnitzer 1990).

1912 Leopold Ruzicka clarifies the structure of pyrethrin (Roth 1996b).

1992 According to Dawson and Strang, direct contact with works of art which contain insecticides with pyrethrins should be avoided.

Present Day

Pyrethrum is hardly used as insecticide in wood preservatives because even moderate long-term effectiveness can be obtained only in combination with piperonyl butoxide. Recent research, however, classifies piperonyl butoxide as toxicologically questionable. Producers of organic paints add pyrethrum to protective varnishes for wood.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

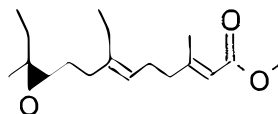
In regard to dry wood: pyrethrum is effective against insects in protecting plants and stored material, and in household uses. However, because of its instability and short-term effectiveness it is hardly suitable for wood preservation. In nature it is degraded rapidly.

7.3.19.7

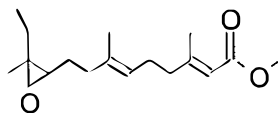
Juvenile Hormones

Occurrence: In insect larvae, butterflies, and certain plants

Formulas: Structure of juvenile hormones (JH)



JH1



JH2

Properties: Properties depend on the specific structure

Toxicology: Because of their specific effects on insects, juvenile hormones are not expected to be particularly harmful to humans or the environment

Biological effects: Juvenile hormones can be used as insecticides specific to certain developmental stages. Their effect extends to the egg stage and to pupation, whereas the development of various larval stages is not affected. The effects are therefore preventive and not applicable to control

Application: Detailed information is not yet available

Analysis: Chromatographic methods, MS

Use with Dry Wood

Historical

1977 Tscholl investigates the effect of juvenoids on *Lyctus brunneus*.

Present Day

Naturally occurring juvenile hormones are not used for the formulation of wood preservatives because of their high cost; synthetic analogs such as fenoxycarb (see under carbamates) are used.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

The, as yet, insufficient long-term stability of the biocides causes problems in the formulation of wood preservatives. Advantages and risks associated with the use of juvenile hormones for cultural property cannot yet be evaluated.

7.3.19.8

α -Ecdysone [(22R)-2 β ,3 β ,14,22,25-Pentahydroxy-5 β -cholest-7-en-6-one]

Occurrence: In insects, crustaceans, worms, but also in certain plants

Formula: α -Ecdysone is a steroid of complex structure

Properties: Colorless crystals; m.p. 242°C; readily soluble in polar solvents but poorly soluble in nonpolar solvents

Toxicology: See under juvenile hormones

Biological effects: α -Ecdysone is an insect growth regulator and causes repeated skin sloughing of *Hylotrupes bajulus* larvae, and especially in male larvae accelerates pupation, which results in deformed male imagoes

Application: Specifics have not yet been determined

Analysis: Chromatographic methods, MS

Use with Dry Wood

Historical

1954 Butenandt and Karlson isolate very small quantities of α -ecdysone from silkworm larvae (Römpf 1995).

1997/1999 Pallaske (1997, 1998, 1999) reports on the status of using ecdysone and ecdysone mimics against wood-destroying insects.

Present Day

The substances are still being investigated as to their effectiveness and suitability for the formulation of wood preservatives against wood-destroying insects.

Use with Waterlogged Wood

No information.

Advantages/Disadvantages

In regard to dry wood: future use of wood preservatives based on α -ecdysone for prevention and control is promising in regard to minimizing harm to humans, works of art, and the environment. The lack of long-term effectiveness which is necessary in wood preservation is problematic.

7.4

Solvents and Additives

As was already pointed out in Section 7.1, wood preservatives can be divided into waterborne and solvent-borne systems. However, there are systems intermediate between these two, for example systems in which the use of emulsifiers and surfactants enables the production of aqueous systems which contain organic solvents. Whereas formerly oil-borne or solvent-borne systems were preferred, the trend is now toward purely aqueous systems or aqueous systems containing smaller proportions of solvents. Solvent-borne wood preservatives can be formulated with polar solvents such as alcohol or with nonpolar solvents such as various fractions of gasoline derived from petroleum distillation. Alcohols and other polar solvents will cause swelling of the wood which nonpolar solvents such as gasoline do not (cf. Chap. 3). Aliphatic and aromatic fractions of gasoline have low viscosity and penetrate wood rapidly and deeply. However, their high volatility can lead to reverse migration by transporting biocides back to the wood surface during evaporation. Thus it is necessary to use cosolvents of higher viscosity, such as glycols and their derivatives, in order to obtain better distribution of biocides and prevent their migration to the wood surface. It must be considered that many solvents are flammable and may represent toxicological problems. Solvents can also either augment or diminish the effectiveness of biocides. If polar solvents must be used, their penetration into wood can be improved by the addition of certain resins and waxes such as those based on palmitic or stearic acids or their esters. These compounds serve as surfactants and facilitate the penetration of polar substances by masking the hydrophilic sites in the wood. Emulsions are formed by taking the biocide which is dispersed in high concentration in an organic solvent, and emulsifying it in water. On the wood surface the emulsion separates into organic solvent and water; the solvent

Table 7.1. Organic solvents for wood preservatives

Group	Examples	Properties
Aliphatic hydrocarbons	Hexane, heptane, white spirit free of aromatics (b.p. up to 140°C), Shellsol T	Poor solvents for most biocides and binders; good solvents for fats, oils, and waxes
Cycloaliphatic hydrocarbons	Cyclohexane and its derivatives, Decalin, Tetralin	Solvents for binders. Some cyclohexane derivatives are also solvents for certain biocides
Aromatic hydrocarbons	White spirit (b.p. 140 to 200°C) such as Sangajol; toluene, xylene	Solvents and diluents for film formers and dyes
Terpenes	Spirits of turpentine, isobornyl acetate	Solubilizers; also improve penetration
Multivalent alcohols such as dioles	Glycols, glycol ether, glycol ester	Improve solvent and penetration properties, solvents for certain binders and consolidants
Heterocyclic compounds	1,3-Dioxolane, tetrahydrofuran	Solvents for biocides and solubilizers
Other compounds	Ethers, ketones, esters	Polar solubilizers

carries the biocide into the wood while the water evaporates. A distinction is made between regular emulsions and microemulsions depending on particle size. Microemulsions penetrate better into wood and the chromatographic effect is less.

Solvent-borne wood preservatives may contain 40–85% solvent, 0.2–5% biocide, 4–40% binders, 0–6% pigments and 4–9% additives. The large variation arises from the intended application, e.g., as undercoating, impregnation for prevention or control, or below-the-surface or film-forming varnish. Table 7.1 lists the most important groups of solvents which are used in the production of wood preservatives. The oily solvents derived from hard coal or petroleum used in the past which often varied in purity and in their properties were at first replaced by solvents with standardized parameters such as white spirit. Later, increased concern about safety and the environment resulted in the discontinuation of many solvents with toxicological damage potential, including among others the glycols, in the formulation of wood preservatives, and replacement with nontoxic compounds. Paralleling this was a trend of reducing the proportion of organic solvent in wood preservatives in favor of water. In the future, an increased use of emulsions can be expected.

The range of binders contained in wood preservatives formerly included mainly natural resins, drying oils and synthetic alkyd resins, but now acrylic resins are also often used. Pigments and dyes in wood preservatives serve as colorants but, in the case of pigments, also impart resistance to UV radiation.

Iron oxides and soot are examples of the pigments used. Coloring of preparations containing solvents and the addition of color to monitor penetration of wood preservatives is done with synthetic organic dyes. Further additives may be siccatives (metal soaps), low viscosity oils, small amounts of monovalent aliphatic and aromatic alcohols, and inorganic thickeners such as montmorillonite (swells in water).

7.5

Treatment Processes

The nature of the treatment process employed determines how much wood preservative is taken up and how deeply it will penetrate into the wood. The processes can be divided into (1) pressureless treatments, (2) pressure treatments, and (3) special treatments. Pressureless treatments can be further divided into surface treatments and immersion treatments. Surface treatments can be carried out by brushing, smoke treatment, fine and coarse spraying, short dipping, and foam application. They will result in surface treatment of little, if any, penetration, or marginal treatment which may extend a few millimeters into the wood but not cover the entire cross section. Immersion treatments include dip treatments of moderate duration and soaking in tanks; these can only effect marginal treatments. Pressure treatments, with and without the use of vacuum in pressure vessels, produce the greatest possible level of treatment, although even they may not lead to complete penetration throughout the cross section, depending on the permeability of the particular wood species and the size of the wood member to be treated. Special processes are diffusion treatments, injection methods, and methods employing bore holes, where particularly threatened areas can effectively be treated in depth.

In cases of historical monuments and museum objects, pest control and remedial treatments are the primary consideration, and therefore pressureless and special treatments which are better suited for these purposes will be discussed in more detail than industrial pressure treatments. Most of the immersion treatments mentioned above are also used for treating wood with consolidants.

7.5.1

Pressureless Treatments

7.5.1.1

Surface Treatments

Brushing

Brush application is the most commonly used method in conservation. Since the amount of preservative taken up per unit of wood surface is low, the concentration of biocide has to be sufficiently high to achieve the desired level of

protection. In most cases two or more applications will be necessary in order to ensure the prescribed amount of treatment. The depth of penetration will be much less than can be achieved by immersion treatments, and for sound wood will be on the order of 1–2 mm. In brush treatments, 10–20% of preservative will be lost. Since the major part of preservative will remain on the surface, even minor scratches into the surface of the sound wood will break the preservative shield against wood-destroying organisms. Old wood with insect damage will take up more preservative via exit holes and the wicking action of the frass within them, and greater depth of penetration can be achieved.

Smoke Treatment, and Fine and Coarse Sprays

These methods differ by the size of preservative droplets, which are $<50\mu\text{m}$ in smoke treatments, $50\text{--}150\mu\text{m}$ in fine sprays, and $>150\mu\text{m}$ in coarse sprays. If an active insect infestation exists in spaces, smoke generators or sprays are often used (Read 1982; Child and Pinniger 1987; Pinniger 1994). Spraying of in situ structural wood members entails high losses of preservative which may reach 20–50%. Spray treatments can also be used for the introduction of consolidants into wood. The treatment of the *Wasa* is an example, where the water contained in her hull was exchanged with PEG. Spray treatments permit faster application compared with brushing, but preservatives of low viscosity are required. The depth of penetration for spraying is as shallow as for brushing; only by way of checks, splits, and insect exit holes can the preservative penetrate somewhat deeper by spraying. A disadvantage of fine sprays is the possible formation of aerosols, and in Germany this method is restricted to specialized applicators. Furthermore, serious damage can be caused by indiscriminate application in valuable historic buildings if, for instance, spray treatments applied in attic spaces leak into rooms below. For this reason, it is best if spray treatments are not used in historic buildings and foam treatments are used instead.

Foam Treatments

As early as 1967 Thele Jr. and Shair were awarded a US patent for the use of foams with fungicides in cooling towers. Foam treatments were of major importance in the former German Democratic Republic for the control of fungi in old buildings and for the preservation of mine timbers (Petermann 1976; Langendorf 1988; Rafalski and Biering 1990). After reunification, German manufacturers of wood preservatives produced commercial preparations suitable for foaming and the necessary equipment to apply foams to treat building timbers and masonry infested by fungi in situ. If the components in the wood preservative do not have sufficient surfactant properties, 2–3% of a surfactant must be added, but this must not react with the biocides. The foams have sufficient adhesion so that even vertical surfaces and the undersides of overhangs can be readily treated. The method is also suitable for remedial treatments of difficult-to-access timber connections and hollow

spaces in ceiling constructions. The thickness of the foam layer is determined by preservative to foam ratio and should be about 2–3 cm. In order to bring the required amount of preservative into the wood, a concentration of 8–13% is necessary. Losses by drip-off during foam application should not be greater than 10%.

Short Dip Treatments

Short dip treatments are a transition form between surface and immersion treatments. Wood will be in contact with preservative for a matter of seconds or at most a few minutes, so that both the amount taken up and the depth of penetration will be small. In order to obtain an acceptable level of treatment, the concentration must be high enough to ensure the necessary effectiveness. Old wood which has already been damaged by biological organisms will tend to take up more preservative and transport it more deeply into the wood, depending on the level of degradation.

7.5.1.2

Immersion Treatments

Extended Dip Treatments

During extended dip treatments the wood is immersed for one to several hours. Compared with surface treatments, extended dip treatments result in only minor improvements in uptake and penetration, and usually only marginal treatment is obtained. Preservatives which may be used with this method are non-fixing aqueous and fixing oil-borne systems. For the aqueous systems, the wood moisture content must be below 30%, and the concentration is about 10–20%. Solvent-borne preservatives are usually used undiluted, and here the wood moisture content should be below 20%. Extended dipping of old wood with insect damage can at times take up large amounts of preservative accompanied by significant mass gain. There may be danger of breakage of frail objects when they are taken out of the bath. For polychromed objects, the extended dip and the tank soaking treatment to be discussed below are hardly suitable because of the danger of damage to paint or gilding.

Soaking Treatments

In this method wood is placed into open tanks and kept completely immersed in wood preservative from one to several days. It is used mainly for treating freshly sawn construction timber. Aqueous solutions of fixing preservatives are used, with a solution concentration of usually 5–10%. This method can also be used for wood with a moisture content between 30 and 50%. The tanks are open, have double walls, and are usually made of steel. Also required are vessels for preparing solutions and for storage, a soaking basket, a device to

prevent the wood from floating, stirring devices, and possibly heating equipment and a balance to determine the uptake. Following treatment, the wood must pass over equipment where excess preservative can drip off, and must then be stacked for drying by separating the pieces with strips of wood to allow for air circulation. Penetration is greater than can be obtained by surface or dip treatments, but more than marginal treatment is not possible.

A special variation of the soaking treatment is the hot-and-cold open tank process, where the dried or partially dry wood is first placed into a tank of preservative at ambient temperature. The temperature is then raised to 85–95 °C for heavy oil-based preservatives, or to about 55 °C for waterborne preservatives. The tank is then allowed to cool, which creates a vacuum inside the wood and draws preservative into it. Soaking times can be reduced from days to hours by this method, while improving penetration. Another variation is partial immersion; this method is still used sometimes to treat one end of stakes for use in gardening, fruit-growing and viticulture. In the past this was also used to treat furniture containing insect pests, by placing the legs into containers filled with preservative.

7.5.2

Pressure Treatments

Pressure processes utilize pressure differentials to introduce preservative into wood. Pressure treatment methods are considered the only reliable methods for the industrial treatment of wood, and generally will result in complete treatment of the sapwood. Because of their industrial nature, these methods are of little importance for remedial treatments of structural timber in old buildings. Pressure treatment methods can be divided into full-cell treatments, conventional or modified empty-cell treatments, sap-displacement methods and the double-vacuum process. Woods which are difficult to treat may be incised to improve penetration, the incisions being made by knives, needles, or laser beams.

7.5.2.1

Full-Cell Treatments

In this method vacuum is drawn before the preservative is introduced into the pressure vessel, and high pressure is then used to force the liquid into the wood. This method was proposed by the Frenchman Bréant in 1831 for treatment with salt solutions, and by the Briton Bethell in 1838 for creosote impregnation. Today, it is used mainly for aqueous salt solutions or emulsions in the treatment of wood for exterior exposure, with or without soil contact, whereby the wood should be below 30% moisture content at the time of treatment.

7.5.2.2

Conventional and Modified Empty-Cell Treatments

Species such as Douglas-fir or spruce, which are difficult to treat, can be preserved by means of the Rüping and Lowry processes and their modifications. Coniferous woods, which may be green, are given many short cycles of vacuum followed by pressure, in the course of which the water in the wood is exchanged for aqueous preservative solution. This process originates from the sap displacement process introduced by Boucherie in 1838. Inevitably, the solution concentration will diminish during the course of the treatment.

7.5.2.3

Double Vacuum Impregnation

This method is used mainly for treating planed or precision-sawn building parts which are at least partially dried, such as siding, balcony balustrades, soffit, and window and door parts with solvent-borne preservatives but also emulsion concentrates which can be diluted with water. This process achieves deeper penetration compared with dip treatments, and can reduce preservative consumption while ensuring the required protection.

7.5.2.4

Special Pressure Treatments

Special methods include pressure injection with hollow needles or hollow drills, and pressure infusion using hollow needles and carbon dioxide gas. In the future, pressure impregnation of lumber with biocides using supercritical fluids (SCF process; Morrell et al. 1997) and vapor phase impregnation with boric acid esters (Vinden et al. 1991) may well come to the foreground.

7.5.3

Special Methods

7.5.3.1

Diffusion Methods (Bandage Methods)

Diffusion methods such as the paste method (Osmose process) are hardly of interest in conservation work. The paste method was used formerly to treat freshly debarked, green logs of species such as spruce and true fir for transmission poles. However, paste methods might possibly gain some importance for the decontamination of cultural property which had earlier been treated with environmentally damaging biocides (cf. Sect. 7.7). Similarly, the bandage method developed for transmission poles in service could find use for the decontamination of wood containing dangerous biocides.

7.5.3.2

Injection and Infusion Methods

These procedures are mainly used in museums to control active insect infestations, and to introduce preventive biocides and consolidants into portions damaged by decay or insects, of sculptures, picture frames, panel paintings, furniture and other objects. Treatment liquids are introduced by means of disposable syringes, spray cans with plastic snouts, or special injection devices into the damaged wood through insect exit holes or cracks caused by decay. If necessary, additional holes may be bored into the wood, especially if consolidants with relatively high viscosity are to be impregnated. Injection methods are labor intensive and time consuming, and often only partial preservative treatment or consolidation can be obtained.

Infusion treatment requires a supply bottle, with stand (Fig. 7.2), for the preservative or consolidant, a ventilation hose, a rubber stopper with glass tube leading to the supply bottle, a distribution hose with drip sphere and hose clamp, and the injection device. The latter consists of a control valve and a hollow needle fitted with a mandrel to prevent clogging of the needle during insertion. Once the needle has been inserted into the object to be treated, the mandrel is withdrawn and the needle connected to the apparatus. The supply bottle is kept elevated above the object, and the drip rate is controlled gradually with the hose clamp according to the uptake capacity of the wood. An excessive drip rate can be recognized if the needle at the point of insertion is surrounded by a wad of cotton with some solvent. Infusion treatments ensure a continuous, largely automatic impregnation by which high loading and deep penetration can be obtained (Aberle and Koller 1989). However, periodic checks are necessary to prevent leakage from the object. If needed, several infusion systems can be attached simultaneously to the same object. Wooden objects with paint or gilding which might be endangered by dip or soaking treatments can be treated by infusion largely without undesirable changes.

7.5.3.3

Impregnation Via Bore Holes

This method is used mainly for controlling insects in structural timbers such as beam ends and to control house fungus in masonry. Normally wood is removed 1–1.5 m beyond the decayed zone and the remaining sound wood is treated in areas susceptible to renewed attack by bore hole impregnation. When treating historic buildings, it is often demanded that as much as possible of the original material should be preserved. For this reason even members with decay may be retained in the structure and must then be treated accordingly. Bore hole impregnation can establish barriers which prevent the spread of the decay to sound wood. Generally, bore holes 10–15 mm in diameter are made to a depth of up to two thirds of the beam thickness, at a spacing of 20 cm and in rows staggered by about 10 cm

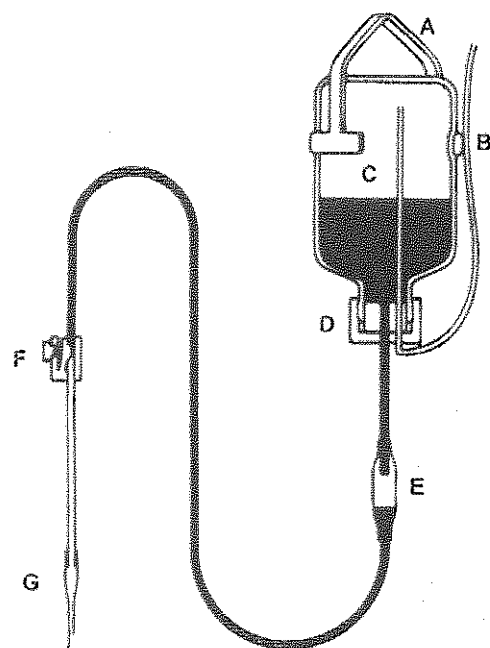


Fig. 7.2. Infusion apparatus. A stand, B ventilation hose, C supply bottle, D rubber stopper with glass tube, E drip sphere, F hose clamp, G injection device. (After Aberle and Koller 1989)

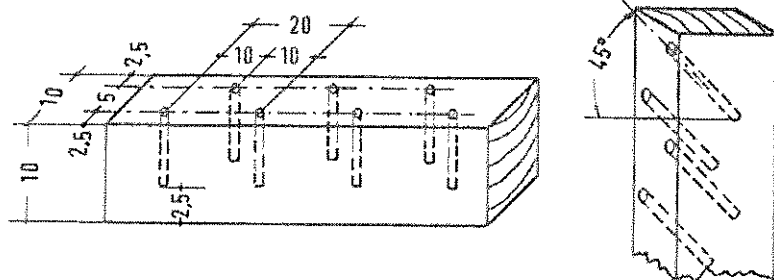


Fig. 7.3. Schematic for impregnation via bore holes. (After Grosser et al. 1991)

(Grosser et al. 1991). Columns have bore holes inserted at 45° with the same spacing (Fig. 7.3). When inserting bore holes, checks and splits must be avoided, and structural engineering requirements must be considered. The bore holes are filled two to five times with preservative in order to get as much penetration as possible. Instead of liquids, cartridges of pressed, salt-like preservative such as boron salts can be inserted into the bore holes which are then closed with treated hardwood dowels.

Masonry infested with decay fungi is first cleaned with steel brushes or brooms, loose mortar is scraped out, and remains of mycelium is burned off

before applying a systematic bore hole impregnation, which should be administered from both sides if the walls are thick.

7.6

Damage by Wood Preservatives

Undesirable changes in cultural property by wood preservatives can be caused by their composition as well as by improper application. Biocides (Dawson 1986), solvents, binders, pigments and dyes in the preservative can all have an effect on objects. Biocides may decompose due to wrong or excessive storage and cause damage to objects. It is possible that biocides, on or inside an object, may be altered chemically by changes in pH, by variations in moisture content in the air or in the wood, by UV radiation or by metal ions in paints or metallic coatings, and then react with components of the object leading to corrosion. For instance, many organic halogen compounds which are used as biocides are not stable against alkali. Furthermore, soluble fluorides, hydrogen fluorides and fluorosilicates can react with the chalk in ground layers, corrode metal coatings such as gilding, and in the case of treated wood windows etch the glass. Certain carbamates will form green or blue reaction products with metal attachments containing copper. Fire retardant salts used in roof timbers can cause the wood to be macerated. There are known cases where the control of house fungi in masonry with borates has diminished plaster adhesion.

If biocides are imperfectly, or not at all, fixed inside the wood, the inorganic or organic biocide may in some cases be displaced successively by water due to variations in relative humidity and wood moisture content, causing the biocide to migrate to the surface. There it may become attached to surface dust, or it may evaporate and pollute the room air. Solvents of low volatility which may remain inside the wood years after treatment can also influence the migration of biocide to the surface. Typical examples are blooms of DDT on the surface of art objects which are caused by excessive application of oily wood preservatives (Fig. 7.4) or by "insect powders" on ethnographic objects (Glastrup 1987). Aqueous or hydrophilic solvents accentuate wood shrinkage and swelling (cf. Chap. 3), which can lead to detachment of surface coatings or paints. If the solvents are acidic, they may react with chalk in ground layers or other mixtures, and color changes may be caused in pigments such as synthetic ultramarine blue. Mixtures of organic solvents can cause swelling of paint binders containing oils or resins, and can effect color changes of natural wood surfaces and paints. Some solvents produce rainbow gleam on metal attachments. Objects treated with oil-borne wood preservatives often develop electrostatic charges and attract dust, the formerly frequently used kerosene being an especially telling example. If half-timbered buildings are treated with oil-borne preservatives, contacting plaster may be discolored by sweating of solvent. When using solvent-borne wood preservatives for cultural property, it is therefore especially important to request detailed information on solvent



Fig.7.4. Sculpture with DDT bloom. (Photograph courtesy of V. Ehlich)

composition from the manufacturer. With respect to potential damaging effects, it would seem to be preferable to use pure solvents for biocides rather than solvent mixtures. Nonpolar organic solvents with low swelling capacity such as aliphatic white spirit free of aromatic components are to be preferred to other solvents. Damage caused by auxiliary components in wood preservatives, among them binders and pigments, manifest themselves in color and texture changes and the formation of undesirably shiny surfaces. Texture changes can go as far as a reversal of the figure in wood.

Much of the damage caused by wood preservatives originates from errors and omissions in application technique. When wood preservatives are sprayed or fogged in interior spaces, uncontrolled overspray or excess can leak into other rooms, especially those below, which do not require treatment and are thereby damaged. Excessive application of oil-borne or solvent-borne wood preservatives can also lead to migration into adjacent areas such as frescoes, with damaging effects.

7.7

Decontamination and Masking of Wood Which Contains Preservatives

7.7.1

Nature of the Problem

Many of the chlorinated hydrocarbons which were used extensively between 1950 and 1980, not only in interior spaces for control of pests or as a preventive treatment in structural members and architectural trim, but also for movable works of art and other cultural property, are now polluting the room air and are a latent danger to people and the environment. Many objects of great art historical significance are now in a condition brought on by excessive use of oil-borne wood preservatives containing PCP, lindane, or DDT that no longer permits their presentation in exhibits. In order to safeguard the original substance, conservators must therefore first solve the problem of removing old wood preservatives and also consolidants. Such decontamination is in many cases not only necessary to avoid health problems but also unavoidable to ensure the long-term stability of subsequent conservation treatments. Residual amounts of solvents of low volatility in objects often prevent new attempts at stabilization. The vapor pressure of biocides (cf. properties in Sect. 7.3) plays an essential role in the extent to which they endanger the object and the environment. PCP and lindane are gradually transferred to dust and the room air because of their high vapor pressure, without causing significant superficial changes of the treated objects. However, DDT which was extensively used in wood preservatives for control measures in the countries of the former East Block is often found as visible surface deposits on objects because the saturation concentration had been exceeded. PCP has a strong tendency to attach itself to dust particles and can effect a secondary contamination of untreated objects.

Undoubtedly the safest method of removal of harmful biocides would be the removal and destruction of the treated objects, but this is not an option for cultural property. Therefore, it is necessary to look for ways to free as much original substance of harmful poisons without further detrimental changes or at least to minimize the harmful effects. The methods for decontaminating treated wood or for masking biocides in wood are discussed below. These are no more than starting points for solving some of the problems found in the practice of pest control and conservation.

7.7.2

Mechanical Procedures

The decontamination of structural wood members containing dangerous biocides in the conservation of historical monuments customarily begins with

various cleaning methods to remove dust and dirt-holding biocides, biocide bloom, old frass and detached wood particles. Particular care must be exercised with painted objects so that loose portions of paint do not separate and get lost. One can distinguish between dry and damp processes; the latter which may use water or solvents will be discussed in Section 7.7.4. Unfinished structural members can be superficially decontaminated with special vacuum cleaners using a variety of brushes. Valuable art objects can have the surface dust and biocide bloom removed dry with soft brushes and simultaneous suction. Strongly adhering dirt with biocide content or biocide crystallized on the surface may, depending on the nature of the object, be removed using ultrasonic scalpels or chisels, or with the aid of laser beams, but these methods are very time consuming and can only be justified for small areas. In clean rooms of the microelectronic industry, sticky foil is used for the elimination of particles. Such foils could also be used for cleaning and surface decontamination of small areas of unfinished objects. Structural members which contain dangerous biocides could possibly be decontaminated by planing or routing off surface material, provided that they have sufficient excess load bearing capacity and the treatment is confined to the surface layers.

7.7.3

Thermal Processes

In interior spaces, PCP and lindane contained in wood can be mobilized and driven off from the surface layers by the introduction of heated and humidified air (von Rotberg et al. 1997). Treatment is carried out at largely constant relative humidity and an entering air temperature of 70°C. The core of the building is held at 60°C, and closed system circulation is monitored and regulated by computer for a period of 3 weeks. Liberated pollutants are oxidized in a parallel air stream. This treatment leads to a marked reduction in room air pollution. Reportedly, structural wood members of historically important monuments will not be damaged by the temperature elevation. This procedure is of questionable efficiency for DDT because of its low vapor pressure.

Contaminated flooring can be heated by means of high frequency electromagnetic fields, which raises the vapor pressure of pollutants so that they can be suctioned off in larger quantities. In principle, this same method could be used for structural members as well, but this would require large investment in equipment and would have to be done with great caution, as hidden metal parts can cause problems. It is also only possible to treat relatively small areas at a time. The method appears to be particularly suited for contaminated built-in structural members because the heating and therefore also the liberation of the biocides proceeds from the inside out.

In contrast to heating procedures which rely on raising the vapor pressure of biocides for their removal, low temperature treatments can only be used

for surface cleaning. In Germany, two cleaning methods have been used for the removal of wax coatings, dirt accumulations, varnish and adhesives, namely impingement with carbon dioxide pellets, the Cryo Brush method, and compression with cold pads cooled with liquid nitrogen, the Cryo Pad method (Besch 1997). Both methods could be used in principle for the removal of biocide blooms, but with the impingement method simultaneous vacuuming of biocide crystals or dust would be necessary. The impingement method requires a pellet gun which shoots a stream of dry ice particles about 1.5mm in diameter at a temperature of -78°C onto the surface to be cleaned. The carbon dioxide pellets have about the same hardness as plaster of Paris. When they hit the surface of the object, they will instantly sublime, accompanied by an increase in volume. The Cryo Pad method uses compresses cooled with liquid nitrogen as low as -196°C which are placed on the object. Both methods rely on differences in the coefficients of thermal expansion of the respective materials. Icing the surface causes embrittlement of the material, and undesirable biocide deposits, wax coatings, and adhesive residues can, in certain cases, be removed more easily.

7.7.4

Solvent-Based Methods

The simplest method of damp cleaning consists of wiping contaminated surfaces with rags or sponges soaked in water, possibly with the addition of a surfactant, or in solvents. Special cloth which has a very large surface and can take up large quantities of biocide and bind it by adsorption is available, but the problem of environmentally safe disposal or washing for reuse is a disadvantage. Valuable single objects can be cleaned with cotton or pulp swabs or pulp compresses using water or solvents. Unpainted structural elements of historic buildings can be cleaned by spraying cold, aqueous cleaning fluids and subsequent vacuum suction of the dirty water, but this method is hardly suitable for painted objects, especially if the paints might be water soluble. The potential swelling effect of the water and the pressure with which the water spray impinges the surface can be very dangerous to paints and other coatings.

Cultural property with or without paints and coatings can, in principle, also be treated with pastes, provided that their constituent solvents do not attack the coatings or the wood (e.g., by swelling) and that the adsorbents can be removed readily. The pastes can be prepared with inorganic or organic agents such as powdered sepiolite, pyrogenic silicic acid and special natural cellulose fibers (trade name Arbocel).

The procedures discussed so far are suitable only for decontaminating the surface or surface layers to varying extents. Biocides which have penetrated much more deeply into wood with fungal or insect damage will be hardly affected. However, it cannot be ruled out that the solvents used to remove dan-

gerous chemicals mobilize biocides located more deeply in the interior and thereby trigger a migration to the surface, where it might lead to clouding or crystallization. In order to remove an old wood preservative almost completely, the entire object must be subjected to some form of extraction. This is only possible for movable cultural property. The simplest form would be immersing the object in a tank with solvent, at or slightly above room temperature, where the solvent should be circulating and be renewed periodically. Another possibility is to apply the Soxhlet or infusion principle by dripping fresh solvent on the top of an object, such as a sculpture, and continuously removing the solvent containing the biocide at the bottom. Although biocides could be removed in this manner, the procedure is probably only applicable to unpainted objects with relatively little damage by decay or insects. With painted objects the great danger of swelling or even dissolution of binders is always present. The redistillation and purification of the contaminated solvent is also very costly.

A much more elegant solution of the contamination problem for movable objects can be found with supercritical fluids (Levien et al. 1994). Carbon dioxide, which in supercritical form is liquid and acts as a solvent, is particularly well-suited for this. If this method, as already alluded to in Section 7.5.2.4, can distribute biocides over the entire cross-section of wood, it should also be possible to use it to remove biocides from wood provided that they are not fixed to the wood substance. Results to date show that 75% of DDT and 90% of lindane can be removed again from structural wood members painted on one side only (Unger 1998). Tempera paint layers merely become lighter due to a cleaning effect after carbon dioxide treatment, but resins in softwoods can be dissolved and mobilized. Although many details for solid wood must still be clarified (Hartung 1999; Kim and Morrell 2000), this treatment appears to be promising and effective, because the biocides can be accumulated in a separator and the carbon dioxide returned to circulation.

7.7.5

Microbial Methods

It is known that old wood containing tar oil or PCP, after suitable processing, can be detoxified by metabolizing with enzymes derived from fungi, or with bacteria. Preliminary experiments have shown that certain white-rot fungi are able to markedly reduce the DDT or lindane content of wood. However, enzymes in aqueous solution are effective only on the surface or at most to a depth of 1–2 mm. Whether enzymes or bacteria can be used for decontamination of cultural property in the future has to wait for clarification of a multitude of problems, such as shelf life, effectiveness, and application of the preparations as well as their compatibility with wood and paint.

7.7.6

Masking Methods

A marked reduction of the emission of biocides into room air can be obtained by covering contaminated structural wood members with largely impermeable metal foil such as aluminum foil or with multiple layers of plastic films. Plaster board (sheet rock) covered with aluminum foil can also effect a reduction in room air pollution. With treatments of that type, all joints have to be carefully taped and made tight. Care must also be taken that no accumulation of moisture can take place behind the barrier to prevent the development and spread of wood-destroying fungi.

Brushing or coating the contaminated wood with special sealers and varnishes offers only temporary protection from biocide emission. None of the commercial varnishes is sufficiently elastic over the long run to tolerate dimensional movements of wood without cracking. The rate of emission will be much reduced, but still takes place by way of hairline cracks in the coating. Practically the same end results occur whether the varnish is based on natural products such as shellac or larch resin for the film former and alcohol from fermentation, or whether they are water-based, solvent-containing resin solutions with a combination of acrylic and natural resins. The sealers and also the varnishes are often formulated basic, in order to effect at least a partial transformation of substances such as PCP, DDT, and lindane (e.g., PCP to Na-PCP) which have low stability in alkaline media. The effectiveness of sealers and varnishes as diffusion barriers extends over a period of 2 to a maximum of 5 years, at the end of which the surface must be coated and sealed again.

References

- Aberle B, Koller M (1968) Konservierung von Holzskulpturen. Probleme und Methoden. Institut für Österreichische Kunstforschung des Bundesdenkmalamtes Wien, 43 pp (AATA 8-761).
- Aberle B, Koller M (1989) Restauratorische Holzfestigung und die Infusionstränkung. Restauratorenblätter 10:73–78
- Adams AJ, Jermannaud A, Serment M-M (1995) Silafluofen: novel chemistry and versatility for termite control. IRG/WP/95-300069
- Alagna P (1977) The construction of the treatment tanks used in the conservation of the wood of the Marsala Punic Ship. Stud Conserv 22(3):158–160 (AATA 15-393)
- American Wood-Preservers' Association, AWP Standards, Woodstock 1999
- Ankner D (1972) Zur Konservierung vorgeschichtlicher Feuchtholzfunde. Arbeitsbl Restaur 5(1) Gruppe 8:58–67 (AATA 9-621)
- Anonymous (1935) Zeittafel zur Holzkonservierung. Holzmarkt 52:102
- Anonymous (1990) Preventol A8. Produkt-Information der Firma Bayer-Materialschut
- Anonymous (n.d.) Silafluofen. Technical information, 2nd edn. Hoechst Schering AgrEvo GmbH, Frankfurt/M., Germany
- Arai H, Kenjo T, Nakasato T, Miura S, Mori H, Emoto Y, Ito N (1991) Studies on the conservation of Shinto and Buddhist buildings in Nikko designated as National Treasure and Important Culture Property. Sci Conserv (Hozon Kagaku) 30:65–128 (AATA 29-1774)
- Baer NS, Ellis MH (1988) Conservation notes on thymol fumigation. Int J Museum Management Curatorship 7(2):185–188 (AATA 30-78)

- Baker JM, Berry RW (1980) Synthetic pyrethroid insecticides as replacements for chlorinated hydrocarbons for the control of wood-boring insects. *Holz Roh Werkst* 38:121–127
- Barkman L (1965) The preservation of the Wasa. Wasastudier Statens Sjöhistoriska Museum, Stockholm (5), 19 pp
- Barkman L (1969) Konservierung von Holz des Kriegsschiffes "Wasa". *Dtsch Kunst Denkmalpflege* 27:138–146
- Barth V, Härtner H (1993) A new type of biocide suitable for use in different fields of wood preservation. Paper presented for the 24th annual IRG-meeting, Orlando, USA, 16–20 May 1993
- Baynes-Cope AD (1975) Fungicides and the preservation of waterlogged wood. *Mar Monogr Rep Natl Maritime Mus Greenwich* 16:31–33
- Becker H (1983) Neuere Fungizide und Insektizide für lösemittelhaltige Holzschutzmittel. *Seifen Öle Fette Wachse* 109(2):49–52
- Becker H (1985) Synthetische Pyrethroide – eine neue Gruppe von Holzschutz-Insektiziden. *Seifen Öle Fette Wachse* 111(19):617–619, 111(20):649–652
- Becker H (1987/1988) Organozinnverbindungen als Holzschutzfungizide. *Seifen Öle Fette Wachse* 113(20):773–776, 114(1):27–30, 114(2):61–63, 114(3):99–100
- Becker H (1989a) Entwicklung auf dem Gebiet neuer Holzschutz-Fungizide. *Seife Öle Fette Wachse* 115:469–475
- Becker H (1989b) Alkylammoniumverbindungen als Holzschutzmittel. *Seifen Öle Fette Wachse* 115(18):681–684
- Berry RW (1976) The toxicity of the synthetic pyrethroid NRDC 143 to some wood-boring insects. *Int Biodeter Bull* 12(2):42–43
- Besch U (1997) Workshop "Einsatz von Kältereinigungstechniken in der Restaurierung" am 8. April 1997 in der Residenz München. Informationsbericht. *Restauro* 103(4):285–286
- Birkholz D Jr (1989) Steamship Wapama finds a cure: remedial treatment of dry rot in a large wooden structure. *CRM Bull* 12(4):18–19 (AATA 27-1942)
- Borgin K (1978) Appendix 2: progress on evaluating the Thessaloniki process in Mombassa wreck excavation. Second preliminary report by Rubin C.M. Piercy. *Int J Naut Archaeol Underwater Explor* 7(4):314–317 (AATA 16-1343)
- Borkovský I (1941) Poznámky ke konservování dřeva na pražském hradě (Notes to the wood conservation on the Prague castle). *Zprávy památkové péče* 5(2):17–20
- Boustead W (1966) Conservation of Australian aboriginal bark paintings with a note on the restoration of a New Ireland wood carving. *Stud Conserv* 11(4):197–204 (AATA 6-C3-52)
- Brachert T (1972) Die Solothurner Madonna von Hans Holbein aus dem Jahr 1522. *Maltechnik Restauro*, p 6
- Broese van Groenou H, Risden HWL, van den Berge J (1952) Wood preservation during the last 50 years, 2nd edn. *Sijthoff's Uitgevers – Maatschappij*, Leiden
- Brokerhof A (1989) Control of fungi and insects in objects and collections of cultural value "a state of the art". Central Research Laboratory for Objects of Art and Science, Amsterdam, 77 pp
- Brorson Christensen B (1970) The conservation of waterlogged wood in the National Museum of Denmark. *Museumstekniske Stud* 1:118 pp
- Broughton HB, Jones PS, Ley SV, Morgan ED, Slawin AMZ, Williams DJ (1986) The chemical structure of azadirachtin. Schmutterer H, Ascher KRS (eds) *Proceedings of the 3rd international neem conference*, Nairobi, 1986, TZ-Verlagsgesellschaft Rossdorf 1987, pp 103–110
- Bub-Bodmar F, Tilger B (1922) Die Konservierung des Holzes in Theorie und Praxis. Parey, Berlin
- Burton R, Bergervoet T, Nasheri K, Vinden P, Page D (1990) Gaseous preservative treatment of wood. *IRG/WP/3631*
- Buschhaus H-U (1992) Tolyfluorid – fungicide against blue stain in service. *IRG/WP/3736-92*
- Butcher JA (1985) Benzalkonium chloride (an AAC preservative): criteria for approval, performance in service, and implications for the future. *IRG/WP/3328*

- Butcher JA, Drysdale JA (1977) Relative tolerance of seven wood-destroying Basidiomycetes to quaternary ammonium compounds and copper-chrome-arsenate preservative. *Mat Org* 12(4):271–277
- Butcher JA, Drysdale JA (1978) Efficacy of acidic and alkaline solutions of alkylammonium compounds as wood preservatives. *NZ J For Sci* 8(3):404–409
- Caputi Jambrenghi E (1989) Il restauro della cassa armonica dell'organo della chiesa di S. Maria Vetere di Andria (Bari) [The restoration of the soundbox of the organ in the church of Santa Maria Vetere in Andria (Bari)]. In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp 228–230, 349–350 (AATA 29-2350)
- Child RE, Pinniger DB (1987) Insect pest control in U.K. Museums. Recent Advances in the Conservation and Analysis of Artifacts. Jubilee Conservation Conference, University of London, Institut of Archaeology: Summer Schools Press, London, pp 303–308 (AATA 26-62).
- Clausnitzer K-D (1990) Historischer Holzschutz. *Ökobuch, Staufeu bei Freiburg*
- Conwentz H (1925) Das Wikingerboot von Baumgarth, Kr. Stuhm (Ostpr.) (1895). *Bl Dtsch Vorgesch* (2):1–24
- Crefield JW, Greaves H, Howick CD (1983) Boracol 40 – a potential remedial and preventive treatment for lyctids. *IRG/WP/1192*
- Csillag G (1961) Insektenvernichtung in Holzobjekten. *Neprijazni Ertesito* 42:181–186
- Cummins JE, Wilson HB (1939) The preservation of timber against attack of the powder post borer *Lyctus brunneus* Steph. by impregnation with boric acid. *J Counc Sci Ind Res Austral* 9:37–56
- Cymorek S, Pospischil R (1982) Über Hormonmimetika und Chitinsynthesehemmer als biologisch wirkende Schutzmittel für den Holzschutz. *Holzschutz – Forschung und Praxis, Symposium* 1982. DRW, Leinfelden-Echterdingen, 1984, pp 64–68
- Dawson J (1982) Some considerations in choosing a biocide. In: Grattan DW, McCawley JC (eds) *Proceedings of the ICOM Waterlogged Wood Working Group Conference*, Ottawa, pp 269–277 (AATA 21-405)
- Dawson JE (1986) Effects of pesticides on museum materials: a preliminary report. Papers presented at the 6th international biodeterioration symposium, Washington, DC, Aug 1984. *Biodeterioration* 6:350–354
- Dawson JE, Strang TJK (1992) Solving museum insect problems: chemical control. *Tech Bull* no 15, Canadian Conservation Institute
- De Jong J (1977) Conservation techniques for old waterlogged wood from shipwrecks found in the Netherlands. In: Walters AH (ed) *Biodeterioration investigation techniques*. Applied Science Publishers, Essex, pp 295–338 (AATA 15-1291)
- De la Baume S (1987) Essais de conservation des bois archéologiques au sucrose. *VALEC-TRA/DER/EDF*. Saint Denis, pp 162–172
- Dickinson DJ, Coggins CR (1975) Xyligen-NCH, an organo aluminum compound: a study of its activity against wood rotting fungi. *Int Pest Control* 17(5):10–12
- Dickinson DJ, Murphy RJ (1996) Sterilization and borate treatment on the RRS *Discovery*. *Proceedings from the 2nd international conference on wood protection with diffusible preservatives and pesticides*, Mobile, Alabama, 6–8 Nov 1996, pp 129–134
- DIN 68800-3 (1990) Holzschutz. Vorbeugender chemischer Holzschutz, Stand April 1990
- Dolenz H (1940) Zwei Einbäume aus dem Sattnitzmoor – II. Beschreibung und Konservierung der Einbäume. *Carinthia* 130(1/2):217–223
- Doppelreiter H (1980) Die Wirksamkeit von Diflubenzuron (Dimilin) auf Eilarven von *Hylotrupes bajulus* (L.). *Mat Org* 15(1):47–52
- Dubois JW, Ruddick JNR (1998) The fungal degradation of quaternary ammonium compounds in wood. *IRG/WP/98-10263*
- Dumkow M, Preuss H (1990) Konservierung von Naßholz mit Rübenzucker. *Arbeitsbl Restaur* 23(1) Gruppe 8:186–192 (AATA 28-655)
- Eaton RA, Hale MDC (1993) Wood: Decay, pests and protection. Chapman & Hall, London
- Elliot M, Farnham AW, Janes NF (1973) Potent pyrethroid insecticides from modified cyclopropane acids. *Nature* 244:456–457

- Emoto Y (1972) Fungi control for the statues of Yakushi (Bhaisajyaguru) Triad in the Hōjōbō Temple. *Sci Conserv* (9):51–53 (AATA 9-626)
- EN 335-1 (1992) Dauerhaftigkeit von Holz und Holzprodukten. Definition der Gefährdungsklassen für einen biologischen Befall. Teil 1: Allgemeines, Stand September 1992
- Feige W (1986) Ger. (East) Patent 232 060
- Feige W (1988) Ger. (East) Patent 243 823
- Gambetta A, Orlandi E, Cramer CR, Maier D, Tscholl HP (1988) Organotin compounds as wood preservatives in ground contact and sea water – a longterm study. *Mat Org* 23(1):61–80
- Garczynski W (1958) Transport i konserwacja wczesno-sredniowiecznej łodzi ze wsi Czarnowsko, pow. Lebork (Transportation and conservation of the prehistoric Czarnowsko boat, district Lebork). *Museum Pomorza Zachodniego, Materiały Zachodnio – Pomorskie, Szczecin* 4:393–397
- Gaudel P (1963) Das Polyglycol-Verfahren. Ein Beitrag zur Konservierung großer Feuchtholzobjekte. *Präparator* 9:202–210 (AATA 13-363)
- Gerard A (1990) Sculptures du retable de Grunewald au Musée Unterlinden de Colmar: traitement de désinsectisation. La conservation du bois dans le patrimoine culturel, Besancon-Vesoul, 8–10 Nov 1990, pp 139–145 (AATA 30-109)
- Glastrup J (1987) Insecticide analysis by gas chromatography in the stores of the Danish National Museum's Ethnographic Collection. *Stud Conserv* 32:59–64
- Göttsche R, Marx H-N (1989) Kupfer-HDO – ein vielseitiger Wirkstoff im Holzschutz. *Holz Roh Werkst* 47:509–513
- Graf E (1987) Biogene Schäden an kulturhistorischen Holzbauteilen und ihre Sanierung. In: Schiessl U (ed) *Bemalte Holzdecken und Tafelungen*. Haupt, Bern, pp 101–105
- Graf E, Manser P, Lanz B (1998) Erfolgreiche Insektenbekämpfung mit Borpräparaten. *Holz-Zentralblatt* 124(121):1774
- Grosser D, Eichhorn M, Grabow F (1991) Merkblatt 1-2-91. Der Echte Hausschwamm – Erkennung, Lebensbedingungen, vorbeugende und bekämpfende Maßnahmen, Leistungsverzeichnis. *Bautenschutz Bausanierung* 14:[45–62]
- Grosso GH (1981) Experiments with sugar in conserving waterlogged wood. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa, Preprints 81/7/7/1-9 (AATA 18-1276)
- Gustafson RA, Modaresi IR, Hampton GV, Chapesiuk RJ, Kelley GA (1990) Fungicidal efficacy of selected chemicals in thymol cabinets. *J Am Inst Conserv* 29:153–168 (AATA 28-1909)
- Hädicke E, Reuther W, Hickmann E (1978) Kurzbericht. *Nachr Chem Techn Lab* 26(3):117
- Hansen J (1984a) IPBC – a new fungicide for wood protection. *IRG/WP/3295/1-6*
- Hansen J (1984b) A new fungicide for wood protection. *Modern Paint Coatings* 74(11):50–54 (AATA 24-652)
- Hartlieb J, Messner K, Riedl H (1982) Wachstum von Schimmelpilzen in Malgründen und ihre Bekämpfung. *Maltechnik Restauo* 88(3):189–197
- Härtner H, Barth V (1996) Effectiveness and synergistic effects between copper and polymer betaine. *IRG/WP/96-30097*
- Hartung F (1999) Untersuchungen zum Verfahren der Supercritical Fluid Extraction (SFE) mittels CO₂ an Holz. Diplomarbeit, Fachhochschule Eberswalde, Fachbereich Holztechnik
- Hedley ME, Preston AF, Cross DJ, Butcher JA (1979) Screening of selected agricultural and industrial chemicals as wood preservatives. *Int Biodet Bull* 15(1):9–18
- Hegarty B (1988) Neue Erkenntnisse über den Echten Hausschwamm *Serpula lacrymans*. *Holz-Zentralblatt* 114(46):655,660–666
- Hegarty B, Yu B, Leightley L (1997) The suitability of isothiazolone microemulsions as long-term wood preservatives. *IRG/WP/97-30150*
- Hof T (1969) Review of literature concerning the evaluation of organotin compounds for the preservative of wood. *J Int Wood Sci* 23:19–28
- Hoffmann P (1990) Sucrose for stabilizing waterlogged wood – some investigations into anti-shrink efficiency (ASE) and penetration. In: Hoffmann P (ed) *Proceedings of the 4th ICOM*

- Group on Wet Archaeological Materials Conference, Bremerhaven. Deutsches Schifffahrtsmuseum, pp 317–328
- Hoffmann P, Perez de Andres C, Sierra Mendes JL, Ramiere R, Tran QK, Weber UM (1994) European inter-laboratory study on the conservation of waterlogged wood with sucrose. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference*, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 309–335
- Holmwood G, Büchel KH, Lürssen K, Frohberger P-E, Brandes W (1981) 1-Hydroxyethyl-azol-Derivate, Verfahren zu ihrer Herstellung sowie ihre Verwendung als Pflanzenwachstumsregulatoren und Fungizide. *Europapaten* no 0040345 vom 21.11.1981
- Horn W, Marutzky R (1994) A rapid pyrolytical method for the determination of wood preservatives in treated wood. *Fresenius J Anal Chem* 384:832–835
- Hug B (1979) Die Methode Carbowachs (PEG)/Gefriertrocknung. *Z Schweiz Archäol Kunstgesch* 36(2):134–137
- Ishikawa R, Miura S, Arai H, Mori H (1976) Gate of the Shrine “Nezu” – X-ray examination and treatment against biodeterioration. *Sci Conserv* 15:19–24 (AATA 14-175)
- Jin L, Preston AF (1991) The interaction of wood preservatives with lignocellulosic substrates. I. Quaternary Ammonium Compounds. *Holzforschung* 45(6):455–459
- Kim GM, Morrell JJ (2000) In-situ measurement of dimensional changes during supercritical fluid impregnation of white spruce lumber. *Wood Fiber* 32(1):29–36
- Kleitz M-O (1987) L'oxyde d'éthylène. Utilisation et limites. In: Grimstad K (ed) *Actions secondaires avec un résidu de traitement antérieur*. ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6–11 Sept 1987, Preprints, vol3, pp 1175–1181 (AATA 25-697)
- Koch AP (1990) Occurrence, prevention and repair of dry rot. Paper prepared for the 21st IRG meeting, 14–18 May 1990, Rotorua, New Zealand, 10 pp
- Koesling V (1991) Konservierung wassergesättigter Holzdosen mit Zuckerlösungen. In: *Arbeitsgemeinschaft der Restauratoren* (ed) *Proceedings of the conference: Konservierung von archäologischem Naßholz mit Zucker*, 31 Jan – 1 Febr 1991, Stade, Germany, pp 98–103
- Koesling V (1992) Konsolidierung wassergesättigter Naßholzfunde mit heißen Zuckerlösungen. *Arbeitsbl Restaur* 25(2) Gruppe 8:209–212 (AATA 31-1702)
- Koesling V (1993) Zwei Kloben aus der Takelage eines hölzernen Kaffenkahns. *Restauo* 99(4):243–245 (AATA 31-1703)
- Koestler RJ, Parreira E, Santoro ED, Noble P (1993) Visual effects of selected biocides on easel painting materials. *Stud Conserv* 38:265–273 (AATA 31-1616)
- Krause E (1883) Die Erhaltung von Gold- und Holzsaachen. *Z Ethnol Verh* 15:360–361
- Krchňavý L (1972) Konzervovanie mokreho dreva z archeologických výskumov polyetylénovou metódou (Conservation of waterlogged wood from archaeological excavations by means of the PEG-method). *Konzervátorské praktikum, Muzeologický kabinet Slovenského národného múzea*, pp 48–50
- Kulzer E (1985) Fledermäuse u. Holzschutzmittel – ein Konflikt? *Prakt. Schädlingsbekämpfer* 37(9):177–178
- Kunz B, Weidenbörner M, Adams S, Strohmeyer M, Wüstenhöfer B, Wegen H-W (1995) Chancen und Möglichkeiten der Entwicklung umweltschonender Holzschutzmittel. *Vortragsband der 20. Holzschutz-Tagung*, Rosenheim/Germany, 18–19 Oct 1995, pp 133–140
- Langendorf G (1988) *Holzschutz*. Fachbuchverlag, Leipzig
- Lefèvre J, Unger A (1996) Dekontamination von Holzkonservierungsmitteln in Kunst- und Kulturgütern. *Holz-Zentralblatt* 152:2440
- Lehmann J (1962) Konserwacja drewnianych zabytków etnograficznych i archeologicznych (Conservation of ethnological and archaeological wooden items). *Ochrona Zabytkow* 15: 24–33
- Leightley LE, Nicholas DD (1990) In-ground performace of wood treated with a substituted isothiazolone. *IRG/WP/3612*
- Leiß B (1992) *Holzschutzmittel im Einsatz*. Bauverlag, Wiesbaden

- Leiß B (1996) Holz natürlich schützen. Schäden vermeiden, Werte erhalten. Reihe Sanfte Chemie, 1st edn. Müller-Verlag, Heidelberg, Alembik-Verlag, Braunschweig
- Levien KL, Morrell JJ, Kumar S, Sahle-Demessie E (1994) Process for removing chemical preservatives from wood using supercritical fluid extraction. US-Patent 5.364.475
- Linnie MJ (1990) Conservation: pest control in museums – the use of chemicals and associated health problems. *Museum Manage Curatorship* 9(4):419–423
- Lohwag K (1967) Zeittafel zur Geschichte des Holzschutzes. *Int Holzmarkt* 58(16/17):45–54
- Lorenz W, Bahadır M, Korte F (1985) Zum Einsatz synthetischer Pyrethroide im vorbeugenden Holzschutz. Ein Beitrag zur Verminderung der Chemikalienbelastung in Innenräumen. *Holz Roh Werkst* 43(8):339–343
- Lutowski K, Skrzypczak P, Gajdzinski M (1988) Použitie chemických prostriedkov na konzervovanie polychromovaného dreva (Application of chemical reagents for the preservation of polychrome wood). *Drevo* 43(1):8–12 (AATA 26-2181)
- Majewski L (1972) On conservation (of objects made of wood). *Museum News* 51(2):13–14 (AATA 10-201)
- Matějková J (1971) Sanaco stavebních památek napadených dřevomorkou domácí (Treatment of architectural monuments attacked by dry-rot). *Památková péče* 31(4):193–209 (AATA 11-122)
- Metzner W, Buchwald G, Cymorek S, Hinterberger H (1977) Neuere Entwicklungen auf dem Gebiet der Insektizide und Fungizide für ölartige Holzschutzmittel. *Holz Roh Werkst* 35:233–237
- Michaelson H (1984) Der Dürerschränk auf der Wartburg. Geschichte, Konservierung, Restaurierung. *Neue Museumskd* 27(4):260–272
- Mihailov A (1970a) Conservation of wooden works of art in Bulgaria. IIC conference on the conservation of stone and wooden objects, New York, pp 115–136 (AATA 8-768)
- Mihailov A (1970b) Conservation of the wooden elements in the Renaissance houses of the People's Republic of Bulgaria. *Stud Conserv* 15(3):221–223
- Mihailov A (1974) Konservácia na rezbovanií proizvedeniá na izkustvoto (Conservation of carved art objects). *Proučvaniá i Konservácia. Nauka i izkustvo* Sofia, pp 137–150
- Mihailov A (1975) Conservation of wood which has stayed in water in the P.R. of Bulgaria. ICOM Committee for Conservation, Venice, 75/8/3:1–11 (AATA 13-926)
- Moll F (1916) Über die Zerstörung von verarbeitetem Holz durch Käfer und den Schutz dagegen. *Naturwiss Z Forst Landwirtsch* 14:494
- Morgós A (1987) Nagymértékben csökkent szilárdságu fatárgyak restaurálása – két rossz állapotú ácsolt láda restaurálása (Restoration of gravely deteriorated wooden objects – restoration of two timbered chests of poor condition). *Múzeumi Műtárgyvédelem* 17: 159–172 (AATA 24-740)
- Morgós A (1992) Erfahrungen bei der Stabilisierung von Naßholz mit Zucker in Ungarn. Konservierung von archäologischem Naßholz mit Zucker. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Febr 1991, 1992, pp 4–8
- Morgós A, Strigazzi G, Preuß H (1994) Microbicides in sugar conservation of waterlogged archaeological wooden finds: the use of isothiazolones. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 463–484 (AATA 32-860)
- Mori H, Arai H (1978) Biodeterioration of wooden cultural properties and its control. *Conserv Wood Int Symp Conserv Restor Cult Prop* 1977, proceedings, pp 1–16 (AATA 16-1385)
- Mori H, Arai H (1981) Protection of underwater cultural properties from marine borers. *Sci Pap Jpn Antiques Art Crafts* 26:89–95 (AATA 19-1367)
- Morrell JJ, Levien KL, Sahle Demessie E, Acda MN (1997) Impregnating wood with biocides using supercritical carbon dioxide: process parameters, performance, and effects on wood properties. American Wood-Preservers Association, 93rd annual meeting, 27–29 April, Pittsburgh, Pennsylvania, USA, pp 249–266
- Mühlethaler B (1973) Kleines Handbuch der Konservierungstechnik. Haupt, Bern. AATA 10-676; 13–585

- Nicholas DD, Preston AF, Greenley DE, Parikj S (1984) Evaluation of substituted isothiazolone as a potential new wood preservative. IRG/WP/3306
- Noack D (1965) Der gegenwärtige Stand der Dimensionsstabilisierung von Holz und Schlußfolgerungen für die Konservierung der Bremer Kogge. *Brem Jahrb* 50:43–72
- Noldt U (1994) Termite bioassays of sucrose-treated waterlogged archaeological wood. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 337–356 (AATA 32-867)
- Oertel J (1965) Neuartige schwer auswaschbare Holzschutzmittel auf der Basis wasserlöslicher organischer Verbindungen und ihre Anwendungsmöglichkeiten. *Holztechnologie* 6(4): 243–247
- Pallaske M (1997) Insect growth regulators: modes of action and mode of action-dependent peculiarities in the evaluation of the efficacy for their use in wood preservation. Paper prepared for the 28th annual IRG-meeting, Whistler, Canada, 25–30 May 1997
- Pallaske M (1998) Insektenhormone als hochselektive Insektizide für den Einsatz in Holzschutzmitteln. Tagungsband der 21. Holzschutz-Tagung, Rosenheim/Germany, 21–23 Apr 1998, pp 125–139
- Pallaske M (1999) Insect growth regulators: modes of action and mode of action-dependent peculiarities in the evaluation of the efficacy for their use in wood preservation. In: Reinprecht L (ed) Rekonstrukcia a konzervácia historického dreva '99, 2nd international symposium, 15–17 June 1999, Zvolen, pp 239–248
- Pallaske M, Wegen H-W (1995) Benzoylharnstoffverbindungen als alternative Insektizide im Holzschutz. Tagungsband der 20. Holzschutz-Tagung, Rosenheim/Germany, 18–19 Oct 1995, pp 259–271
- Pallaske M, Metzner W, Wegen H-W (1993) Deutsche Patentschrift: Mittel zum Schutz technischer Materialien, insbesondere Holz und Holzwerkstoffe, DE 4303012 A1
- Parrent JM (1983a) The conservation of waterlogged wood using sucrose. Master's Thesis Texas, A and M University, College Station, Texas USA
- Parrent JM (1983b) The conservation of waterlogged wood using sucrose. Paper presented to the joint CUA/SMA Meeting Denver, Colorado, January 1983
- Parrent JM (1985) The conservation of waterlogged wood using sucrose. *Stud Conserv* 30:63–72 (AATA 22-2009).
- Perkow W, Ploss H (1999) Wirksubstanzen der Pflanzenschutz- und Schädlingsbekämpfungsmittel. 3. Aufl., Parey Buchverl., Berlin
- Petermann H (1976) Holzschutzmittelschaumverfahren – Möglichkeiten der Schutzbehandlung von Hölzern in Bauholzkonstruktionen. *Holzindustrie* 30:267–270
- Petrowitz H-J (1986) Zur Abgabe von Holzschutz-Wirkstoffen aus behandeltem Holz an die Raumluft. *Holz Roh Werkst* 44:341–346
- Petrowitz H-J, Wagner M (1987) Dünnschichtchromatographie von synthetischen Pyrethroiden in öligen Holzschutzmitteln. *Holz Roh Werkst* 45(12):514
- Petrowitz H-J, Wagner M (1992) Nachweis von Fungiziden in Holzproben. *Prakt Schädlingsbekämpfer* (6):140–142
- Peylo A (1998) Schnellerkennung von Holzkontaminationen (1),(2). *Holz-Zentralblatt* 124(46): 690,692, (54):823
- Pinniger D (1994) Insect pests in museums, 3rd edn. Archetype Publications Limited, London
- Pirling R, Buchwald G (1974) Ein Schiff aus karolingischer Zeit und seine Konservierung. *Naturwissenschaften* 61:396–398
- Plackett DV (1981) Anti-stain field trials in British Columbia. IRG/WP/4174
- Plackett DV (1984) Spot-tests for TnBTO and AAC preservatives. IRG/WP/3279
- Plenderleith HJ (1956) The conservation of antiquities and works of art. Oxford University, London, part 1/5:116–143
- Post LC, Vincent WR (1973) A new insecticide inhibits chitin synthesis. *Naturwissenschaften* 60:431–432

- Preston AF (1983) Dialkyldiammonium halides as wood preservatives. *J Am Oil Chem Soc* 60(3): 567–570
- Preston AF, Nicholas DD (1982) Efficacy of series of alkylammonium compounds against wood decay fungi and termites. *Wood Fiber* 14(1):37–42
- Rafalski H-J, Biering B (1990) Holzschutz-Beschäumverfahren. Die ökologische Alternative zum Spritzverfahren. Leipziger Gesellschaft für Bausanierung mbH, Leipzig
- Rama Rao N, Pandit Rao V (1990) Conservation of an old wooden bullock cart. *Indian J Chem Sci* 4:69–71 (AATA 29–697)
- Rathgen F (1924) Die Konservierung von Altertumsfunden, Teile II u. III. De Gruyter, Berlin, pp 133–149 (Holz)
- Read SJ (1982) Control of death-watch beetle (*Xestobium rufovillosum* Deg.) with experimental permethrin smoke generators. IRG/WP/3199 (AATA 20–463)
- Richardson BA (1993) Wood preservation, 2nd edn. E & FN SPON, London (AATA 32–2299)
- Römpf H (1995) Chemie-Lexikon. Falbe J, Regitz M (eds). Thieme, Stuttgart
- Rosenqvist AM (1959) The stabilizing of wood found in the viking ship of Oseberg. *Stud Conserv* 4(1):13–22; 4(2):62–72 (AATA 13–216)
- Rosenqvist AM (1973) Versuche zur Konservierung von Naßhölzern durch Gefriertrocknung. *Arbeitsbl Restaur* 6(2) Gruppe 8:69–74 (AATA 12–242)
- Roth L (1996a) Chlorierte Kohlenwasserstoffe. Ecomed, Landsberg
- Roth L (1996b) Pyrethroide. Ecomed, Landsberg
- Rustenburger G, Klaver CJ (1991) Silafluofen, a new insecticide against wood-boring insects and termites. IRG/WP/3666
- Sakai H, Imazu S, Morgós A (1997) Protection of waterlogged wooden objects kept in water against decay. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York, UK, 1996, Bremerhaven 1997, pp 295–316
- Sanchez Ledesma A, Castro Boch J, Martinez Outorino P (1990) Experiencia cubana en la consolidación de maderas arqueológicas deterioradas por el agua empleando azúcar de caña: estudio microbiológico. Documentos (Grupo de Información Esfera de las Artes Visuales) 2/3:1–47 (AATA 30–1293)
- Schiessl U (1984) Historischer Überblick über die Werkstoffe der schädlingsbekämpfenden und festigkeitserhöhenden Holzkonserverung. *Maltechnik Restau* 90:9–40 (AATA 22–739)
- Schmidt H (1971) Holzminierende Käferlarven. 2. Nage-, Klop- oder Pockkäfer (Anobiidae). *Holz Roh Werkst* 29:201–204
- Schmidt O, Müller J, Moreth U (1996) Zur möglichen Schutzwirkung von Chitosan gegenüber Holzpilzen. Bundesforschungsanstalt für Forst- und Holzwirtschaft Hamburg, Jahresbericht, pp 40–41
- Schmutterer H, Ascher KRS, Rembold H (eds) (1981) Natural pesticides from the neem tree (*Azadirachta indica* A. Juss). Proceedings of the 1st international neem conference, Rottach-Egern, 1980, 297 pp
- Schoknecht U, Gunschera J, Marx H-N, Marx G, Peylo A, Schwarz G (1998) Holzschutzmittelanalytik. Forschungsbericht 225. BAM, Berlin
- Schultze-Dewitz G (1969) Geschichte der Holzpathologie und des Holzschutzes. *Holzindustrie* 22(9):257–261
- Schweizer F, Houriet C, Mas M (1985) Controlled air drying of large Roman timber from Geneva. Les Bois Gorgés d'Eau. Actes de la 2e conference du groupe de travail de l'ICOM 1984, Grenoble, pp 327–338 (AATA 24–796).
- Seifert K, Unger W (1994) Insecticidal and fungicidal compounds from *Isatis tinctoria*. *Z Naturforsch* 49c:44–48
- Serck-Dewaide M (1978) Disinfestation and consolidation of polychrome wood at the Institut Royal du Patrimoine Artistique, Brussels. Conservation of wood in painting and the decorative arts. Preprints of the contributions to the Oxford Congress, 17–23 Sept 1978. IIC, 81–83 (AATA 16–449)
- Serck-Dewaide M (1990) Le retable de Sainte Colombe à Deerlijk XVIe siècle: étude et restau-

- ration. La conservation du bois dans le patrimoine culturel. Besancon-Vesoul, 8–10 Nov 1990, pp 113–124 (AATA 30–1297)
- Stoia NA, Lambrou A (1975) Wood preservative for art objects. Roman Patent 59354 (30 Oct 1975) (AATA 15–1335)
- Straub RE (1963) Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich
- Su N-Y, Freytag E, Bordes ES, Dycus R (2000) Control of Formosan subterranean termite infestations using baits containing an insect growth regulator. *Stud Conserv* 45:30–38
- Suthers T (1975) The treatment of waterlogged oak timbers from Ferriby boat III using polyethylene glycol. *Mar Monogr Rep Natl Mar Museum Greenwich* 16:115–119 (AATA 15–448)
- Thele EA Jr, Shair SA (1967) US-Patent no 1578751 AO 1N
- Thevenon M-F, Pizzi A, Haluk J-P (1997) Non-toxic albumin and soja protein borates as ground-contact wood preservatives. *Holz Roh Werkst* 55:293–296
- Thevenon M-F, Pizzi A, Haluk J-P (1998) One-step tannin fixation of non-toxic protein borates wood preservatives. *Holz Roh Werkst* 56:90
- Thompson WS (1965) Response of *Poria monticola* and *Polyporus versicolor* to aliphatic amines. *For Prod J* 15(7):282–284
- Troschel E (1916) Handbuch der Holzkonserverung. Springer, Berlin
- Tscholl HP (1977) Entwicklung von Methoden zur Prüfung von Juvenoiden als Holzschutzmittel gegen Insekten, insbesondere Bewertung von 3 Juvenoiden auf den Splintholzkäfer, *Lyctus brunneus* Steph. (Col.: Lyctidae). Diss. ETH no 5990, 180pp
- Tsunoda K, Nishimoto K (1987) Fungicidal effectiveness of amended alkylammonium compound. IRG/WP/3421
- Turner WS (1978) Conservation of the finds. *Int J Naut Archaeol Underwater Explor* 7:317–319 (AATA 16–1150)
- Unger A (1998) Organolösliche Holzkonserverungsmittel. Dekontaminierungsprojekt. *Restau* 104(1):13
- Unger W, Sallmann U, Henkel T, Herrmann R (1989) Zum Einsatz des Holzschutzmittels Deltax IT in der Restaurierung. *Holztechnologie* 30(5):260–263
- Valcke A (1989) Suitability of Propiconazole (R 49362) as a new-generation wood-preserving fungicide. IRG/WP/3529
- Valcke A, Pallaske M (1995) FLUROX™, a new breakthrough in insect control for wood preservation. IRG/WP/95–30079
- Van Dyk P, Ligthoet T, van Leemput L (1984) Water dilutable wood-preserving liquids. EU-Patent no 0148526, 2 Dec 1984
- Vinden P, Burton RJ, Bergervoet AJ (1991) Vapour phase treatment of wood with trimethyl borate. In: Thompson R (ed) The chemistry of wood preservation. Royal Society of Chemistry, London, pp 265–274
- Vinden P, Fenton T, Nasheri K (1985) Options for accelerated boron treatment: a practical review of alternatives. IRG/WP/3329
- Von Rotberg W, Gagelmann M, Wilke N, Piening H, Sicke RW, Roux K, Michaelis S (1997) PCP-Pilotsanierung durch ein feuchtegekoppeltes thermisches Verfahren. *Umwelt* 27(5):56–59
- Von Stokar W (1939) Ein neues Verfahren zur Konservierung von Moorböhlzern. *Nachrichtenbl Dtsch Vorzeit* 15(5/6):145–149
- Voss A, Esser PM, Suitela WLD (1999) Chemical analysis of TnBTO in lap-joints. IRG/WP/99–20173
- Wallhäusser KH, Fink W (1976) Konservierung von Dispersionen und Dispersionsfarben. *Farbe Lack* 82(2):108–125
- Weber R (1965) Neue Beiträge zum Fund der Bremer Kogge. 1. Zu der Geschichte des Fundes, seiner Bergung und wissenschaftlichen Betreuung. *Brem Jahrb* 50:27–37
- Wegen H-W (1996) Häutungshemmer für den alternativen Holzschutz. *Holz-Zentralblatt* (57): 937, 944
- Wegen H-W, Platen A, Höllbacher G (1996) Suitability of benzoyl urea compounds as insecticides in a new generation of wood preservatives. BWPDA Convention, 6 pp + figures

- Wehlte K (1961) Verölte Holzskulpturen. *Maltechnik* 67:23–24
- Willeitner H, Brandt K, Illner HM (1988) Nachweis von Pentachlorphenol im Holz: Hinweis für die Praxis. *Holz-Zentralblatt* 114:265–266
- Wirth P (1977) A szatmárcseki református temető védelme (The protection of the Calvinist graveyard of Szatmarcseke). *Műemlékvédelem* 21(2):96–102 (AATA 15-461)
- Wittenzellner J, Hettler W, Maier M (1999) Determination of bis-(N-cyclohexyl-diazonium-dioxy)-copper in different matrices by photometer, thermal energy analyzer and HPLC. *IRG/WP/99-20179*
- Wróblewska K, Tomaszewski K, Wieczorek K (1990) Conservation of waterlogged wood from excavation at Pultusk. Comparison of different treatment methods. In: Hoffmann P (ed) *Proceedings of 4th ICOM Group on Wet Organic Archaeological Materials Conference*, Bremerhaven. Deutsches Schiffahrtsmuseum, pp281–317
- Wüstenhöfer B, Wegen H-W, Metzner W (1990) Tebuconazole, a new wood-preserving fungicide. *IRG/WP/3634*
- Wüstenhöfer B, Wegen H-W, Metzner W (1993) Triazole – eine neue Fungizidgeneration für Holzschutzmittel. *Holz-Zentralblatt* 119(58):984,988
- Ypey J (1964) Zusammenhänge zwischen der Konservierung während der Grabung und der Behandlung der Funde im Labor. *Präparator* 10:39–47
- Zimmermann J (1977) Pilz- und Bakterienbekämpfung in Feuchtholzlagerbecken. *Arbeitsbl Restaur* 10(2) Gruppe 8:85

8 Fumigants

8.1

Nature and Scope of Fumigant Treatments

Fumigation is a part of wood preservation and is used mainly for the control of wood-destroying insects, but sometimes also to control decay fungi. Fumigation normally does not achieve a preventive treatment, because following the required ventilation the fumigants escape from the wood completely, leaving no residuals.

Fumigants are characterized by being present in sufficiently high concentration in the gas phase under ambient conditions of temperature and pressure, and by having biocidal effects. They will include gases as well as readily volatilized liquids and solids. Fumigants are used to protect plants, stored products and materials, objects, rooms and buildings by eradicating pests from them. Their effectiveness depends on the nature of the fumigant; concentration (c), length of exposure (t), and their product ($c \times t$ product); temperature and pressure, as well as the ambient relative humidity and the moisture content of the material.

Fumigants will penetrate into wood faster, more deeply, and more uniformly than liquid wood preservatives. Large numbers of objects can be treated with fumigants simultaneously and in less time than they could be treated with wood preservatives. The disadvantages are that some fumigants have very high toxicity and that not every gas is suited for a given problem situation.

Based on their chemical reactivity and degree of toxicity, fumigants can be divided into very reactive substances which are highly toxic to people and the environment, and substances which are inert or of low reactivity and are of little or no direct danger to health. Whereas liquid wood preservatives can usually be used by conservators without restrictions, the application of highly toxic fumigants is limited to specialized commercial applicators with appropriate licenses. Some odorless, reactive fumigants contain an added indicator gas because of their danger potential. Reactive fumigants may sometimes remain inside treated objects for long periods and may, under conditions of high ambient relative humidity and material moisture content, lead to permanent detrimental changes in certain materials. With inert fumigants, the

clearly longer exposure times are a disadvantage. In general, exposure times can be shortened by increasing temperature and/or pressure.

Portable objects can be treated in tents (bubbles), containers or pressure chambers. Rooms and buildings must be sealed inside and out, or entire buildings may be tented (covered with gas-tight film). Special cases of fumigation involve the control or modification of the surrounding atmosphere.

Fumigants were used in historic times (cf. Appendix, Table 2). In future, the highly reactive fumigants will be replaced in all those cases where remedial treatments of works of art and other cultural property can be done with inert fumigants or those of low reactivity, or by physical control methods.

In industrial practice of remedial treatments for decaying wood a different form of fumigation is used, which is referred to as long-term fumigation as opposed to short-term fumigation as usually used by conservators. The main application of long-term fumigation is to extend the service life of utility poles, marine pilings and bridge timbers. Long-term fumigants are introduced into the wood where they volatilize over time and spread through the wood. The most commonly used fumigant is Vapam (32.1% sodium *n*-methylthiocarbamate); others are Vorlex (20% methylisothiocyanate in chlorinated C₃ hydrocarbons) and chloropicrin (trichloronitromethane; Morrell and Corden 1986; Morrell 1989).

Since fumigants are of no significance for waterlogged wood, the following discussions of fumigants are not divided into separate sections on dry wood and waterlogged wood in most cases.

8.2

Inorganic Fumigants

8.2.1

Reactive Gases

8.2.1.1

Sulfur Dioxide

Formula:	SO ₂
Properties:	Colorless, incombustible gas with pungent odor; m.p. -72.7°C; b.p. -10°C; density ca. 2.3 times that of air; readily soluble in water under formation of sulfurous acid (18.6% mass basis at 20°C and 101.3 kPa) and very soluble in ethanol
Toxicology:	Very toxic; sulfur dioxide causes poisoning symptoms at concentrations of 0.04% and higher in air (corneal opacity, difficulty in breathing, inflammation of respiratory organs); prolonged inhalation can affect conscious-

ness and lead to lung edema. Great damage to plants, especially conifers. Water pollutant

Biological effects: Insecticide and microbiocide

Application: Against insect pests in closed spaces with 2% volume basis SO₂ for 6h. Against microorganisms through smoking with burning sulfur (16 g sulfur per m³)

Analysis: Detector tubes, microchemically by reduction of Cu²⁺ to Cu⁺; also by colorimetry or by fluorescence spectroscopy.

Uses

Historical

- ca. 900 B.C. SO₂ mentioned as disinfectant smoking substance in Homer's *Odyssey* (Römpf 1995).
- 1493–1541 Paracelsus knows of the bleaching effects of the gas (Römpf 1995).
- Before 1900 Control of pests in libraries and art galleries by smoking with burning sulfur (Schiesl 1984).
- 1963 Straub mentions the gas for controlling wood-destroying insects in art objects.
- 1993 Williams et al. expose 34 artists' pigments for 12 weeks to 93 ± 5 ppb sulfur dioxide in air, and only triphenylmethane pigments (fuchsin and brilliant green) are affected.

Present Day

Not used for fumigating works of art, only for disinfecting wood barrels (e.g., wine barrels).

Advantages/Disadvantages

Sulfur dioxide is not sufficiently effective for the control of wood-destroying insects. At high concentrations and with increasing relative humidity and material moisture content dyes, pigments and their wood supports can be affected. Sulfur dioxide is desorbed slowly, and is very health threatening.

8.2.1.2

Hydrogen Cyanide (Prussic Acid)

Trade name:	Cyanogas (USA), Zyklon B, Cyanosil (Germany)
Formula:	HCN

- Properties:** Colorless, combustible liquid with characteristic odor; m.p. -14°C ; b.p. 25.6°C ; vapor pressure 83 kPa at 20°C ; density 0.94 times that of air; freely miscible with water and ethanol but low solubility in ether
- Toxicology:** Extremely toxic. Dosage of 1 mg CN⁻/kg body mass is lethal. Blocks oxygen transfer, leading to difficulty in breathing, loss of consciousness and suffocation. Damages the central nervous system, and can be absorbed through the skin
- Biological effects:** Hydrogen cyanide is an insecticide which affects cell respiration by blocking respiratory enzymes and oxygen transfer. It has weak fungicidal effectiveness
- Application:** Used in buildings against wood-destroying insects (Coleoptera), by setting out cardboard sheets or scraps of pulp soaked in prussic acid. Halogen carbonic acid ester and other chemicals may be added as warning indicators. Required are 20–30 g/m³ of air space for 72 h and at a minimum temperature of 5°C . Lighting must be limited to explosion-proof, electric lights. Low relative humidity and low material moisture content are advantageous, because the substance is readily soluble in water and can then attack materials more severely. Therefore, fumigation and subsequent ventilation should not be carried out at high interior relative humidity or during rain. Desorption from wood is slow, and buildings must therefore be ventilated for several days or even weeks. Freedom of residual gas must be checked in the rooms and on wood test samples
- Analysis:** Generally with detector tubes; in wood by reaction with benzidine-copper acetate according to Pertusi and Gastaldi. Test paper soaked in the reagent will turn blue when HCN is present

Uses

Historical

- 1880 Use of prussic acid against pests of plants and stored materials in America (Grosser and Roßmann 1974).
- 1915 Kemner reports on a successful fumigation of anobiid larvae with HCN (Grosser and Roßmann 1974).
- 1921 Control of Anobiidae with prussic acid in the Swedish royal palace in Kalmar (Grosser and Roßmann 1974).

- 1924 Rathgen cautions against the use of the Zyklon procedure.
- 1928 Control of the house longhorn beetle with prussic acid in the Emmaus Church in Copenhagen (Grosser and Roßmann 1974).
- 1929 Treatment of the altar in the Kefermarkt church (Austria) with Zyklon B (Oberwalder 1930; cf. Chap. 1, Fig. 1.1).
- After 1945 Fumigation of numerous churches in Bavaria (Germany) with prussic acid (Biebl 1995).
- 1954/1955 According to Mori and Kumagai, various polished metals, except gold, are attacked considerably after an exposure to hydrogen cyanide for 48 h. Unprotected and oil-bound pigments are also altered, but pigments with glue as a binding medium are not affected.
- 1974 Grosser and Roßmann publish their detailed contribution on the fumigation of works of art with hydrocyanic acid.
- 1978 DEGESCH-Technician conference in Baden-Helental near Vienna. Bäumert and Wentzel report among other topics on the use of prussic acid, and Bachmann reports on damage to precious metal overlays and to some non-ferrous metals by the substance.
- 1980 Weber reports on the formation of Prussian blue by fumigation with prussic acid of a damp lime cement plaster containing iron compounds.
- 1981 Publication by Bachmann on the attack of metals by prussic acid.
- 1983 Prussic acid fumigation of a village church infested with house longhorn beetles after tenting with film (Unger).
- 1986 Sutter, also Unger and Unger publish comprehensive accounts of the use of fumigants.
- 1987 Checks of buildings previously fumigated with prussic acid do not show any new infestation (Biebl 1995).
- 1988 Unger publishes the book *Holzkonservierung (Wood Conservation)* which includes sections on fumigants. Becker publishes an overview of fumigants.
- 1989 Bauer, also Brokerhof in their reviews discuss the advantages and disadvantages of hydrogen cyanide and other gases. Ognibeni tests the effect of prussic acid on pigments and binders.
- 1990 Irreversible discolorations are detected on gilding and copper-rich hammered metal overlays after fumigation with prussic acid (Anonymous). French publication on fumigation of wood (Vieillemand).
- 1992/1993 Continuing education events at the Bavarian State Institute for Conservation in Munich (Germany) on the themes of 'preservation, consolidation, and fills for wood' and 'Fumigation as a means of wood pest control'. During both conferences hydrogen cyanide was discussed (Emmerling 1995; Unger and Unger 1995).
- 1997 Fuchs describes changes of various dyes after fumigation with 20 mg/l HCN at 50 and 70% relative humidity. At 70% relative humidity there are great changes of chroma and value.

Present Day

In Europe hydrogen cyanide is now used only occasionally for insect control in historic structures because of its high toxicity and incompatibility with certain materials.

Advantages/Disadvantages

Hydrogen cyanide is highly toxic to humans and the environment. Insect pest are killed fast and completely. Normally there are no preventive effects, but hydrogen cyanide is easily adsorbed by walls, ceilings, floors, and wood artifacts and may remain there for extended periods. The gas is probably adsorbed extensively or may even react with the polysaccharides in wood under formation of cyanogenic glycosides, which may later liberate prussic acid again by hydrolysis. These processes could be the reason that until now no new insect infestations have been observed in objects that had been fumigated with hydrogen cyanide (Biebl 1995). However, this means that there would also be a latent danger to people and the environment. Especially at high levels of relative humidity and material moisture content, great changes can occur in various materials associated with wood in art objects.

8.2.1.3

Hydrogen Phosphide (Phosphine)

Trade name:	In Germany: PHOSTOXIN; Detia-Gas-Ex-B; Cartox, for a mixture of 10% ethylene oxide and 90% phosphine; Frisin, for a mixture of 1.7 vol% phosphine and 98.3 vol% nitrogen. In the former German Democratic Republic: Delicia-GASTOXIN, for 56.7% aluminum phosphide and 43.3% additives
Formula:	PH_3
Properties:	Colorless, combustible gas, odorless in its pure form; the technical gas has odors resembling technical calcium carbide, garlic, or fish; m.p. -132.5°C ; b.p. -87.4°C ; density 1.17 times that of air; solubility low in water, good in organic solvents such as acetone, benzene, and cyclohexanol
Toxicology:	Phosphine is a metabolic and nerve poison; sudden exposure causes nausea, daze, and cramps; slow intake leads to difficulty in breathing and lung edema; it has carcinogenic potential. In the environment it is degraded to phosphoric acid and phosphates
Biological effects:	Phosphine is an insecticide which is also effective against insect eggs (ovicide). The gas interferes with the redox

system of the mitochondria and disrupts the respiratory chain. At high doses it has a weak fungicidal effect

Application: Against wood-destroying insects (Coleoptera) inside buildings, tablets containing aluminum phosphide are laid out. Dosage is 2–4 g phosphine/ m^3 air space for 5–10 days, at normal pressure and a minimum temperature of 15°C . The aluminum phosphide reacts slowly with the moisture in the air to form hydrogen phosphide and aluminum hydroxide (powdery). Ammonium carbamate is added to the tablets as a fire retardant, and degrades to ammonia and carbonic acid. For this reason ammonia odor can be detected in the early stages of hydrogen phosphide fumigations. The gas is given off again quickly by the wood, among other reasons because it has very low solubility in water

Analysis: Gas detection tubes or sensors for PH_3

Uses

Historical

- 1936 Delicia-process for the fumigation of stored grain. Generation of hydrogen phosphide by hydrolysis of aluminum phosphide (Anonymous 1978).
- 1969 Attempts to control wood-destroying insects with hydrogen phosphide (Lehmann et al.).
- 1978 Instructions on the use of PHOSTOXIN against wood-destroying insects at the DEGESCH Technician Conference (Bäumert and Wentzel).
- 1984 Control of house longhorn beetle infestations in three Norwegian stave churches with an ammonia-free hydrogen phosphide preparation by the Rentokil Company (Anonymous 1985) Fumigation of a baroque village church in Germany with Delicia-GASTOXIN (Unger et al.).
- 1986 Hydrogen phosphide is mentioned as a fumigant by Sutter and by Unger and Unger.
- 1988 cf. hydrogen cyanide.
- 1989 cf. hydrogen cyanide. Ognibeni notes a susceptibility of Naples yellow bound with egg yolk to attack by the gas.
- 1990 Vieillemand mentions the gas.
- 1993 cf. hydrogen cyanide.

Present Day

Because of its detrimental effects on certain materials relevant to cultural property, hydrogen phosphide is scarcely used anymore in Western and

Central Europe. Mixtures of phosphine and either nitrogen or carbon dioxide are used for the preservation of materials and supplies.

Advantages/Disadvantages

Hydrogen phosphide is highly toxic and produces a high mortality rate among all insect stages, but it has no preventive effects. It is easy to use, but compared with other reactive fumigants requires longer exposure times. Out-gassing from wood is faster than with hydrogen cyanide. Concentrations which are too low can lead to development of insect resistance. The gas is very corrosive to metals.

8.2.1.4

Sulfuryl Fluoride (Sulfuryl Difluoride)

Short designation: SF

Trade name: Vikane (USA); Altarion Vikane, for 99.0–99.7% sulfuryl fluoride (Germany)

Formula: SO_2F_2

Properties: Colorless, non-flammable, odorless gas; the technical gas contains chloropicrin as a warning indicator; m.p. -135.8°C ; b.p. -55.2°C ; vapor pressure 1.55 MPa at 20°C , 1.789 MPa at 25°C ; density 3.52 times that of air; solubility in water is 0.75 g/l at 25°C and 101.3 kPa, somewhat soluble in acetone and chloroform. The technical gas contains chlorine, hydrogen chloride, hydrogen fluoride, sulfur dioxide, hydrogen sulfide, and thionyl fluoride as impurities

Toxicology: Highly toxic; irritates eyes, respiratory organs and the skin, and has suffocating effects. It is not absorbed through the skin and is less toxic to warm-blooded animals than bromomethane. To date no indication of carcinogenic effects. It is damaging to aquatic life because of its low pH value. Does not affect ozone, but contribution to acid rain possible by way of hydrolysis

Biological effects: Sulfuryl fluoride is an insecticide; it is more toxic to larvae, pupae, and adults but less toxic to eggs than bromomethane. In insects it acts by disrupting the glycolysis cycle. Its fungicidal effect has not been sufficiently investigated. It inhibits activity of *Aspergillus niger*, *A. flavus* and *Penicillium* spp. but is less effective than ethylene oxide. Spores will survive exposure (Derrick et al. 1990). The oak wilt fungus *Ceratocystis fagacearum* can be

killed, but other fungi (e.g. *Trichoderma* spp. and *Penicillium* spp.) and bacteria will survive (Schmidt et al. 1997)

Application: Used against wood-destroying insects. The gas is introduced from steel cylinders; liquid SF must not come into contact with objects. Recommended dosages: 15–60 g/m³ for 24 h at 20°C (Brokerhof 1989); in buildings 36 g/m³ for 162.5 h at 6–9.5 $^\circ\text{C}$ (Binker 1993b); against house longhorn beetle 7 g/m³ and against Anobiidae 21 g/m³ for 72 h at 20°C (Binker 1995a). Maximum permissible concentration is 35 g/m³ in Germany. To kill insect eggs the dosage must be raised or the exposure time extended (Williams and Sprenkel 1990). The minimum temperature is 6–12 $^\circ\text{C}$. Sulfuryl fluoride penetrates hardwoods and softwoods faster than bromomethane, even through paint layers. It will desorb in 4–6 h compared with a minimum of 12 h for bromomethane. SF is disposed of using scrubbers with alkaline solutions (e.g. of sodium hydroxide or soda). Against wood-destroying fungi: specifically the oak wilt fungus, in stacks under tents of nylon film; dosage 280 g/m³, c $\times$ t product: 27,400 g $\times$ h/m³ (Schmidt et al. 1997) Temperature range: 10–20 $^\circ\text{C}$

Analysis: By fumiscope (measurement of thermal conductivity)

Uses

Historical

- 1950–1955 The Dow Chemical Company develops SF for fumigation (Schneider 1993).
- 1957 Kenaga tests SF against various developmental stages of 14 insect species, and Stewart uses it to control dry-wood termites.
- 1963 Straub mentions the gas to control wood-destroying insects in works of art.
- 1978 Mori and Arai list SF as a fumigant against wood-destroying insects. Renshaw-Beauchamp describes the use of the substance in remedial treatments of cultural property.
- 1985 According to Arnold, SF should be preferred to bromomethane for cultural property, but should not be used at high temperature or high relative humidity. Tang et al. fumigate insect-infested, tropical hardwoods with 40 g SF/m³ for 48 h or 60 g SF/m³ for 60 h. In both cases 100% mortality was achieved.
- 1989 Brokerhof reviews publications on SF to date.
- 1990 Baker et al. note changes in materials relevant to cultural property following exposure to technical SF at a dosage of 15–36 g/m³. Overview of SF use published by Derrick et al.

- 1991 Lignocellulosic materials are attacked by technical SF but not by purified SF (Burgess and Binnie).
- 1992 First fumigation with SF of a church infested with Anobiidae in Germany (Binker 1993b). Compared with bromomethane, more SF diffuses per unit of time through hardwood and softwood (Scheffrahn et al.).
- 1993 Conference "Fumigation as a means of wood pest control" in Munich, Germany. Emmerling (1995) describes the material changes caused by SF, and Unger (1995) compares bromomethane and SF. Ten of 11 tested pigment systems are affected negatively by technical SF (Koestler et al.). Schneider comprehensively describes the application technology and the biocidal properties of SF.
- 1994 Binker describes technical innovations of SF fumigation, and Binker and Binker obtain a patent for the removal of SF after fumigation.
- 1995 The addition of 10% carbon dioxide to SF permits a reduction in dosage for control of termites (Scheffrahn et al.).
- 1996 Eggs of stored-materials pests are killed with an application of 35 g/m³ for 24 h at 20°C (Drinkall et al.).
- 1997 Control of the oak wilt fungus with the gas (Schmidt et al.).

Present Day

Sulfuryl fluoride is increasingly used for the fumigation of buildings because of plans to discontinue the use of bromomethane worldwide.

Advantages/Disadvantages

Sulfuryl fluoride has good insecticidal effectiveness; compared with bromomethane it is more effective against all insect stages except the egg stage. It has fungistatic effects (*Aspergillus* spp., *Penicillium* spp.) and acts as a fungicide (oak wilt fungus). It performs well with respect to penetration, diffusion, and desorption, especially when compared with bromomethane. Sulfuryl fluoride is highly toxic, but less damaging to the environment than bromomethane. Technical SF corrodes many materials, but even purified SF causes changes in some materials. The addition of carbon dioxide to SF produces a synergistic effect in the control of insect pests. SF fumigation of buildings housing bats are possible when the animals are in their winter quarters (e.g. October/November, March/April; Binker 1995b).

8.2.2

Gases of Low Reactivity and Inert Gases

Wood-destroying insects require oxygen for their life processes, but because of their tracheal respiration they can subsist on small amounts of oxygen. Nevertheless, it is possible to inhibit their development or to exterminate them by changing the air they respire, which normally consists of 78.09%

nitrogen, 20.95% oxygen, 0.93% rare gases, and 0.03% carbon dioxide, on a volume basis. So-called controlled or modified atmospheres are produced by the following methods:

1. Reduction of the oxygen concentration by:
 - a. Use of oxygen absorbers,
 - b. Displacement of oxygen by repeated purging with nitrogen or argon,
 - c. Withdrawing the respiration air, burning off the oxygen, and re-introducing the resulting nitrogen atmosphere.

The nitrogen content of the controlled atmosphere must be above 99% by volume in order to kill the insects.
2. Raising the carbon dioxide concentration.

The carbon dioxide concentration of the modified atmosphere must be above 60% by volume in order to guarantee destruction of the insects by acidification of their blood (hemolymph) and by suffocation.
3. Use of inert gas mixtures.

Production of oxygen-poor atmospheres by displacement with mixtures of carbon dioxide and nitrogen.

Temperature, relative humidity, and pressure influence the fumigation time and the killing effect. Insect pests are exterminated faster and with more certainty the higher the temperature and the pressure and the lower the relative humidity. Pests of stored products and materials, the various species and their developmental stages require different fumigation parameters. Fungal mycelium will not be killed by controlled or modified atmospheres, but merely have their growth inhibited. Spores are also not destroyed, but their germination is prevented.

8.2.2.1

Carbon Dioxide

Trade name:	Altarion Carbo-Gas (Germany)
Formula:	CO ₂
Properties:	Colorless, incombustible gas with a slightly acidic odor and taste; m.p. -56.6°C at 0.52 MPa; b.p. -78.5°C; density 1.9768 g/l or 1.529 times that of air; solubility 0.870 l gas/l of water at 20°C
Toxicology:	At a concentration of >4% in the air being breathed headaches occur; 8–10% leads to loss of consciousness and death by respiratory stoppage under cyanosis; 20% causes instant paralysis and death. The gas is one of the reasons for the greenhouse effect on earth

Biological effects: Carbon dioxide is an insecticide effective against larvae, pupae, and adults of wood-destroying insects, but is a weak ovicide. The gas acts initially as an anesthetic; an increase in the partial pressure of CO_2 in the blood leads to stimulation of the respiratory musculature (respiratory analeptic) and to hyperventilation. Finally the hemolymph becomes excessively acidified. Carbon dioxide has fungistatic effects by inhibiting mycelial growth and suppressing spore germination

Application: Used against wood-destroying insects via exposure in portable tents of plastic film (bubbles), plastic film chambers which can be dismantled, stationary containers or chambers, and buildings (Fig.8.1). The CO_2 is introduced from gas cylinders and must first be humidified. The concentration should be $>60\%$ but $<100\%$, by volume. Exposure time, depending on the species to be controlled and its developmental stage, and the room temperature will range from 14–28 days. Low levels of relative humidity and material moisture content are advantageous for exterminating the pests and to prevent corrosion processes. The gas will penetrate wood more slowly the higher its moisture content, and high moisture content will also delay the desorption of the gas. However, care must be taken that the relative humidity is not too low to avoid wood shrinkage which could damage the object to be treated. Portable objects can be treated in pressure vessels with CO_2 to shorten the exposure time (Binker 1993a)

Analysis: Gas detection tube, CO_2 sensors

Uses

Dry Wood

Historical

- ~ Carbon dioxide formed naturally during storage of grain supplies has been used to control pests for centuries (Pinniger 1990).
- 1985 Story describes the use of gases found in the atmosphere to control pests in museums. At a CO_2 concentration of 60%, all developmental stages of most insect pests should be exterminated within 4 days at a temperature of 21°C .
- 1987 According to Paton and Creffield, larvae of *Hylotrupes bajulus* and *Lyctus brunneus* survived a 7-day treatment with 100% CO_2 . Three termite species, however, were exterminated at 30, 60 and 80% CO_2 . *Ste-*

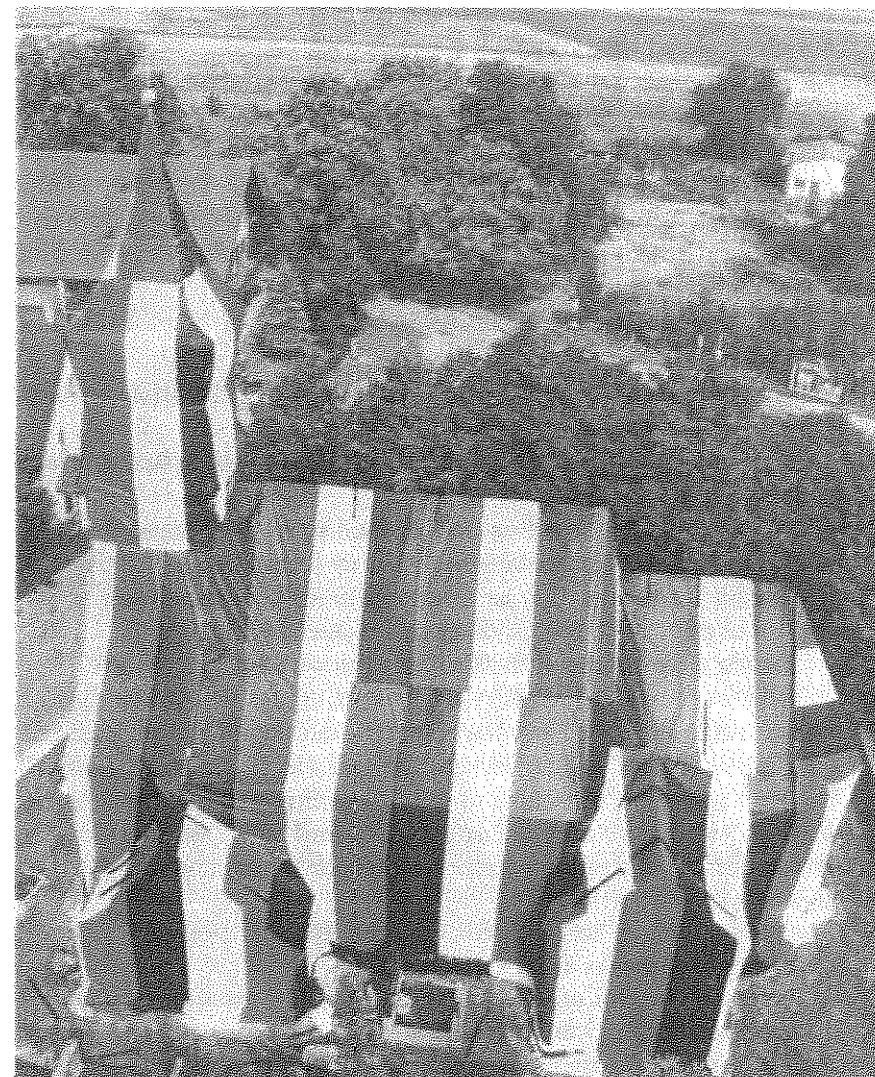


Fig.8.1. Fumigation of a church with carbon dioxide. (Photograph courtesy of G. Binker)

gobium paniceum died after 10 days in air with 35% CO_2 . Three days of CO_2 treatment causes no pH changes or deleterious effects in paper, bark and tanned goat skin (Sanders).

- 1988 According to statements of the Rentokil company, most pests of stored products and materials (including *Anobium punctatum*, among others) are exterminated within 14 days with 60% CO_2 (Smith).

- 1989 Adler and Reichmuth investigate the effectiveness of CO₂ against pests of stored products. Brokerhof presents an overview of the use of atmospheres modified with CO₂.
- 1991 An infestation of art objects with *Anobium punctatum* is eliminated within 14 days by CO₂ at 35°C (Smith and Newton).
- 1992 According to Valentin et al., insect pests of the families Cerambycidae and Anobiidae with a long generation period are very resistant to CO₂. Mixtures of 90% nitrogen and 10% carbon dioxide do not show any clear improvement in the control of *Hylotrupes bajulus* and *Anobium punctatum*.
- 1992/1993 Piening investigates the diffusion behavior of carbon dioxide and nitrogen in wood.
- 1993 Pressure fumigation of a polychromed wood sculpture with CO₂ (Binker 1993a).

First fumigation in Europe of an entire church with CO₂ by the Binker company (Hering 1994).

Binker (1995a), Emmerling (1995), and Unger (1995) report on CO₂ at a conference on control of wood pests by fumigation.

Newton introduces CO₂ as a substitute for bromomethane in the control of pests of stored products and materials.

Piening tests the compatibility of the gas with painted objects.

Valentin compares the effect of nitrogen, argon, and carbon dioxide on various insect pests and their respective developmental stages. Some Coleoptera species (e.g., *Hylotrupes bajulus* and *Anobium punctatum*) show an increased resistance to CO₂. To exterminate old larvae of *H. bajulus*, 3 weeks are required at 60% CO₂ and 30°C. Moisture loss by larvae during fumigation accelerates their extermination and leads to shorter exposure times.

- 1994 For fumigations of large spaces, concentrations of >60–65% CO₂ are necessary for 3 weeks at 20°C (Hering).

Review of control of insect pests in works of art with nitrogen or carbon dioxide (Reichmuth et al.).

- 1995 Carbon dioxide as synergist in mixtures with bromomethane or sulfuryl fluoride (Scheffrahn et al.).

- 1996 Controlled heat treatment of art objects including the use of nitrogen and carbon dioxide mixtures (Nicholson and von Rotberg). Protection of pigments and binders by the reduced CO₂ content.

Adding 5% CO₂ to a nitrogen atmosphere reduces the fumigation time of various pests of stored products and materials (Reierson et al.).

- 1997 Destruction of textile pests in a museum storage area with CO₂ (Brand and Wudtke).

- 1998 Selwitz and Maekawa report results of insect control in cultural property with CO₂ in the USA, Canada, and Germany.

- 1999 Binker describes the great technical efforts required for CO₂ fumigation of buildings.

Present Day

Carbon dioxide is the preferred fumigant for built-in works of art and cultural property (including buildings) where nitrogen or argon cannot be used. Also used as fumigant in plastic film tents (bubbles) and for pressure fumigation of individual objects in stationary equipment.

Waterlogged Wood

Carbon dioxide is not used to fumigate waterlogged wood, but is used for supercritical drying (SCD). It also serves in the supercritical state for the impregnation of wood with PEG (cf. Chap. 11). Prior to drying with CO₂ it is necessary to exchange the water in the wood (e.g., methanol).

Advantages/Disadvantages

Carbon dioxide has insecticidal effects on pests of stored products and materials, but it is not effective against wood-destroying fungi. When used at a concentration of 60–70% CO₂, a residual oxygen content of about 6–8% is tolerated, which is an advantage over nitrogen or argon fumigations. For controlling wood-destroying insects in particular, long exposure times (3–4 weeks) are required. Carbon dioxide is less expensive than nitrogen or argon and special licenses are not required. Requirements for gas permeability of the plastic films are less stringent than for nitrogen or argon. The dry gas must be humidified. There is danger of suffocation if ventilation after fumigation is insufficient. High levels of relative humidity and material moisture content may lead to attack on paint and certain other materials.

8.2.2.2

Nitrogen

Trade name:	Altarion Nitrogeno Gas (Germany)
Formula:	N ₂
Properties:	Colorless, incombustible gas without odor or taste; m.p. –209.86°C; b.p. –195.8°C; mass of 1.2505 g/l; density 0.967 times that of air; solubility 0.0156 l gas/kg water
Toxicology:	At concentrations >80% nitrogen causes daze, nausea, loss of consciousness, and death by suffocation. In small rooms with poor ventilation loss of consciousness can occur within seconds. Installation of an oxygen monitor with alarm is therefore to be recommended.

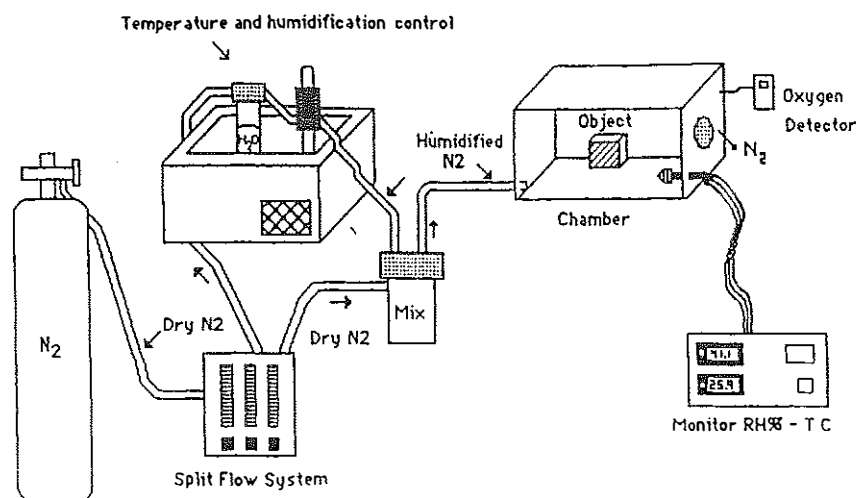


Fig.8.2. Method of nitrogen treatment. (After Valentin and Preusser 1990)

No effect on the environment of which it is a major constituent

Biological effects: Insecticide, effective against larvae, pupae and adults of wood-destroying insects, but a weak ovicide. Nitrogen causes death by dehumidification and suffocation. For fungal pests of wood, mycelial growth is inhibited and spore germination is suppressed, but fungi are not killed off

Application: Exposure in portable tents of plastic film (bubbles), plastic film chambers which can be dismantled, and stationary containers or chambers. Nitrogen is dispensed from gas cylinders, containers with liquid nitrogen, or nitrogen generators with molecular sieves or hollow fibers. Dry gas must be humidified (Fig.8.2). N_2 concentration in the fumigation space must range from 99.0–99.98% by volume. Exposure time for wood-destroying insects, at 20°C and 0.03% residual oxygen is 7–20 days, depending on species. The lower the residual oxygen concentration and relative humidity or the higher the temperature, the shorter the fumigation time. Diffusion is affected less by wood moisture content than in the case of carbon dioxide

Analysis: During fumigation indirectly by measuring residual oxygen concentration with sensors

Uses

Dry Wood

Historical

Antiquity Hermetically enclosed grain stores deplete the oxygen; any insect pests present fail to survive (Levinson and Levinson 1990).

Since ca. 1860 Nitrogen is mentioned as a control substance (Koestler 1993).

Since ca. 1960 Use of nitrogen to control insects in the preservation of stored products (Koestler 1993).

1985 Bibliography by Story on pest control in museums, including the use of inert gases from the atmosphere for the preservation of stored products and materials.

1989 Overview by Brokerhof. Use of controlled nitrogen atmospheres in museums (Gilberg).

1990 Description of properties and use of the oxygen absorber AGELESS [mixture of activated iron(II) hydroxide and potassium chloride, which takes up oxygen under formation of iron(III) hydroxide] to produce inert atmospheres for the destruction of insect pests in museums (Gilberg).

Exterminating termites (*Cryptotermes brevis*) in wood (Valentin and Preusser) and in books infested with *Anobium punctatum* (Valentin) by displacing oxygen with nitrogen.

Inhibiting growth of microorganisms on parchment in a nitrogen atmosphere with low relative humidity (Valentin et al.). Storage of valuable documents and objects in protective atmospheres.

1991 Gilberg investigates the effectiveness of oxygen-poor atmospheres (0.4% O_2 , 30°C, 3 weeks) on various developmental stages of important museum pests.

Fumigation of insect-infested sculptures by flooding with nitrogen in a plastic bag, utilizing larvae of wood-destroying insects enclosed inside test samples to monitor the results (Reichmuth et al.).

1992 2nd International Conference on Biodeterioration of Cultural Property (Proceedings 1993) with contributions on controlled atmospheres by Gilberg and Roach (application of AGELESS; 1993a), Hanlon et al. (dynamic nitrogen treatment of large objects), Maekawa et al. (display cases with inert gas), and Unger et al. (effect of temperature on the control of wood-destroying insects with nitrogen).

Contribution to the reaction kinetics of AGELESS in closed containers and its suitability for the production of oxygen-poor atmospheres in display cases (Lambert et al.).

Compared with carbon dioxide, nitrogen and argon are more effective for the control of wood-destroying insects (Valentin et al.).

1992/1993 Report on the diffusion of nitrogen through wood (Piening).

- 1993 Conference on control of wood pests by fumigation; Binker (1995a), Emmerling (1995), and Unger (1995) report on use of N_2 as fumigant, and Gilberg and Roach (1995) report on AGELESS.

Description of various technologies for producing oxygen-deprived atmospheres (anoxia) for control of insects, and data on plastic films with low permeability to oxygen (Daniel et al.).

According to Gilberg and Roach (1993b), at least 12 days at 0.4% residual oxygen content, 30°C, and 70% relative humidity are required to kill all developmental stages of *Lyctus brunneus* in wood.

Koestler et al. cannot detect any visible changes in pigment/binder systems caused by exposure to nitrogen.

Control of organic-material pests with fumigation by nitrogen flooding (Reichmuth et al.).

According to Rust, 72h are required to destroy dry-wood termites in wood blocks at a residual oxygen content of 0.1%. The role of moisture loss in extermination is pointed out.

Nitrogen acts more slowly on insect pests than argon (Valentin).

- 1994 Nitrogen as a remedy for cultural property of wood infested with insects (Reichmuth et al.).

- 1995 Review by Hanlon and Daniel (1998) on the use of modified atmospheres against wood-destroying insects in panel paintings.

- 1996 Description of reusable fumigation tents made of laminated films for the control of pests with nitrogen, including information on the calculation of the required amount of nitrogen (Maekawa and Elert).

Combination of controlled heating and use of modified atmospheres (Nicholson and von Rotberg).

According to Reiersen et al. and Rust et al., some species of insects, including the Lyctidae, can tolerate oxygen deficiency for extended periods.

- 1997 Contributions to the technical aspects of nitrogen fumigation by Binker et al. and Elert and Maekawa.

- 1998 Comprehensive exposition by Selwitz and Maekawa on the use of inert gases against insect pests in museums, including biological mechanisms, materials and treatment methods as well as the construction of fumigation chambers and tents.

- 1999 Nitrogen fumigation of two anobiid species (*Anobium punctatum* and *A. fagi*) by Despot et al.

Review by Maekawa of control of insects in nitrogen atmospheres and by use of low temperatures.

Present Day

Nitrogen is used as an inexpensive, inert gas for the gentle control of active insect infestations in museum objects. It can also be used for infested built-in works of art, such as altars, but not for buildings.

Waterlogged wood

Nitrogen is not used as a fumigant but finds application in freeze-drying at atmospheric pressure and for controlled drying of the wood (cf. Chap. 11)

Advantages/Disadvantages

When nitrogen is used properly, insect pests are destroyed completely, but fungi are not killed. However, growth rates of fungi and wood decomposition are reduced (Kazemi et al. 1998). It is an inexpensive inert gas, and easy to use since there are no licensing or reporting requirements. Technological limitations, i.e., the concentration requirement of >99% by volume, make it unsuitable for the fumigation of buildings. Continuous monitoring is necessary to guarantee the stability of the fumigation system and to prevent the ingress of oxygen. Humidification of the gas and climate control inside the fumigation space are necessary. For the control of wood-destroying insects, longer exposure times (2–4 weeks) will be required, depending particularly on temperature. There is danger of suffocation if nitrogen is allowed to escape in poorly ventilated rooms. Until now there is no evidence of detrimental changes in paint materials. Nitrogen fumigation is not preventive.

8.2.2.3

Argon

Formula:	Ar
Properties:	Colorless, incombustible gas without odor or taste; m.p. -189.2°C ; b.p. -187.5°C ; density 1.7837 g/l or 1.38 times that of air; solubility 52 ml Ar/l water at 0°C
Toxicology:	Suffocating in very high concentrations; compatible with the environment
Biological effects:	Effective against all developmental stages of wood-destroying insects, but also against pests of stored materials. Argon acts faster than nitrogen. Insect pests suffocate, but argon has no fungicidal effect
Application:	Exposure in plastic bags, plastic film tents (bubbles), containers, or vacuum fumigation chambers. Argon is introduced from gas cylinders. Humidification of the dry gas is necessary. Required argon concentration in the fumigation space is 99.9–99.97% by volume. Exposure time for wood-destroying insects at 20°C and 0.03% residual oxygen content is 5–14 days, depending on the species. The influence of fumigation parameters is the same as for nitrogen. Wood moisture content has less effect on diffusion of argon than of carbon dioxide

Analysis: By spectroscopy; during fumigation indirectly by measuring residual oxygen concentration with sensors

Uses

Historical

1985 Bibliography by Story with recommendations for the use of rare gases against stored-material pests.

1992 Instructions by Koestler for fumigation with argon of museum objects.

Compared with carbon dioxide, nitrogen and argon are more effective for the control of insect species with a long generation period (Valentin et al.).

1993 Koestler monitors the activity of insect pests before and after argon fumigation by measuring the CO₂ content in the fumigation chamber with FTIR spectroscopy.

Compilation of data on the argon fumigation of wood-destroying organisms (Unger 1995).

Detailed testing of the effects of argon atmospheres on insect pests found in museums and archives (Valentin). Exposure time is reduced markedly compared with nitrogen and carbon dioxide.

1998 Report by Selwitz and Maekawa (cf. nitrogen).

Present Day

Because argon is gentle on materials it is used to control insect pests in especially valuable, unique objects such as paintings and sculptures.

Advantages/Disadvantages

At equal levels of residual oxygen content, temperature and relative humidity, argon is more rapidly effective against insect pests than nitrogen. Under practical conditions argon is not fungicidal. The high gas concentration required of 99.9% or more makes argon unsuitable for fumigating buildings. Argon is more expensive than nitrogen; therefore it is preferably used for particularly delicate and valuable art objects. Care must be taken in small rooms with insufficient ventilation. The gas is heavier than air and can cause suffocation. Argon has no preventative effects against insects. It poses no danger to the environment. The dry gas must be humidified in order to prevent damage to objects by drying.

8.3

Organic Fumigants

8.3.1

Carbon Disulfide

Formula: CS₂

Properties: Colorless, somewhat volatile liquid; in its pure form it has an aromatic odor, which becomes unpleasant through impurities. Turns yellow on exposure to light. Extremely combustible; forms explosive mixtures with air in the range of 1–60% by volume. m.p. –111.6°C; b.p. 46.3°C; vapor pressure 36.3 kPa; density 2.67 that of air; low solubility in water (2 g/l), dissolves well in ethanol, ether, benzene, tetrachloromethane, chloroform and essential oils

Toxicology: Highly toxic; primarily affects the nervous system. Contact of the liquid with the skin or mucous membranes causes strong irritation, burning, reddening, and possibly skin defects. Inhaling the vapor leads to mucous membrane irritation, restlessness, vision impairment, nausea, vomiting, headaches, loss of consciousness and paralysis of respiration. Prolonged inhalation also leads to joint pains and muscular weakness

Biological effects: The vapors act as an insecticide

Application: Used against wood-destroying insects (Coleoptera) in fumigation chests or chambers, or in polyethylene bags. Dosage is 28 g/m³ air space for 2–3 weeks (Plenderleith 1956). Open containers (bowls) with the liquid are placed into the fumigation space above the objects to be treated. The carbon disulfide vapors, being heavier than air, sink to the bottom and kill the insects. After 1 week the carbon disulfide is replenished

Analysis: Detection tubes; carbon disulfide reacts with diethylamine in the presence of a copper salt to form the characteristic yellowish copper[di-(ethyl-dithiocarbamate)]

Uses

Historical

ca. 1907 Use of carbon disulfide in “poison boxes” (Aberle and Koller 1968).

1924 Rathgen recommends the following: 150–200 g CS₂/m³ air space in bowls distributed with the objects inside an air-tight box and left for 3–4

weeks. For polychromed wood sculptures, the air should first be displaced with dry carbon dioxide.

- 1956 Plenderleith lists carbon disulfide among the substances for control of wood-destroying insects. Carbon disulfide reportedly does not attack paint layers on picture frames. For unpainted art objects he recommends a mixture of carbon disulfide and tetrachloromethane in the ratio of 1:4.
- 1963 According to Straub, carbon disulfide vapors can attack varnishes and paints.
- 1968 Prussic acid is more effective against wood-destroying insects than carbon disulfide (Aberle and Koller).
- 1986 Overview of the properties of carbon disulfide, and its advantages and disadvantages as a fumigant (Unger and Unger).

Present Day

Carbon disulfide is practically no longer used for control of wood-destroying insects because of its disadvantageous chemical and toxicological properties.

Advantages/Disadvantages

Insufficient effectiveness against wood-destroying insects, and no preventive effects. It attacks various materials because of its solubility and reactivity. It is very toxic to humans and the environment, and dangerous because it is combustible and forms explosive mixtures.

8.3.2

Carbonyl Sulfide (Carbon Oxysulfide)

Formula:	COS
Properties:	Colorless gas; odorless in its pure state but otherwise malodorous; ignites easily; m.p. -138°C ; b.p. -50.2°C ; density 1073 kg/m^3 ; solubility 1.4 g/l water at 25°C
Toxicology:	A poison which is an anesthetic at high concentrations, and an irritant. Can hydrolyze with traces of water to form very toxic hydrogen sulfide and carbon dioxide. Reportedly the gas, unlike bromomethane, effects no changes in the environment
Biological effects:	Carbonyl sulfide is an insecticide
Application:	Against termites (nymph stage): $288\text{ mg h}^{-1}\text{ l}^{-1}$ at 30°C or $600\text{ mg h}^{-1}\text{ l}^{-1}$ at 27°C for 24 h. Fumigation in closed glass containers with a relative humidity of 55–60% (Desmarchelier 1994)
Analysis:	GC

Uses

Historical

- 1867 Discovery of the gas (Zettler et al. 1997).
- 1957 The properties of carbonyl sulfide are intermediate to those of carbon disulfide and carbon dioxide (Zettler et al. 1997).
- Ca. 1993 Carbonyl sulfide is patented as a fumigant for stored materials (Zettler et al. 1997).
- 1994 Desmarchelier publishes an overview of properties and potential applications of carbonyl sulfide in insect control.
- 1997 Investigation of gas diffusion, adsorption and desorption of bromomethane and carbonyl sulfide in wood (Ren et al.). Carbonyl sulfide penetrates wood better than bromomethane and is adsorbed less by wood.

Present Day

Carbonyl sulfide is being tested as a substitute for bromomethane for the protection of stored products. It also has possibilities for the control of insect pests in wood. However, changes must be expected in painted objects.

Advantages/Disadvantages

Probably effective against wood-destroying insects, and inhibits fungal growth. It is less damaging to the environment than bromomethane and has better penetration, adsorption and desorption properties in wood. Carbonyl sulfide would probably attack materials relevant to cultural property.

8.3.3

Tetrachloromethane (Carbon Tetrachloride)

Short designation: Tetra

Trade name:	Dowfume 75, for tetrachloromethane/ethylene dibromide, 30:70 (USA)
Formula:	CCl_4
Properties:	Colorless, volatile, incombustible liquid; m.p. -22.9°C ; b.p. 76.7°C ; vapor pressure 11.6 kPa at 20°C ; density of the vapor 5.3 times that of air; barely soluble in water (0.8 g/l), readily soluble in ethanol, ether, chloroform, benzene, gasoline, essential and fatty oils. Solvent for fats, oils, and resins
Toxicology:	Tetrachloromethane is a highly toxic cell poison which mainly affects liver and kidneys. It is absorbed readily

through the skin, which loses its fat. Concentrated vapors lead to loss of consciousness and respiration stoppage. Lesser concentrations lead to indisposition, headaches, nausea, dizziness, and loss of consciousness. Alcohol increases the effect. Carcinogenic potential is suspected

Biological effects: The vapors are insecticidal

Application: Specific data are lacking, but against wood-destroying insects (Coleoptera) the application should be similar to carbon disulfide, although higher doses may be required because of reduced effectiveness. Direct spraying of the substance into exit holes is also being used

Analysis: GC

Uses

Historical

- ca. 1907 Use in "poison chests" (cf. carbon disulfide).
- 1916 Bolle notes that compared with carbon disulfide, tetrachloromethane is significantly less effective. About five times the concentration and exposure time are needed.
- 1924 Rathgen also points out the lower effectiveness of tetrachloromethane, but notes the advantage of incombustibility.
- 1956 Mixture of carbon disulfide and tetrachloromethane for fumigation (cf. carbon disulfide).
- 1968 Aberle and Koller mention tetrachloromethane.
- 1983 According to Fey a minor anobiid infestation can be controlled by spraying tetrachloromethane into exit holes.
- 1987 Treatment of an insect-infested chest with tetrachloromethane vapors in a fumigation chamber (Petrovszki).

Present Day

Only occasional use for small infestations. In addition to tetrachloromethane, trichloroethene (trichloroethylene) and tetrachloroethene (perchloroethylene) are also used (Sutter 1986).

Advantages/Disadvantages

Tetrachloromethane is insufficiently effective against wood-destroying insects. As a solvent it attacks various materials and also effects corrosion processes. It is chemically unstable and highly toxic but, unlike carbon disulfide, it is incombustible.

8.3.4

Bromomethane (Methyl Bromide)

Short designation: MeBr

Trade name: Dow-Fume MC-2 (USA), Meth-O-Gas, Terr-O-Gas, Maltos (Canada), Altarion-Mebrofum, Detia Gas Ex-M, Haltos, Rabasan, Zedesa-Methylbromid (Germany), S-Gas (Switzerland), ISRAEL BROMINE (Israel), EKIBON, for a mixture of ethylene oxide and bromomethane, 13:87 (Japan)

Formula: CH_3Br

Properties: Colorless, incombustible gas, odorless in its pure form, otherwise odor similar to chloroform or ether; m.p. -93.6°C ; b.p. 3.6°C , other report 4.5°C ; vapor pressure 189.3 kPa at 20°C , other reports 161 kPa at 25°C , 227 kPa at 25°C ; density 3.27 times that of air; solubility is 13.4 g/l water at 25°C ; readily soluble in ethanol and ether

Toxicology: Bromomethane is highly toxic. The vapors greatly irritate eyes, respiratory tract, lungs (lung edema possible) and the skin. Resorption through the skin. It damages the central nervous system (neurotoxin); the liquid causes severe inflammation and blisters on the skin. Toxic concentrations cannot be detected by smell. There is reason to suspect carcinogenic effects. Bromomethane damages the environment (destruction of the ozone layer)

Biological effects: Bromomethane is effective against all developmental stages of wood-destroying insects, including good ovicidal effects. It acts by methylation of enzymes containing-SH groups. The addition of small amounts of carbon dioxide stimulates respiration and increases the toxic effect of bromomethane. Killing of the mycelium of brown rotters such as *Serpula lacrymans* is possible. Spores are sterilized only at very high dosages; mold fungi and their spores can also be controlled. In fungi it probably acts by direct chemical attack on the cell substance (cytoplasm), with the following possible reactions: N-methylation of amino acids, proteins, and also attack on aminomercapto-carbonic acids, e.g., cysteine

Application: Bromomethane fumigations are carried out in gas-tight film tents (bubbles), atmospheric and reduced pressure chambers, and buildings. The gas is dispensed from steel cylinders (Fig. 8.3). Dosage against wood-destroying

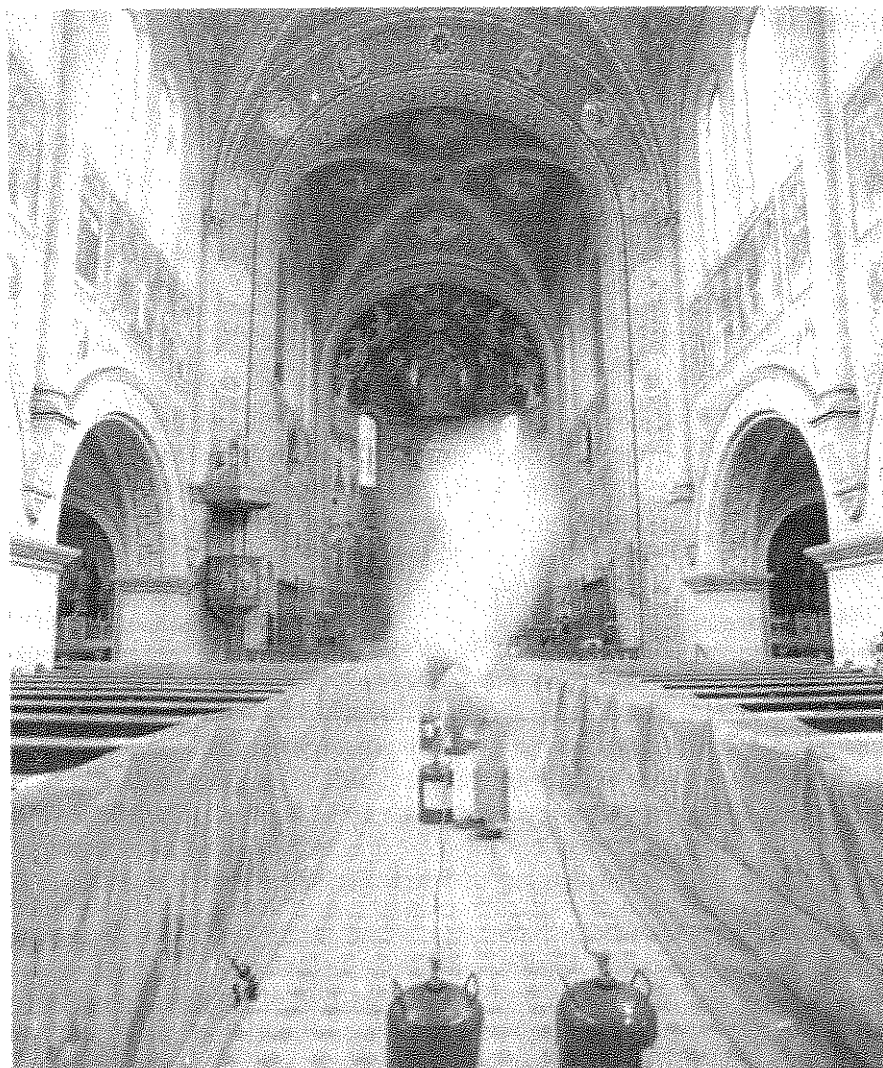


Fig.8.3. Fumigation of a church with bromomethane from steel cylinders. (Photograph courtesy of G. Binker)

insects in buildings is $20\text{--}60\text{ g/m}^3$ with exposure times of 24–72h, in reduced-pressure chambers $16\text{--}20\text{ g/m}^3$. Against fungi (Basidiomycete mycelium) the dosage in buildings is $30\text{--}50\text{ g/m}^3$, with an exposure time of about 96h. In order to kill spores, about ten times the dosage is required. Minimum temperature for fumigating buildings is about 4°C , but temperatures $>12^\circ\text{C}$ are advantageous.

The gas must be circulated during fumigation because it is heavier than air. Relative humidity and material moisture content should be in the lower to medium range. Fumigated buildings must be ventilated at least 12 h in Germany and 72 h in the USA, because desorption of the gas is relatively slow

Analysis: Generally by fumiscope (measurement of thermal conductivity of the air), and gas detection tubes. Leaks can be detected with a gas-test lamp (halogen detector based on the Beilstein test)

Uses

Dry Wood

Historical

- 1932 Discovery of the insecticidal effect of MeBr by Le Goupil (Grosser 1975).
 - Since ca. 1950 MeBr is used especially in England, Denmark, USA, Australia, New Zealand and Japan to control wood-destroying insects including termites.
 - 1954/1955 Mori and Kumagai investigate the effects of the gas on metals and pigments.
 - 1956 Plenderleith recommends MeBr for the extermination of insects in dense woods, where it should penetrate better than prussic acid.
 - 1963 Straub lists changes caused by the gas and recommends the application of a thin coat of varnish or wax to prevent discoloration.
 - 1968 Aberle and Koller describe advantages and disadvantages of the use of MeBr.
 - 1972 Control of *Nicobium castaneum* in a temple gate. The gate is tented with several layers of PVC film, followed by fumigation (40 g/m^3 , 72 h) (Arai et al.).
 - 1975 MeBr as fumigant against wood-destroying insects (Grosser)
 - 1977 Fumigation of registered historical buildings with MeBr in Japan (ca. $50\text{--}55\text{ g/m}^3$, 36h; Mori and Kadokura): 100% of the rice beetles (*Sitophilus zeamais*) used as test insects were killed.
 - 1978 Instructions on the use of Haltox (a bromomethane preparation) at the DEGESCH-Technician conference by Bäumert and Wentzel.
- Contribution to the control of wood-destroying insects with gases including bromomethane in Japan (Mori and Arai).
- Detailed description of a MeBr fumigation by Renshaw-Beauchamp.
- 1982 Improvements in MeBr fumigation of works of art in Japan (Mori and Arai).

Monograph on MeBr by Weller.

- 1983 First fumigation of an iconostasis with MeBr by the Archaeological Service of Greece (Paterakis).
Dissertation by Ruetze on the control of the oak wilt fungus with MeBr.
- 1985 Description of endangerment of materials by MeBr (Story).
Use of the gas to control wood-destroying insects in tropical woods (50 g/m³, 60 h: Tang et al.)
- 1986 Sutter, also Unger and Unger describe the properties and use of MeBr for the fumigation of cultural property.
- 1987 Child and Pinniger list the disadvantages of the gas (toxicity, attack of materials).
- 1988 Overview of fumigants by Becker.
Fumigation of wooden church doors with MeBr (Canuti).
- 1989 Publications by Bauer and by Brokerhof on the fumigation of cultural property with detailed instructions on MeBr.
Fumigation of a polychromed crucifix with the gas in Italy (Castelli and Ciatti).
Ognibeni tests various pigments and binders for their susceptibility to attack by MeBr.
- 1990 Contributions by Linnie on the use of fumigants, including MeBr, in museums and by Vieillemand on the control of wood-destroying insects.
- 1992 Information on the use of the gas in museums (Dawson and Strang).
Comparison of the diffusion of MeBr and SF through wood (Scheffrahn et al.).
Control of *Serpula lacrymans* in buildings with the gas (Unger et al.).
Contribution on control of wood pests (among others by MeBr) at the conference on 'preservation, consolidation, and fills for wood' in Munich, Germany (Unger and Unger 1995).
Fungicidal effects of the gas, and problems of residues (Yulin 1993).
- 1993 MeBr is mentioned at the conference "Fumigation as a means of wood pest control" by Binker (1995a), Emmerling (1995), and Unger (1995).
Experiments on killing off mycelium of various basidiomycetes and ascomycetes with MeBr by Unger and Unger.
- 1994 Fumigation of painted pine panels with MeBr (Howarth).
- 1995 Synergy effect through the addition of carbon dioxide to MeBr for control of termites (Scheffrahn et al.).
- 1999 Miura pleads for limited use of MeBr on cultural property in Japan even after it becomes illegal in 2005.

Present Day

The use of bromomethane has fallen off considerably because, following the Montreal Conference of September 1997 and the Clean Air Act of the USA the stepwise cessation of MeBr use (presently by 1 January 2010; planned for 1 January 2001) has been determined or planned. So far, it is still used to dis-

infect North American oak logs of the oak wilt fungus. Sulfuryl fluoride and iodomethane are being tested as a substitute for bromomethane for log disinfection. Central European wood products are fumigated with MeBr against *Sirex noctilio* for export to Australia and New Zealand (*Sirex* certificate). In Germany MeBr is also used as a supplementary procedure in remedial treatments to control house fungus in registered historical buildings.

Waterlogged wood

- 1981 According to Mori and Arai, remedial treatments with MeBr of underwater cultural property infested by shipworms are possible.

Advantages/Disadvantages

Bromomethane is a good insecticide and also has fungicidal effects. It also kills insect eggs. It is highly toxic and a suspected carcinogen. Relatively long ventilation periods are required. MeBr attacks natural products containing sulfur and other materials. It damages the environment by destroying ozone. Preventive effects are not assured. As the gas is released from its cylinder, a "fog-out effect" – formation of water vapor – can occur, making hydrolysis of the gas and its impurities such as hydrogen bromide possible. The resulting hydrobromic acid causes corrosion of metals and other materials. The gas is heavier than air; care must be taken during fumigation of buildings by providing for circulation during treatment and making certain that ventilation has been adequate before reentering the building at the conclusion.

8.3.5

Ethylene Oxide (Oxirane, 1,2-Epoxyethane)

Short designation: ETO

Trade name: In the USA: Oxyfume; and Penngas for 12% ethylene oxide and 88% dichlorodifluoromethane. In Germany: T-Gas; ETOX for 90% ethylene oxide and 10% carbon dioxide; ETOXIAT for 45% ethylene oxide, 45% methylformiate, and 10% carbon dioxide; Cartox for 10% ethylene oxide and 90% phosphine; In Japan EKIBON for 13% ethylene oxide and 87% bromomethane

Formula: $\begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$

Properties: ETO is a colorless gas with a sweetish odor; m.p. -111 °C; b.p. 10.7 °C; vapor pressure 142.4 kPa; density 1.52 times that of air; dissolves in water without limit, soluble in

ethanol, ether, acetone, and benzene. In water it is slowly changed to glycol; it reacts with alcohols and other compounds with active hydrogen atoms; it can polymerize spontaneously, and forms explosive mixtures with the air. The addition of carbon dioxide reduces the danger of explosions

Toxicology: ETO is highly toxic and carcinogenic. It irritates eyes, mucous membranes, and respiratory organs. On inhalation it causes nausea and vomiting. It pollutes the environment and is dangerous to bees

Biological effects: ETO is an insecticide, a fungicide, and a bactericide. It poisons the protoplasm since ethylene oxide reacts with proteins. In insects the initial effect is anesthetic, and after a recovery phase death sets in. Addition of bromomethane improves the bactericidal effect, while addition of carbon dioxide stimulates respiration of insects and increases the absorption of the poison

Application: Fumigation takes place in stationary, reduced-pressure chambers; mixtures of ETO and carbon dioxide in the ratio of 1:9 can also be used in gas-tight containers at atmospheric pressure. The gas is dispensed from steel cylinders; trichloronitromethane (chloropicrin) and ethylbromoacetate are added as warning indicators

For control of wood-destroying insects in reduced-pressure chambers, dosage is 150–200 mg/m³ for 4–6 h (ETOX, ETOXIAT; Bäumert and Wentzel 1978); 1000 g/m³ for 0.5–2 h at 50–55°C (pure ETO) (Unger et al. 1988); in closed containers with 1:9 mixture of ETO/CO₂ 1000 g/m³ for 12–24 h (Unger et al. 1990)

For control of fungi and bacteria in vacuum fumigation equipment, dosage of ETO mixed with Freon or CO₂ (1:9) is 250–800 g/m³ for 72 down to 1.5 h at a temperature of 20–35°C (Gallo 1975); with 1:9 mixture of ETO/CO₂ in closed containers dosage is 1000 g/m³ for 12 h against Basidiomycete mycelium (Unger et al. 1990). For the control of soft-rot fungi higher dosages are necessary. Minimum temperature for application is 11°C. High relative humidity and material moisture content improve effectiveness, but increase the risk of hydrolysis. Forced circulation of the gas during treatment is necessary since ETO is heavier than air. ETO desorbs slowly from wood and other materials. The fumigation chamber must there-

fore be purged with fresh air up to 30 times in order to attain the threshold limit value (TLV) of 0.5 ppm (USA). Disposal is by catalytic combustion or by gas scrubber

Analysis: Test strips, gas detection tubes, GC

Uses

Historical

- 1928 Discovery of the effectiveness of ETO against insects in foodstuff and in wood by Cotton and Roark.
- 1929 Addition of carbon dioxide improves the effectiveness of ETO (Cotton and Young).
- 1960 Kowalik and Sadurska investigate the effect of ETO on wood-destroying fungi.
- 1963 According to Straub a 1:9 mixture of ETO/CO₂ should kill off *Serpula lacrymans*.
- 1968 Aberle and Koller recommend a 1:9 mixture of ETO/CO₂ from steel cylinders for reduced-pressure fumigation to control insects in wood sculptures.
Smith investigates the effect of wood moisture content during sterilization of wood with ETO and propylene oxide.
- 1970 Dominik et al. kill off larvae of *Hylotrupes bajulus* in old wood with a 1:9 mixture of ETO/CO₂.
The British Museum begins to use a mixture of ETO/CO₂ in a reduced-pressure fumigation chamber (Green and Daniels 1987).
- 1975 Gallo treats books with ETO/Freon or ETO/CO₂ mixtures.
- 1978 DEGESCH-Technician conference. Bäumert and Wentzel report on the use of ETOX and ETOXIAT.
Fumigation of buildings under a plastic film tent with a 87:13 mixture of bromomethane/ETO for the control of wood-destroying fungi, at a dosage of 100 g/m³ (Mori and Arai).
- 1981 ETO is considerably more toxic than previously assumed (Dawson).
- 1982 ETO as sterilizing agent for wood (Clark and Smith).
- 1986 Reports on ETO as a fumigant for cultural property by Sutter, and by Unger and Unger.
Disinfection of museum objects with 1:9 mixture of ETO/CO₂ (Wolinski).
- 1987 Child and Pinniger list the disadvantages of ETO.
The strength of paper is increased by ETO fumigation (Florian).
Report on residue problems of museum objects fumigated with ETO (Green and Daniels).
ETO reacts with textiles treated with Na-PCP (Kleitz).
- 1988 Report by Becker on ETO.
Unger et al. fumigate a wood sculpture infested by *Lyctus* with ETO

1989 Comprehensive description of ETO use for cultural property by Bauer and by Brokerhof.

Ognibeni tests the effect of ETOX on various pigments and binders.

1990 Detailed investigation of the suitability of ETO, alone or in mixtures, for the control of wood-destroying insects and fungi (Unger et al.).

1992 Safety regulations for the use of ETO for museum objects (Dawson and Strang).

Conference "preservation, consolidation, and fills for wood"; report on ETO by Unger and Unger (1995).

1993 Antimicrobial treatment of cultural property with ETO in a reduced-pressure fumigation chamber at a dosage of ca. 600g/m³ (Elmer et al.).

Emmerling (1995) discusses the use of ETO at the conference "Fumigation as a means of wood pest control".

Present Day

Use is sharply decreasing because of the danger of the substance, especially in regard to residues remaining inside treated objects. Occasional use for cultural property infested with mold fungi or bacteria, by fumigation in reduced-pressure equipment.

Advantages/Disadvantages

Fumigants based on ethylene oxide are good insecticides, and also have fungicidal and bactericidal effects at higher dosages. Next to gamma-rays, ETO is the surest means for killing off fungal mycelium and spores, especially of mold fungi. Insect egg stages are also destroyed. ETO is highly toxic and carcinogenic. Mixtures with air are explosive from 2.6%, by volume, of ETO; therefore it must be used undiluted only in vacuum fumigation equipment, and objects must be transported there. Dilution with carbon dioxide, Freon, bromomethane, or phosphine reduces the tendency to explode, and the mixtures can also be used at atmospheric pressure. However, it should be noted that Freon and bromomethane damage the ozone layer. The addition of other gases also increases the effectiveness. The fumigation period is short, but ventilation times are long and repeated purges with fresh air are necessary. Material changes and the formation of toxic residues in the objects fumigated are possible because of the high reactivity of ETO. There is no preventive effect.

8.3.5.1

Additional Compounds: Propylene Oxide

Fumigation of cultural property attacked by pests with pure propylene oxide has been investigated by Yamazaki et al. (1993) and Arai (1995), and with propylene oxide/bromomethane mixtures by Kimura et al. (1993).

8.3.6

Formaldehyde (Methanal)

Trade name: Formalin (35–40% aqueous solution)

Formula: $\text{H}_2\text{C}=\text{O}$

Properties: Colorless, combustible gas with a pungent odor; it forms explosive mixtures with air; m.p. -117 to -118°C ; b.p. -19.2°C , other report -21°C ; density 1.067 times that of air; readily soluble in water, alcohols, acetone, and other polar solvents

Toxicology: Strong caustic and irritant effects on skin, eyes, and the respiratory tract. Possible sensitization through contact with the skin. The gas is a protoplasmic poison, with possible damage to kidneys, liver, and lungs. Inhalation causes severe internal trauma. It is suspected of being a potential carcinogen, and it damages the environment

Biological effects: Formaldehyde is a good microbicide but less effective as an insecticide. Dry formaldehyde does not kill fungal spores. The gas reacts with the amino groups of proteins and inhibits mainly the activity of catalases and dehydrogenases. The insects become paralyzed, affecting the legs and the mouth extremities

Application: In gas sterilizers and fumigation equipment, and by action of formaldehyde vapors, e.g., the low temperature steam with formaldehyde (LTSF) process with a formaldehyde content of 2–3%. Rooms are disinfected by spraying formaldehyde solutions. For the disinfection of objects 4.5% formaldehyde in ethanol or 4.2% formaldehyde in soap solution. Penetration into wood is slow, and good ventilation of fumigated objects is necessary

Analysis: Gas detection tubes; color reaction with chromotropic acid, or the pararosaniline procedure (adsorption on silica gel followed by photometry)

Uses

Dry Wood

Historical

1963 Fumigation of wood infested by insects with formaldehyde vapors is not sufficiently effective (Straub).

- 1975 Treatment of library spaces with formaldehyde by Gallo.
 1988 Review of the use of formaldehyde for wood objects (Unger).
 1989 Report on the technical properties of formaldehyde as they relate to its use as fumigant, by Brokerhof.

Present Day

No application as fumigant.

Waterlogged wood

In the past, aqueous solutions of formaldehyde were added to storage tanks for waterlogged wood to prevent fungal and bacterial attack.

Advantages/Disadvantages

For dry and waterlogged wood the biocidal effect on wood-destroying insects and fungi is not sufficient. Some materials relevant to cultural property are damaged but wood itself is hardly affected. The ability of formaldehyde to penetrate and permeate is not good. It has high affinity for moisture, and does not provide preventive effects.

8.4 Processes

Fumigation processes can be classified either on the basis of exposure location or based on technological procedures. Objects can be fumigated in mobile equipment, such as bags, sacks, pockets, tents (bubbles), and transportable plastic containers, as well as in stationary fumigation chambers or silos of corrosion-resistant metallic materials. A special variation of the fumigation chamber is the treatment of suitably sealed rooms in buildings or an entire building.

Fumigation inside spaces enclosed by plastic film is carried out under atmospheric or slightly elevated pressure to maintain the shape of the enclosure and to prevent the entrance of air. If reactive gases are used, the air inside the tenting is enriched with the gas, but with inert fumigants or those of low reactivity the air is displaced by repeated purging. In stationary fumigation chambers, such as silos, the gas is often circulated inside. Elevated pressure and vacuum fumigations are also possible. In vacuum fumigation the air is first evacuated, followed by drawing in the gas up to atmospheric pressure. The gas may be circulated as well. Vacuum fumigation is very effective and reduces the treatment time significantly. The use of stationary equipment requires transport of the infested objects to the treatment site.

The first consideration for any fumigation treatment is the choice of a suitable fumigant. This will depend on the pest to be controlled, its stage of development, the object to be treated, and the type of space within which the

treatment is to be carried out. Whenever possible, inert gases or those of low reactivity should be used in preference to highly reactive gases (Selwitz and Maekawa 1998). For fumigations, sealing of the fumigation space must be accorded priority because it largely determines if the pests will be exterminated completely, how much fumigant will be used and thereby what the cost of the fumigation will be. In fumigations under plastic film tenting the gas permeability of the film, the tightness of the seams, and of the connectors for gas inlet, gas outlet, sensors etc. play a large role. The oxygen permeability of the films used should be as low as possible. Generally, films with an oxygen permeability of about $50 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1}$ can be considered suitable (Elert and Maekawa 1997). Reichmuth et al. (1994) have compiled data on the gas permeability of various film types. Films of proven suitability are simple and laminated films based on polyvinylidene chloride (Saranex®; Daniel et al. 1993; Valentin 1993), biaxially oriented nylon (coated with PVDC; Gilberg 1990), coextruded ethylvinylalcohol/nylon/ethylvinylalcohol (Koestler 1993), polyethylene terephthalate (Valentin 1990), polychloroethylen (Aclar; Daniel et al. 1993) as well as laminates of low-density polyethylene (LDPE), polyethylene terephthalate and aluminum foil (Newton et al. 1996). The films must also be tear and burst resistant and be well-suited for heat sealing or gluing. Selwitz and Maekawa (1998) give an overview of the films and laminates used to date and their properties.

Small fumigation chambers can be constructed with acrylic sheet about 6-mm thick (Lambert et al. 1992; Rust et al. 1996), and these can be tested for tightness with leak detectors. In buildings which have been tented with plastic film, a pressure test is made. Air is drawn from inside the building until a pressure differential of about 20 Pa between interior and exterior is reached. The air pump is then stopped suddenly, and using a stopwatch and pressure sensors, the half-time to pressure equalization is determined. The half-time is a measure of the tightness of a building and, with careful sealing of the tenting, should be 3.6 s or greater, depending on the enclosed volume (Binker 1995a).

The following parameters must be considered in calculating fumigant quantity: type of pest and its developmental stage, volume and temperature of the fumigation space, tightness of the enclosure, planned concentration and exposure time ($c \times t$ product), wind velocity for buildings and pressure for stationary pressure chambers. The calculated quantity can be reduced by a number of measures, including:

1. Temperature elevation,
2. Increasing the exposure time,
3. Decreasing the interior air space by inserting gas-tight, hollow objects or balloons,
4. Increasing the pressure,
5. Circulating the gas,
6. Fumigating buildings when wind velocity is low,

7. Addition of carbon dioxide to reactive gases, and
8. Reduction of relative humidity and material moisture content.

Temperature elevation and increased exposure times are the methods most often used to reduce dosage. Heat exchangers must be selected such that there will be no detonation of explosive air-gas mixtures or that degradation reactions cannot occur. Gases which are heavier than air must be circulated in order to prevent insufficient or excessive exposure of the infested areas. With some gases, explosion-proof circulation fans must be used. The addition of carbon dioxide as a respiratory analeptic to reactive gases increases their effectiveness against insect pests. Often mixtures of several fumigants are more effective against pests than pure substances. Reduction of relative humidity and material moisture content has to be used with great caution, because although the drying increases the mortality of insect larvae, certain reactive gases become less effective and significant drying can lead to damage of the objects being treated.

When reactive gases such as bromomethane or ethylene oxide/carbon dioxide mixtures are introduced into buildings from gas cylinders, when containers of cardboard sheets soaked in prussic acid must be opened, or when aluminum phosphide tablets must be laid out, gas masks and protective clothing are required. For sulfuryl fluoride the normal adsorptive filters based on activated charcoal are not sufficient, and a full mask with external air supply must be used (Fig. 8.4). The emission of liquefied gases such as bromomethane or carbon dioxide from gas cylinders and their subsequent vaporization will cool the room air, and formation of ice is possible. When large quantities must be vaporized as in fumigation of buildings, heat exchangers and associated equipment are necessary to maintain acceptable air temperature levels. Under no circumstances should liquid, reactive fumigants come into contact with objects as this could cause serious damage. Some gases, such as carbon dioxide, nitrogen, or argon, are very dry when they are let out of their gas cylinders and must be humidified in order to avoid drying cracks in objects. Reactive gases in particular in their technical grades contain a series of impurities which can cause damage to valuable cultural property. These fumigants should therefore be cleaned with suitable high-efficiency filters before they are introduced into fumigation chambers or buildings. When insect pests are to be exterminated by fumigation, it is important that the egg stage is also controlled. Some gases are only weak ovicides, and two possible methods may be used to compensate for this: (1) fumigating at two separate times, using a lower dosage for the second fumigation, and (2) increasing the exposure time.

In the first variation the second fumigation is delayed until after all larvae are hatched from the eggs (vulnerable phase). In the second one, which is usually preferred, the exposure time includes the change from eggs to larvae. In order to monitor the effectiveness of the fumigation, it is recommended that a lethality check with all developmental stages of the particular insect

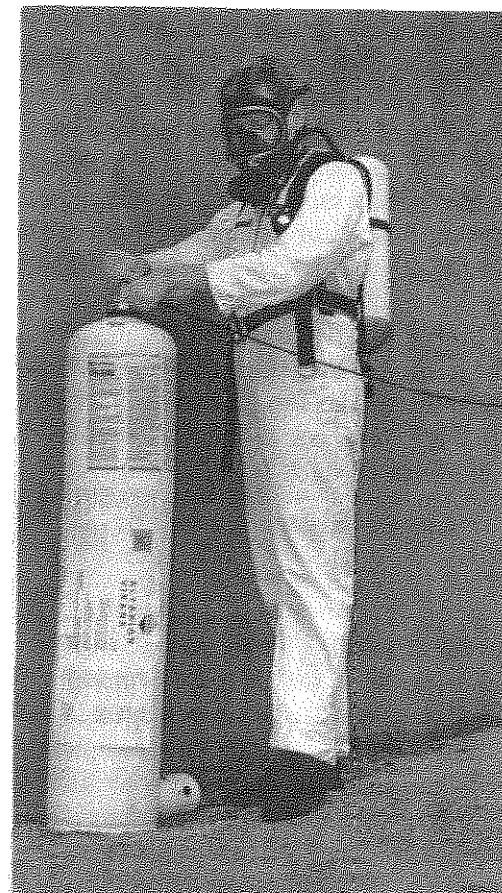


Fig. 8.4. Full masking with external air supply for fumigation with sulfuryl fluoride. (Photograph courtesy of G. Binker)

pest is carried out. For insects which live inside wood, special test specimens have been developed (Unger 1983, 1998; Rust et al. 1996).

Until recently, fumigants were simply let out into the atmosphere after the treatment was completed, which does not present any problems for nitrogen, argon, or carbon dioxide. For reactive gases such as bromomethane, hydrogen phosphide, sulfuryl fluoride and ethylene oxide, protection of the environment means that as much gas as possible is recovered and disposed of suitably. The tighter the container or the sealing or tenting of buildings, the more gas can be recovered. Technologies which remove the gas and then recycle it for additional applications are ideal.

Following the fumigation, objects or buildings must be ventilated sufficiently to eliminate residual gases. Fumigated objects should be kept in well-ventilated quarantine rooms before they are returned to storage or exhibit

spaces. The determining factor for release of treated objects, rooms, or buildings is freedom of gas residues, and this requires certain proof that the concentration of toxic residuals is below the levels permitted by applicable regulations. Particularly porous materials such as wood and bricks, but also plastics can adsorb considerable quantities of reactive gases which are later given off only slowly. Thus checking whether these materials are free from gas residues must also be determined by test specimens. The use of reactive gases is dependent on the awarding of relevant licenses or permits, whereas inert gases such as nitrogen or argon can be used by conservators without limitations.

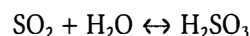
For long-term fumigation, angled holes are drilled into the pole or timber, the liquid fumigant is poured into the holes, and the opening is closed with a tight-fitting dowel. Since it is inevitable that some of the vapors will eventually escape from the wood, this method is appropriate only in well-ventilated spaces where there is no likelihood of human contact.

8.5

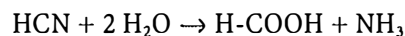
Damage Caused by Fumigants

The most important factor leading to damage during fumigation is the chemical reactivity of the fumigant, which depends on the chemical composition and structure of the specific compound. In the case of hydrogen cyanide the cyanide group readily forms addition compounds or molecule complexes. Hydrogen phosphide is a strong reducing agent because of its constituent hydrogen and its pyramidal structure. The reactivity of sulfuryl fluoride is due to its SO_2 group and its constituent fluorine. The methyl group or the bromine atom in bromomethane can produce methylation or bromination reactions. The ethylene oxide molecule forms an unstable, three-member ring which can easily be split open, and the substance polymerizes quickly. The aldehyde group and the steric structure of formaldehyde make it a strong reducing agent, and it also polymerizes easily. Carbon dioxide is merely a weak oxidizing agent. Nitrogen and argon can be considered inert under normal conditions.

Most fumigants are capable of reacting with water to form new compounds. Sulfur dioxide dissolves in water to form sulfurous acid which is a reducing agent with bleaching action.



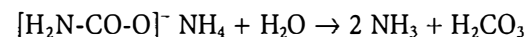
Hydrogen cyanide reacts with water to form formic acid and ammonia, which can damage paint and cause swelling of wood supports.



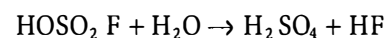
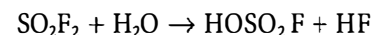
The formation of cyanides is also a possibility.

Hydrogen phosphide oxidizes to phosphoric acids in the presence of water, where copper appears to act as a catalyst. The acids react further under for-

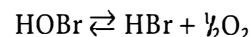
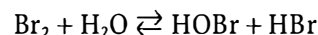
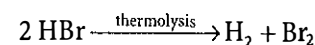
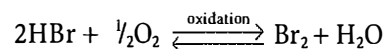
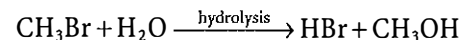
mation of salts. Metal phosphide tablets are sometimes coated with ammonium carbamate, which forms ammonia and carbonic acid in the presence of water.



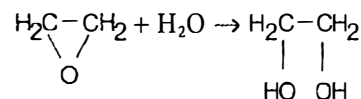
Sulfuryl fluoride is subject to hydrolysis, especially in alkaline media, with sulfuric acid and hydrofluoric acid as the end products. In the neutral region hydrolysis is kinetically hindered.



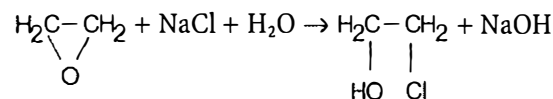
Bromomethane and water at first form hydrobromic acid and methanol. Hydrobromic acid can form bromine either by reaction with oxygen in the air or by thermolysis at heaters. Bromine is somewhat soluble in water, forming bromine water, whereby sometimes hypobromous acid and hydrobromic acid will be present. Bromine water is very aggressive, and gives off oxygen in direct sunlight.



Ethylene oxide and water form ethylene glycol with known solubility and swelling properties.



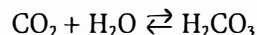
In the presence of chlorides ethylene chlorohydrin is formed.



Ethylene chlorohydrin is a strong poison, which can cause death if inhaled. Historic woods, papyrus, and paper often contain chlorides and therefore ethylene oxide should not be used for objects of that type. Secondary reactions with biocides based on chlorinated phenols such as PCP or Na-PCP are possible, which may be present in impregnated wood or textiles treated with fungicides. The toxicity of the resulting products should not be underestimated.

Formaldehyde reacts with water to form paraformaldehyde, which precipitates as a white coating on objects.

Small quantities of carbon dioxide will change to carbonic acid in water, but since the concentration is low, the solution as a whole acts like a weak acid.



The danger of hydrolytic decomposition of fumigants is especially acute when relative humidity and material moisture content are high. Relative humidity above 65% must be considered questionable, and if elevated temperatures are added, the probability of occurrence of the reactions discussed above is very high. The capability of some materials for retaining certain gases, such as hydrogen cyanide in wood and ethylene oxide in binders and polymers, is considerable, so that ample time is available for the reactions to take place.

The presence of contaminants and additives in fumigants can also cause damage to works of art and cultural property (Table 8.1). Especially impurities found in reactive fumigants are capable of causing corrosive effects, and it is advisable to check in each case if additional purification of fumigants by filtering should be carried out. Most fumigants will contain traces of water in addition to impurities and additives.

Damage can also be caused by improper application of fumigants. Excessive dosage, uneven distribution of gases which are heavier than air, and unsuitable climatic conditions during fumigation are the most important. Damage by fumigants to materials will be discussed separately for wood sup-

Table 8.1. Impurities and additives in fumigants

Fumigant	Impurities	Additives ^a
Hydrogen cyanide	Ammonia	Bromoacetic acid (W)
Hydrogen phosphide	Diphosphine	Ammonium carbamate (S)
Sulfuryl fluoride	Hydrogen fluoride, hydrogen chloride, chlorine, sulfur dioxide, ethylene dichloride, thionyl fluoride	Trichloronitromethane (chloropicrin) (W)
Bromomethane	Bromine water, methanol	Trichloronitromethane (chloropicrin) (W)
Ethylene oxide	Ethylene chlorohydrin, hydrogen chloride, ethylene glycol	Carbon dioxide (S), dichlorodifluoromethane (S)
Formaldehyde	Methanol	—
Carbon dioxide	Oxygen, nitrogen, carbon monoxide, hydrocarbons	—
Nitrogen	Oxygen, argon, hydrocarbons	—
Argon	Nitrogen, oxygen, hydrocarbons	—

^aS, stabilizer; W, warning indicator

ports and for coatings. Since wood is often used in combination with other materials, such as metals, paper, leather, plastics, etc., the damaging effects of fumigants on these will also be discussed. A comprehensive description of the chemical action of fumigants on museum materials has been presented by Sano (1999).

8.5.1

Possible Damage by Specific Fumigants

8.5.1.1

Hydrogen Cyanide

- Wood The gas is adsorbed markedly. Cyanide residues probably remain in the wood due to glycosidic bonds.
- Coatings Paint pigments containing significant amounts of iron may undergo blue discoloration. Copper pigments and plant dyes may be altered (Hahn 1999). Gilding and copper-rich hammered metal overlays can also be discolored by formation of gold or copper cyanides. Animal glues can become somewhat brittle.
- Others Polished metal surfaces such as gold and copper lose their shine and become corroded (Grosser 1975). Fresh whitewash becomes discolored by the formation of calcium cyanide and other compounds. Lime plasters containing iron compounds can undergo a bluish discoloration by the formation of Prussian blue after fumigation; since this is not resistant to alkali, the blue coloring gradually changes to brown by the formation of rust-like substances. In paper color changes to yellow are possible (Brokerhof 1989).

8.5.1.2

Hydrogen Phosphide

- Wood To date no noticeable changes have been observed.
- Coatings Ultramarine and copper-based pigments such as Schweinfurt green may discolor. Gilding and silvering on objects turn pale, and copper-rich hammered metal overlays turn black.
- Others The surfaces of objects made of copper and its alloys, gold, silver, steel, aluminum and nickel become corroded by the formation of phosphoric acids (Brokerhof 1989). Sometimes blackening occurs, e.g. in copper and copper alloys.

8.5.1.3

Sulfuryl Fluoride (Used as Technical Grade)

- Wood So far no changes have been observed, but phenolic groups found in lignin and some extractives catalyze the decomposition of the gas.

- Coatings** Unprotected azurite and malachite can discolor. Pigments with linseed-oil binder have also been observed to deviate from their original color and gloss. Cobalt blue and Prussian blue have been found to be particularly sensitive (Koestler et al. 1993). Binders containing proteins become lighter in color.
- Others** The surfaces of metals and metal alloys such as brass tarnish and discolor through the formation of corrosion products such as fluorides, sulfates, and hydrates. With purified sulfuric acid (Binker and Binker 1993) no changes were found on polished organ pipes of Zn-Pb alloy. Glass can be etched by traces of hydrofluoric acid. Paper exhibits some bleaching. Chemical changes have been observed in polymers such as PVA and epoxy resins. Textile dyes are attacked even when purified gas is used.

8.5.1.4

Bromomethane

- Wood** When liquid bromomethane comes into contact with wood it leaves dark spots.
- Coatings** White lead, Naples yellow, chrome yellow and red lead can blacken. Animal glues suffer some swelling and embrittlement. Natural resins and varnishes soften. If bromine water is formed, gilding and silvering will be attacked.
- Others** Polished metal surfaces will show corrosion by the formation of bromic acid, bromine water and oxygen (cf. reactions above). Materials containing sulfur such as leather book bindings or leather wall coverings, parchment, wool, hair and fur will emit foul odors of thioalcohols (mercaptans) after fumigation. The color of leather and parchment will also change. Varnishes, plastics and foam rubber will be softened by the gas. Photo and film materials with silver coatings become brominated and methylated (Brokerhof 1989), leading to color changes.

8.5.1.5

Ethylene Oxide

- Wood** In materials containing hydroxyl groups, such as wood and paper, cross-linking of free hydroxyl groups (acetalization) takes place, which increases some mechanical properties and reduces the hygroscopicity.
- Coatings** To date, color changes have been observed in lead-tin yellow, in plant dyes (Hahn 1999) and also loss of adhesion in casein and hen's egg binders.
- Others** Copper and its alloys such as brass become oxidized. In leather and parchment a reaction with the proteins takes place, making the

material harder and more brittle and leading to decreased biological resistance. Polymers such as poly(vinyl chloride) absorb the gas greatly, and the tensile strength of the plastic is decreased. Textiles which had been treated with Na-PCP exhibit secondary reactions (Brokerhof 1989).

8.5.1.6

Formaldehyde

- Wood** Only minor changes occur.
- Coatings** Spontaneous polymerization of the gas leads to the formation of white surface deposits (which are also formed on uncoated objects). The gas reacts with free amino groups in binders containing proteins and causes them to harden.
- Others** The gas makes leather and parchment hard, and leads to accelerated aging of wool, hair, and fur (Brokerhof 1989).

8.5.1.7

Carbon Dioxide

- Wood** Wood is not damaged under normal conditions.
- Coatings** Massicot, red lead, zinc white and ultramarine pigments can change color, especially at high relative humidity. Linseed oil varnish, gum arabic, and shellac also are sensitive to the gas at high relative humidity (Piening 1993).
- Others** Silvering and silver objects become tarnished (Piening 1993). The upper patina layers of Jura marble are solubilized by the formation of calcium hydrogen carbonate (Hering 1994).

8.5.1.8

Nitrogen

- Wood** Wood is not damaged.
- Coatings** Kenjo (1980) found that pigments such as cinnabar, litharge, and sienna which are stable in normal atmospheric conditions did undergo slight color changes when exposed to an inert gas such as nitrogen or argon. These changes did not occur when the gas contained about 5% oxygen, suggesting that an appropriate concentration of oxygen must be considered in the conservation of polychromed cultural property. Koestler et al. (1993) did not observe any changes in color or gloss for lead white, zinc white, cobalt blue, Prussian blue, raw sienna, chromium oxide, burnt umber, viridian green, alizarin crimson, cadmium red, ivory black, and yellow ochre in oil-based binders if the residual oxygen content is equal to or less than 0.1%.

References

- Aberle B, Koller M (1968) Konservierung von Holzskulpturen. Probleme und Methoden. Institut für Österreichische Kunstforschung des Bundesdenkmalamtes, Vienna (AATA 8-761)
- Adler C, Reichmuth C (1989) Zur Wirksamkeit von Kohlendioxid bzw. Stickstoff auf verschiedene vorratsschädliche Insekten in Stahl-Getreidesilozellen. *Nachrichtenbl Dtsch Pflanzenschutz* 41(11):177-183
- Anonymous (1978) Vorschrift zur Anwendung von Delicia-GASTOXIN im Vorratsschutz. Prospekt der Fa. Delicia, Delitzsch, Stand: Dezember
- Anonymous (1985) Hausbockbekämpfung in einer Stabkirche. *Denkmalpflege durch Begasung sichert schonende Behandlung*. *Holz-Zentralblatt* 111(67/68):1020
- Anonymous (1990) Metallfärbung durch Blausäurebegasung. *Restauratorenblätter* 11:11
- Arai H (1995) Maßnahmen gegen biologische Schäden in Japan: Experimente und Forschungsergebnisse. *Holzschädlingsbekämpfung durch Begasung*. Fumigation as means of wood pest control. *Arbeitshefte Bayer Landesamt Denkmalpflege* 75:37-39, English version, pp 40-42
- Arai H, Mori H, Harada T (1972) Fumigation of the San-Gedatsu Gate of the Zōjōji-Temple, Tokyo. *Sci Conserv* 9:55-62 (AATA 9-622)
- Arnold WJ (1985) Fumigation for insect control: sensitive structures, museums and art and valuable repositories. *Newsletter (Western Association for Art Conservation)* 7(1):6-7 (AATA 29-1124)
- Bachmann HG (1978) Die Einwirkung gasförmiger Blausäure auf Edelmetallüberzüge und einige NE-Metalle. *DEGESCH-Technikertagung in A-Baden-Helental bei Wien*, 15-21 Oct 1978. *DEGESCH GmbH, Frankfurt/M*, pp 68-76
- Bachmann HG (1981) Prevention of biodeterioration of wooden objects of art: influence of fumigation with hydrocyanic acid on metals. *Stud Conserv* 26(3):111-118 (AATA 18-1239)
- Baker MT, Burgess HD, Binnie NE, Derrick MR, Druzik JR (1990) Laboratory investigation of the fumigant Vikane. *ICOM Committee for Conservation, 9th Triennial Meeting, Dresden 1990*, vol II, pp 804-811
- Bauer WP (1989) Methoden und Probleme der Bekämpfung von Holzschädlingen mittels toxischer Gase. *Restauratorenblätter* 10:58-63
- Bäumert K, Wentzel G (1978) Holzschädlinge und deren Bekämpfung. *DEGESCH-Technikertagung in A-Baden-Helental bei Wien*, 15-21 Oct 1978. *DEGESCH GmbH, Frankfurt/M*, pp 9-16
- Becker H (1988) Der Einsatz von Begasungsverfahren zur Bekämpfung holzerstörender Insekten. *Prakt Schädlingsbekämpfer* 5:114-118
- Biebl W (1995) Erfahrungsbericht über die Langzeitwirkung von Begasungen in Bayern. *Holzschädlingsbekämpfung durch Begasung*. Fumigation as a means of wood pest control. *Arbeitshefte Bayer Landesamt Denkmalpflege* 75:70-71, English version, pp 72-73
- Binker G (1993a) Mit Kohlendioxid gegen Insektenbefall. *Restauro* 99(4):222
- Binker G (1993b) Report on the first fumigation of a church in Europe using sulfuryl fluoride. In: Wildey KB, Robinson WH (eds) *Proceedings of the 1st International Conference on Insect pests in the urban environment - St. John's College, Cambridge*, 30 June-3 July, pp 51-55
- Binker G (1994) Sulfuryl fluoride fumigations in Europe. *Fumigants and pheromones technical seminar, Indianapolis*, 6-8 Dec, pp 230-235
- Binker G (1995a) Umweltschutzkonzepte und Neuentwicklungen bei Kulturgutbegasungen. *Holzschädlingsbekämpfung durch Begasung*. Fumigation as a means of wood pest control. *Arbeitshefte Bayer Landesamt Denkmalpflege* 75:77-89, English version, pp 90-100
- Binker G (1995b) Schutz von Fledermäusen während Kirchenbegasungen im Altarion Vikane-Verfahren. *Vortrag auf der Tagung der Südbayerischen Fledermausschützer, Ottenhofen*, 25 March 1995

- Binker G (1999) Application of carbon dioxide for pest control of buildings and large objects. The 23rd International Symposium on the Conservation and restoration of cultural property, 27-29 Sept 1999, Tokyo. Abstracts, p 14
- Binker G, Binker J (1993) Verfahren und Vorrichtung zur Begasung eines Raumes mit Sulfurylfluorid. *German Pat* 4343689
- Binker G, Binker J (1994) Verfahren zum Ableiten eines Gas-Luftgemisches aus einem Raum. *German Pat* 4401338
- Binker G, Binker J, Fröba G (1997) Binker Materialschutz GmbH: Innovative Stickstoffbegasung gegen Schadinsekten in Museen. *Dem Zahn der Zeit entrissen - neue Forschungen und Verfahren zur Schädlingsbekämpfung im Museum*. Rheinland-Verlag GmbH Köln in Kommission bei Dr. Rudolf Habelt GmbH, Bonn, pp 127-141
- Bolle J (1916) Über die Bekämpfung des Holzbohrwurmes (Anobium) in einem alten Kunstwerke. *Z Angew Entomol* 3:172-178
- Brand SJ, Wudtke A (1997) Bekämpfung von Textilschädlingen mit Kohlenstoffdioxid. *Restauro* 103(4):272-276
- Brokerhof A (1989) Control of fungi and insects in objects and collections of cultural value "a state of the art". *Central Research Laboratory for Objects of Art and Science, Amsterdam*
- Burgess HD, Binnie NE (1991) The effect of Vikane on the stability of cellulosic and ligneous materials - measurement of deterioration by chemical and physical methods. *Mat Res Soc Symp Proc* 185:791-798
- Canuti V (1988) Il restauro di due porte lignee intarsiate della chiesa di S. Sigismondo a Cremona. *Kermes* 1(3):34-39 (AATA 28-2253)
- Castelli C, Ciatti M (1989) La croce dipinta di Lippo di Benivieni: un esempio di risanamento ligneo. In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp 293-295, 352 (AATA 29-2353)
- Child RE, Pinniger DB (1987) Insect pest control in U.K. museums. *Recent Advances in the Conservation and Analysis of Artifacts*. Jubilee Conservation Conference, University of London, Institute of Archaeology, Summer Schools Press, pp 303-305
- Clark JE, Smith RS (1982) Efficacy of quenched ethylene oxide as a sterilant for wood at room temperature. *Wood Fiber Sci* 14(3):200-203 (AATA 20-434)
- Cotton RT, Roark RC (1928) Ethylene oxide as a fumigant. *Ind Eng Chem* 20:805
- Cotton RT, Young HD (1929) The use of carbon dioxide to increase the insecticidal efficiency of fumigants. *Proc Entomol Soc* 31:97
- Daniel V, Maekawa S, Preusser FD (1993) Nitrogen fumigation: a viable alternative. *ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 1993*, vol II, pp 863-867
- Dawson JE (1981) Ethylene oxide fumigation. *IIC-Canadian Group Newslett* 7(2):8-11
- Dawson JE, Strang TJK (1992) Solving museum insect problems: chemical control. *Techn Bull* 15. Canadian Conservation Institute, Ottawa
- Derrick MR, Burgess HD, Baker MT, Binnie NE (1990) Sulfuryl fluoride (Vikane): a review of its use as a fumigant. *J Am Inst Conserv* 29:77-90
- Desmarchelier JM (1994) Carbonyl sulphide as a fumigant for control of insects and mites. In: Highley E, Wright EJ, Banks HJ, Champ BR (eds) *Stored product protection. Proceedings of the 6th International Working Conference on Stored-product protection, Canberra, Australia*, 17-23 April 1994, Wallingford, Oxon, CAB International 1994, vol 1, pp 78-82
- Despot R, Hrašovec B, Trajković J (1999) Experimental sterilization of wooden artifacts by nitrogen (N₂). In: Reinprecht L (ed) *Rekonstrukcia a konzervacia historického dreva '99*, 2nd International Symposium, 15-17 June 1999, Zvolen
- Dominik J, Rudniewski P, Wazny J (1970) Badania nad zastosowaniem tlenku etylenu do dezynsekcji drewna zabytkowego (Study of the application of ethylene oxide for the disinfection of ancient wood). *Zeszyty Naukowe Szkoły Główniej Gospodarstwa Wiejskiego, Lesnictwo XIV*:165-170 (AATA 8-1296)
- Drinkall MJ, Dugast JF, Reichmuth Ch, Schöller M (1996) The activity of the fumigant sulfuryl fluoride on stored product insect pests. In: Wildey KB (ed) *Proceedings of the 2nd Interna-*

- tional Conference on Insect pests in the urban environment. Heriot-Watt University, Edinburgh, Scotland, 7–10 July, pp525–528
- Elert K, Maekawa S (1997) Projekt zur Schädlingsbekämpfung am GCI. *Restauro* 103(4):260–266
- Elmer K, Rose E, Fitzner B, Krumbein WE, Warscheid T (1993) Sterilisation of cultural objects by ethylene oxide – application for conservation practice by laboratory-based or mobile treatments. In: Thiel H-J (ed) *Conservation of stone and other materials, volIII: prevention and treatments. Proceedings of the International RILEM/UNESCO Congress, Paris, 1993*, Verlag E & FN Spon, London, pp581–588
- Emmerling E (1995) Holzschädlingsbekämpfung durch Begasung. Probleme in der Praxis und Wünsche aus der Sicht des Restaurators. *Holzschädlingsbekämpfung durch Begasung. Fumigation as means of wood pest control. Arbeitshefte Bayer Landesamt Denkmalpflege* 75:43–56, English version, pp57–69
- Fey H (1983) *Wörterbuch der Schädlingsbekämpfung*. Wissenschaftliche Verlagsgesellschaft, Stuttgart
- Florian M-L (1987) The effect on artifact materials of the fumigant ethylene oxide and freezing used in insect control. ICOM Committee for Conservation, 8th Triennial Meeting, Sydney 1987, voll, pp199–208
- Fuchs R (1997) Schädlingsbekämpfung an befallenen Schrift- und Archivgut: Vergleich alter und neuer Verfahren – moderne Untersuchungen zur Veränderung der Molekülstruktur. Dem Zahn der Zeit entrissen – neue Forschungen und Verfahren zur Schädlingsbekämpfung im Museum. Rheinland-Verlag GmbH Köln in Kommission bei Dr. Rudolf Habelt GmbH, Bonn, pp53–83
- Gallo F (1975) Recent experiments in the field of disinfection of book materials. ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/15/7
- Gilberg M (1989) Inert atmosphere fumigation of museum objects. *Stud Conserv* 34:80–84
- Gilberg M (1990) Inert atmosphere disinfestation using AGELESS® oxygen scavenger. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden 1990, volII, pp812–816
- Gilberg M (1991) The effects of low oxygen atmospheres on museum pests. *Stud Conserv* 36:93–98
- Gilberg M, Roach A (1993a) Inert atmosphere disinfestation of museum objects using Ageless oxygen absorber. In: Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, 5–8 Oct 1992. *Proceedings 1993*, pp397–406
- Gilberg M, Roach A (1993b) The effects of low oxygen atmospheres on the powderpost beetle, *Lyctus brunneus* (Stephens). *Stud Conserv* 38:128–132
- Gilberg M, Roach A (1995) Entwesung von Museumsobjekten in Inertgasen mit dem Sauerstoffabsorber AGELESS. *Holzschädlingsbekämpfung durch Begasung. Fumigation as a means of wood pest control. Arbeitshefte Bayer Landesamt Denkmalpflege* 75:101–104, English version, pp105–108
- Green L, Daniels V (1987) Investigation of the residues formed in the fumigation of museum objects using ethylene oxide. Recent Advances in the Conservation and Analysis of Artifacts, Jubilee Conservation Conference, University of London, Institute of Archaeology, Summer Schools Press, pp309–313
- Grosser D (1975) Über die Bekämpfung holzzerstörender Insekten mit Begasungsmitteln. *Prakt Schädlingsbekämpfer*, no. 5
- Grosser D, Roßmann E (1974) Blausäuregas als bekämpfendes Holzschutzmittel für Kunstobjekte. *Holz Roh Werkst* 32:108–114
- Hahn O (1999) Chemische Schädlingsbekämpfung. Risiken für Pigmente und Farbstoffe. *Restauro* 105(4):275–279
- Hanlon G, Daniel V (1998) Modified atmosphere treatments of insect infestations. The structural conservation of panel paintings. In: Dardes K, Rothe A (eds) *Proceedings of a Symposium at the J. Paul Getty Museum, 24–28 April 1995, the Getty Conservation Institute Los Angeles*, pp69–78

- Hanlon G, Daniel V, Ravenel N, Maekawa S (1993) Dynamic system for nitrogen anoxia of large museum objects: a pest eradication case study. In: Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, 5–8 Oct 1992, *Proceedings 1993*, pp387–396
- Hering MHB (1994) Anobienbekämpfung in der Erzdiözese München und Freising. Jahresbericht, im Auftrag des Erzbischöflichen Ordinariates München, Kunstreferat
- Howarth G (1994) Conservation of the mortification boards of the city of Aberdeen. *SSCR J* 5(2):15–16 (AATA 32–835)
- Kazemi SM, Dickinson DJ, Murphy RJ (1998) The influence of gaseous oxygen concentration on fungal growth rates, biomass production and wood decay. *IRG/WP/98-10283*
- Kenaga EE (1957) Some biological, chemical and physical properties of sulfonyl fluoride as an insecticidal fumigant. *J Econ Entomol* 50(1):1–6
- Kenjo T (1980) Studies on the long-term conservation of cultural properties (part 1). 2. Effects of different concentrations of oxygen on pigments used for cultural properties. *Sci Pap Jpn Antiques Art Crafts* 25:103–107 (AATA 18-1405)
- Kimura H, Miyachi H, Inoue I, Yamazaki S, Yamano K, Arai H (1993) On the mixed fumigants comprising of propylene oxide and methyl bromide. In: Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, 5–8 Oct 1992, *Proceedings 1993*, pp425–433
- Kleitz M-O (1987) L'oxide d'éthylène. Utilisation et limites. Actions secondaires avec un résidu de traitement antérieur. ICOM Committee for Conservation, 8th Triennial Meeting, Sydney 1987, vol III, pp1189–1196
- Koestler RJ (1992) Practical application of nitrogen and argon fumigation procedures for insect control in museum objects. Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, 5–8 Oct 1992, preprints pp94–96
- Koestler RJ (1993) Insect eradication using controlled atmospheres and FTIR measurement for insect activity. ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 1993, vol II, pp882–886
- Koestler RJ, Parreira E, Santoro ED, Noble P (1993) Visual effects of selected biocides on easel painting materials. *Stud Conserv* 38:265–273
- Kowalik R, Sadurska I (1960) Wpływ tlenu etylenu na kilku przedstawicieli grzybów niszczyjących drewno (Effectiveness of ethylene oxide against wood-destroying fungi). *Acta Microbiol Polon* 9:67–69
- Lambert FL, Daniel V, Preusser FD (1992) The rate of absorption of oxygen by AGELESS™: the utility of an oxygen scavenger in sealed cases. *Stud Conserv* 37:267–274
- Lehmann G, Kerner G, Schultze-Dewitz G (1969) Zur Bekämpfung von Holzzerstörern in Bauten. *Arch Forstwesen* 18(9/10):1163–1166
- Levinson HZ, Levinson AR (1990) Die Ungezieferplagen und Anfänge der Schädlingsbekämpfung im Alten Orient. *Anz Schädlingskd Pflanzenschutz Umweltschutz* 63:81–96
- Linnie MJ (1990) Conservation: pest control in museums – the use of chemicals and associated health problems. *Museum Management Curatorship* 9(4):419–423
- Maekawa S (1999) Overview of oxygen-free methods and thermal methods for insect control in museums. The 23rd International Symposium on the Conservation and restoration of cultural property, 27–29 Sept 1999, Tokyo. Abstracts, p12
- Maekawa S, Elert K (1996) Large-scale disinfestation of museum objects using nitrogen anoxia. ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland 1996, vol I, pp48–53
- Maekawa S, Preusser F, Lambert F (1993) An hermetically sealed display and storage case for sensitive organic objects in inert atmospheres. In: Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, 5–8 Oct 1992, *Proceedings 1993*, pp374–386

- Miura S (1999) Methyl bromide phase out: controversial points for the future of pest control. The 23rd International Symposium on the Conservation and restoration of cultural property, 27–29 Sept 1999, Tokyo. Abstracts, p 8
- Mori H, Arai H (1978) Biodeterioration of wooden cultural properties and its control. Conserv Wood, Int Symp Conserv Restor Cult Prop, Tokyo 1977, Proceedings 1978, pp 1–16
- Mori H, Arai H (1981) Protection of underwater cultural properties from marine borers. Sci Pap Jpn Antiques Art Crafts 26:89–95 (AATA 19-1367)
- Mori H, Arai H (1982) Means of shortening fumigation time for wooden statues and other cultural properties. Sci Conserv 21:33–39 (AATA 19-1366)
- Mori H, Kadokura T (1977) Tarpaulin-covered fumigation of the tea-arbor "Joan" (National Treasure) and the old study "Seidenin" (Important Cultural Property). Sci Pap Jpn Antiques Art Crafts 20/21:93–100
- Mori H, Kumagai M (1954) On the damage to antiques and art crafts by several fumigants. I. Effects of fumigants on some kinds of metals. Sci Pap Jpn Antiques Art Crafts 8:17–21
- Mori H, Kumagai M (1955) On the damage to antiques and art crafts by several fumigants. II. Effects of fumigants upon different kinds of pigments. Sci Pap Jpn Antiques Art Crafts 11:21–28
- Morrell JJ (1989) Fumigation. In: Schniewind AP (ed) Concise encyclopedia of wood & wood-based materials. Pergamon Press, Oxford, MIT Press, Cambridge, Massachusetts, pp 119–122
- Morrell JJ, Corden ME (1986) Controlling wood deterioration with fumigants: a review. For Prod J 36(10):26–34
- Newton J (1993) Carbon dioxide as a fumigant to replace methyl bromide in the control of insects and mites damaging stored products and artefacts. In: Wildey KB, Robinson WH (eds) Proceedings of the 1st International Conference on Insect pests in the urban environment, St. John's College, Cambridge, 30 June–3 July 1993, pp 329–338
- Newton J, Abey-Koch M, Pinniger DB (1996) Controlled atmosphere treatment of textile pests in antique curtains using nitrogen hypoxia – a case study. In: Wildey KB (ed) Proceedings of the 2nd International Conference on Insect pests in the urban environment. Heriot-Watt University, Edinburgh, Scotland, 7–10 July 1996, pp 329–339
- Nicholson M, von Rotberg W (1996) Controlled environment heat treatment as a safe and efficient method of pest control. In: Wildey KB (ed) Proceedings of the 2nd International Conference on Insect pests in the urban environment. Heriot-Watt University, Edinburgh, Scotland, 7–10 July 1996, pp 263–265
- Oberwalder O (1930) Die Vergasung der Pfarrkirche in Kefermarkt und ihres gotischen Schnitzaltars. Frühere Sicherungsarbeiten am Altare und Durchführung der Vergasung. Denkmalpflege, Sonderbeilage, pp 251–261
- Ognibeni G (1989) Die Bekämpfung von Holzschädlingen – gefaßte Holzobjekte unter Einsatz von Gas. Restauro 95(4):283–287
- Paterakis A (1983) Apentomosi xyloglypton I. Naou Agias Triadas Spetson me ti methoda ton aerion (Fumigation). Archaeologika Analekta ex Athinon (Athens Anal Archaeol) 15(1): 65–70 (AATA 21-439)
- Paton R, Creffield JW (1987) The tolerance of some timber pests to atmospheres of carbon dioxide in air. Int Pest Control 29(1):10–12
- Petrovski Z (1987) A gyulai ácsok és közművesek legényládájának restaurálása (The restoration of a carpenter-mason journeyman's chest from Gyula). Műz Műtárgyvédelem 16:289–316 (AATA 24-765)
- Piening H (1992/1993) Untersuchungen zum Diffusionsverhalten von Kohlendioxid und Stickstoff bei der Begasung holzzerstörender Insekten. Semesterarbeit, Fachhochschule Köln
- Piening H (1993) Die Bekämpfung holzzerstörender Insekten mit Kohlendioxid sowie die Verträglichkeit des Gases an gefaßten Objekten. Diplomarbeit, Fachhochschule Köln
- Pinniger D (1990) Insect pests in museums. Archetype Publications, Clwyd
- Plenderleith HJ (1956) The conservation of antiquities and works of art. Oxford University, London, part 1/5 (wood), pp 116–143

- Rathgen F (1924) Die Konservierung von Altertumsfunden, Teil II u. III. De Gruyter, Berlin, pp 133–149
- Reichmuth C, Unger A, Unger W (1994) Schadinsekten in Kunst- und Kulturgut – Bekämpfungsmaßnahmen mit Stickstoff oder Kohlendioxid. Prakt Schädlingbekämpfer 46(3):81–87
- Reichmuth C, Unger W, Unger A (1991) Stickstoff zur Bekämpfung holzzerstörender Insekten in Kunstwerken. Restauro 97(4):246–251
- Reichmuth C, Unger A, Unger W, Blasum G, Piening H, Rohde-Hehr P, Plarre R, Pöschko M, Wudtke A (1993) Nitrogen-flow fumigation for the preservation of wood, textiles, and other organic material from insect damage. In: Navarro S, Donahaye E (eds) Proceedings of the International Conference on Controlled atmosphere and fumigation in grain storage, Winnipeg, Canada, June 1992, Caspit Press, Jerusalem 1993, pp 121–128
- Reiersen DA, Rust MK, Kennedy JM, Daniel V, Maekawa S (1996) Enhancing the effectiveness of modified atmospheres to control insect pests in museums and similar sensitive areas. In: Wildey KB (ed) Proceedings of the 2nd International Conference on Insect pests in the urban environment, Heriot-Watt University, Edinburgh, Scotland, 7–10 July 1996, pp 319–327
- Ren Y, O'Brien G, Desmarchelier JM (1997) Improved methodology for studying diffusion, sorption and desorption in timber fumigation. J Stored Prod Res 33(3):199–208
- Renshaw-Beauchamp R (1978) Fumigation – to purify with fumes. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, 78/3/1, 34pp
- Römpf H (1995) Chemie-Lexikon. Falbe J, Regitz M (eds) Thieme, Stuttgart
- Ruetze (1983) Untersuchungen zur Biologie der amerikanischen Eichenwelke [*Ceratocystis fagacearum* (BRETZ) HUNT] und Entwicklung eines Verfahrens zur Desinfektion von Eichenholz. Dissertation, Fachbereich Biologie, Universität Hamburg
- Rust MK (1993) The potential use of modified atmospheres to control household insect pests. In: Wildey KB, Robinson WH (eds) Proceedings of the 1st International Conference on Insect pests in the urban environment, St. John's College, Cambridge, 30 June–3 July 1993, p 473
- Rust MK, Daniel V, Druzik JR, Preusser FD (1996) The feasibility of using modified atmospheres to control insect pests in museums. Restaurator 17:43–60
- Sanders S (1987) Effects of CO₂-fumigation on pH. ICOM Committee for Conservation, 8th Triennial Meeting, Sydney 1987, vol III, pp 945–946
- Sano C (1999) Chemical effects of various insecticides and fungicides on museum materials; reviews cited from Western papers and case studies to Japanese antiques. The 23rd International Symposium on the Conservation and restoration of cultural property, 27–29 Sept 1999, Tokyo. Abstracts, p 20
- Scheffrahn RH, Su N-Y, Hsu R-C (1992) Diffusion of methyl bromide and sulfuryl fluoride through selected structural wood matrices during fumigation. Mat Org 27(2):147–155
- Scheffrahn RH, Wheeler GS, Su N-Y (1995) Synergism of methyl bromide and sulfuryl fluoride toxicity against termites (Isoptera: Kalotermitidae, Rhinotermitidae) by admixture with carbon dioxide. J Econ Entomol 88:649–653
- Schiessl U (1984) Historischer Überblick über die Werkstoffe der schädlingbekämpfenden und festigkeitserhöhenden Holzkonservierung. Maltechnik Restauro 90(2):9–40
- Schmidt E, Juzwik J, Schneider B (1997) Sulfuryl fluoride fumigation of red oak logs eradicates the oak wilt fungus. Holz Roh Werkst 55:315–318
- Schneider BM (1993) Characteristics and global potential of the insecticidal fumigant, sulfuryl fluoride. In: Wildey KB, Robinson WH (eds) Proceedings of the 1st International Conference on Insect pests in the urban environment – St. John's College, Cambridge, 30 June–3 July, pp 193–198
- Selwitz C, Maekawa S (1998) Inert gases in the control of museum insect pests. Research in conservation. The Getty Conservation Institute
- Smith CP (1988) Fumigation – a new concept. BPCA Paper (Rentokil PLC)
- Smith RS (1968) Effect of moisture content on the sterilization of wood, under vacuum, by propylene and ethylene oxides. Can J Bot 46:299–303

- Smith C, Newton J (1991) Carbon dioxide: the fumigant of the future. In: Saur KG (ed) International seminar on research in preservation and conservation, May 1991. Columbia University, New York/International Federation of Library Associations, New York
- Stewart D (1957) Sulfuryl fluoride – a new fumigant for control of the drywood termite *Kaloterme minor* Hagen. *J Econ Entomol* 50(1):7–11
- Story KO (1985) Pest management in museums. Conservation Analytical Laboratory, Smithsonian Institution Suitland, Maryland
- Straub RE (1963) Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich
- Sutter H-P (1986) Holzschädlinge an Kulturgütern erkennen und bekämpfen. Haupt, Bern
- Tang ZT, Jin ZW, Zhou ZJ, Wang CH, Li ZS (1985) Some tropical hardwood-destroying insects and their control methods. *Nan-Ching Lin Hsueh Yuan Hsueh Pao* (1):38–43 (AATA 27–674)
- Unger A (1988) Holzkonservierung. Schutz und Festigung von Kulturgut aus Holz. Fachbuchverlag, Leipzig
- Unger A (1995) Begasung von Kulturgütern: Grundlagen – Materialien – Entwicklungen. Holzschädlingsbekämpfung durch Begasung. Fumigation as a means of wood pest control. Arbeitshefte Bayer Landesamt Denkmalpflege 75:19–27, English version, pp 28–36
- Unger A, Unger W (1986) Begasungsmittel zur Insektenbekämpfung in hölzernem Kulturgut. *Holztechnologie* 27(5):232–236
- Unger A, Unger W (1995) Die Bekämpfung tierischer und pilzlicher Holzschädlinge. Holzschutz, Holzfestigung, Holzergänzung. Arbeitshefte Bayer Landesamt Denkmalpflege 73:7–14
- Unger A, Rößner P, Schirarend C, Unger W (1988) Ethylenoxidbegasung einer afrikanischen Holzplastik. *Holztechnologie* 29(5):234–236
- Unger A, Unger W, Reichmuth C (1993) The fumigation of insect-infested wood sculptures and paintings with nitrogen. In: Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, October 5–8, 1992, Proceedings 1993, pp 440–446
- Unger W (1983) Die Begasung der denkmalgeschützten Fischerkirche in Ferch (Kreis Potsdam-Land) mit Blausäure. *Holztechnologie* 24(3):241–244
- Unger W (1998) Methoden zum Nachweis der biologischen Wirksamkeit alternativer Bekämpfungsvarianten gegen holz-zerstörende Insekten. Vortragsband der 21. Holzschutz-Tagung, Rosenheim/Germany, 21–23 Apr 1998, pp 185–192
- Unger W, Unger A (1993) On the effectiveness of fumigants against wood-destroying insects and fungi in wooden cultural property. *IRG/WP/93-10030*
- Unger W, Bischoff J, Fielitz L (1984) Zum Einsatz von Phosphorwasserstoff gegen holzzerstörende Insekten in denkmalgeschützten Gebäuden. *Holztechnologie* 25(5):229–232
- Unger W, Sallmann U, Unger A (1990) Eignet sich Ethylenoxid zur Hausschwamm- und Holzwurmbekämpfung in musealem und denkmalgeschütztem Kulturgut? *Holztechnologie* 30(5):255–259
- Unger W, Reichmuth C, Unger A, Detmers H-B (1992) Zur Bekämpfung des Echten Hausschwamms [*Serpula lacrymans* (WULF.:FR.) SCHROET.] in Kulturgütern mit Brommethan. *Kunsttechnol Konserv* 6(2):244–259
- Valentin N (1990) Insect eradication in museums and archives by oxygen replacement, a pilot project. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden 1990, vol II, pp 821–823
- Valentin N (1993) Comparative analysis of insect control by nitrogen, argon and carbon dioxide in museum, archive and herbarium collections. *Int Biodeter Biodegrad* 32:263–278
- Valentin N, Preusser F (1990) Insect control by inert gases in museums, archives and libraries. *Restaurator* 11:22–33
- Valentin N, Algueró M, Martín de Hijas C (1992) Evaluation of disinfection techniques for the conservation of polychrome sculpture in Iberian museums. In: Hodges HWM, Mills JS, Smith P (eds) Proceedings of an international institute for conservation meeting on conservation of the Iberian and Latin American cultural heritage, Madrid, Spain, Sept 1992. The International Institute for Conservation, London, pp 165–167

- Valentin N, Lidstrom M, Preusser F (1990) Microbial control by low oxygen and low relative humidity environment. *Stud Conserv* 35:222–230
- Vieillemand E (1990) La fumigation des bois. La conservation du bois dans le patrimoine culturel, Besançon-Vesoul, 8–10 Nov 1990, pp 173–176 (AATA 30-1306)
- Weber H (1980) Blaufärbung von Kalkzementputz. *Dtsch Architekturbl* 12(1):106
- Weller D (1982) Methylbromid. DEGESCH, Frankfurt/M
- Williams EW Jr, Grosjean E, Grosjean D (1993) Exposure of artists' colorants to sulfur dioxide. *J Am Inst Conserv* 32:291–310
- Williams LH, Sprengel RJ (1990) Ovicidal activity of sulfuryl fluoride to anobiid and lyctid beetle eggs of various ages. *J Entomol Sci* 25(3):366–375
- Wolinski L (1986) Dezynsekcja muzealio w tlenkiem etylenu (Disinfection of museum exhibits by means of ethylene oxide). In: Lehmann J (ed) Ochrona obiektów muzealnych: symposium konserwatorskie, Warszawa 2–4 X 1984. Biblioteka muzealnictwa i ochrony zabytkow, Seria B, no t 80:107–111 (AATA 28-1438)
- Yamazaki M, Arai H, Yamano K, Kenjo T, Lee K-S (1993) On propylene oxide as a fumigant. *Sci Conserv* (32):1–8
- Yulin X (1993) Fungicidal effectiveness of methyl bromide fumigant and its residue after fumigation. In: Toishi K, Arai H, Kenjo T, Yamano K (eds) 2nd International Conference on Biodeterioration of cultural property, Yokohama, Japan, 5–8 Oct 1992, Proceedings 1993, pp 407–414
- Zettler JL, Leesch JG, Gill RF, Mackey BE (1997) Toxicity of carbonyl sulfide to stored product insects. *J Econ Entomol* 90(3):832–836

9 Physical Control Methods

9.1

Characteristics

The activity of wood-destroying insects and fungi depends greatly on environmental factors such as ambient temperature, moisture content of air and host materials, and atmospheric pressure. These factors are thus the basis for the application of physical control methods. The objective is to stop the multiplication of the damaging organism and to liquidate any existing infection by changes in the environment. Since insects belong to the cold blooded (poikilothermic) animals, the temperature of their environment has the greatest effect on their metabolism. Accordingly, extreme temperatures become lethal within a short time of exposure. Fungi are also killed off quickly by high temperatures, but low temperatures will only retard their activity.

In regard to toxicological and ecological considerations, physical control methods are better suited for the treatment of works of art and cultural property than liquid wood preservatives or fumigants. In contrast to liquid preservatives, which leave some of their components permanently inside treated objects, physical control methods leave no residues, and there are no problems of compatibility of preservatives with the original substance. However, as in the case of fumigation, there is the possibility of more or less serious changes in the treated material. Treatment conditions must therefore be considered very carefully. In each case the aging processes of the treated materials are accelerated, but the extent of any changes varies as a function of the physical effect employed and the length of exposure. Once they have occurred, such changes are often irreversible. Depending on the particular pest organism, changes are not always disadvantageous but may be beneficial. Heat treatments, for example, can lead to partial denaturation of proteins in wood or in paint layers. This alters the food source for some wood-destroying insects and impedes their attack. However, sufficient preventive effects cannot be obtained in this manner. Physical methods generally do not result in a preventive treatment. In contrast to the positive effect of heat treatments on the resistance of wood to biological attack, gamma radiation treatments can make wood more susceptible to attack by certain fungi because of chain scission of cellulose and hemicelluloses. Changes in moisture content which occur with

some remedial treatment technologies can also have detrimental effects on objects.

With some physical methods there is greater risk that pest organisms survive, compared with fumigation treatments. Treatment technologies must therefore be carefully designed, and selection and application must be specific to the object. In situ controls of biological effectiveness of each treatment applied are to be recommended. Following pest control with physical treatments, further work on the objects can be done sooner, compared with fumigation treatments where ventilation is required, or liquid wood preservatives which require drying time.

Since physical control methods do not impart preventive effects, it has to be ascertained whether liquid preservatives need to be applied or whether control of the object's environment will allow little or no chance of renewed attack.

9.2

Control Through Temperature Changes

9.2.1

Heat Treatments

Technology

Heat treatments of wood objects attacked by pest organisms can be done with or without measures to maintain constant wood moisture content. Hot air control treatments of structural wood members in buildings which are infested with insects (sometimes also with fungal decay) will lead to a loss of moisture from the wood to the air. For valuable objects such as polychromed wood sculptures, panel paintings, and furniture, such moisture loss must be avoided to prevent the occurrence of drying cracks and splits. Processes for controlled heating with simultaneous regulation of relative humidity (Thermo-Lignum process and klav-Ex process in Germany) offer the possibility of relatively gentle treatments of objects.

Hot-air treatments without moisture content regulation are used primarily for the control of house longhorn beetles in attics. Air is heated in oil or gas fired generators to 100–120°C and blown through ducts into the attic (Fig. 9.1). The air in the attic should maintain temperatures in the range of 80–100°C so that the wood reaches a temperature of 55°C in 3–8 h, depending on cross section. The temperature of 55°C must be maintained over the entire cross section for at least 1 h. This requires continuous readings of temperature with sensors at strategic locations placed in the center of the thickest timbers, or inside masonry in the case of controlling decay fungi. During this exposure the proteins of the larvae of *Hylotrupes bajulus* coagulate, causing them to die. Care must be taken that the air discharge openings are

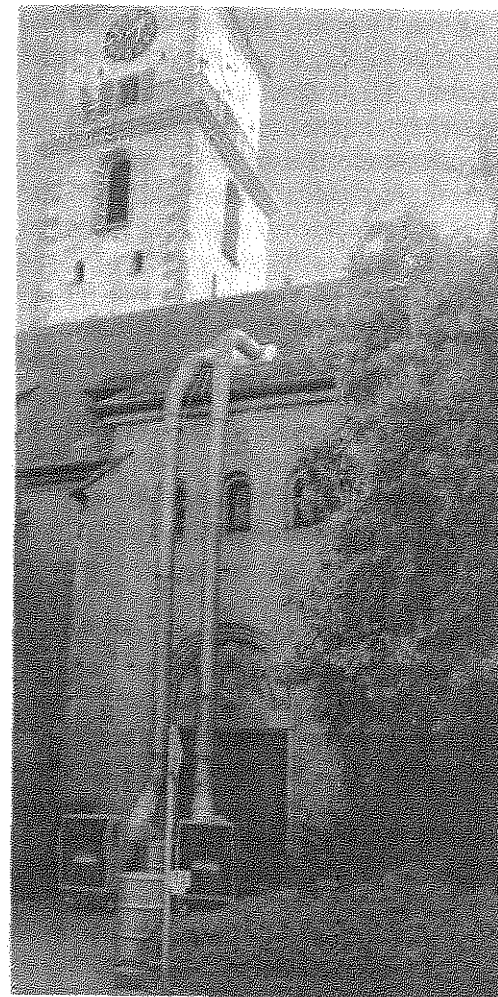


Fig. 9.1. Hot-air treatment for the control of house longhorn beetles in an attic. (Photograph courtesy of G. Binker)

placed to assure uniform air flow, and they should not be within 1 m of easily flammable materials. Prior removal of deteriorated portions of wood are not necessary. Wood more than 60 years old does not need to be treated with preventive wood preservatives, since the probability of renewed attack by the house longhorn beetle is very low.

Hot air treatments can also be used for building timbers attacked by termites. The objects are surrounded with tents which are heated with propane heaters to 66°C for at least 4h. When the interior of the wood reaches 49°C, the termites will die within 30min (Pearce 1997).

In historic buildings attacked by the decay fungus *Serpula lacrymans*, good conservation practice dictates that as much original substance as possible be retained. Hot-air treatments offer the possibility of reducing the material losses which accompany more traditional methods of controlling *Serpula lacrymans* in buildings. To kill off mycelium, strands and hyphae inside the wood, as well as the spores, different temperatures and exposure times are necessary. The moisture content of mycelium, strands, hyphae and wood and the relative humidity of the air affect the lethal temperature and the treatment time. The drier the fungi and the wood, the higher the temperatures and the longer the exposure times will need to be. Mycelium of *Serpula lacrymans* can be killed off at the relatively low temperatures of 37–40°C and exposure times of 3–6 h (Miric and Willeitner 1984). For the eradication of other decay fungi found in buildings such as *Coniophora puteana* and *Gloeophyllum sepiarium*, considerably higher temperatures and longer exposure times may be required. In contrast to requirements for mycelium, the eradication of spores of *Serpula lacrymans* under field conditions will require at least 10 h at 80°C or 4 h at 100°C (Hegarty 1988). Spores of *Coniophora puteana* and *Gloeophyllum sepiarium* are much less heat tolerant than those of *Serpula lacrymans* so that lethal effects are obtained sooner. Remarkably, the spores of other *Serpula* species are sometimes much more susceptible to temperature exposure. The use of hot air to kill off *Serpula lacrymans* mycelium in buildings is being promoted, particularly in Denmark.

Contact heating processes are suitable for difficult control problems such as ceiling beams, certain roof beams, beam ends set into masonry, and timbers extending outside the building envelope which are in the initial stages of an attack by *Serpula lacrymans* (Teichert 1996). The SELAREX process, which was developed in Germany, uses equipment consisting of a regulator, heating rods 200 mm in length and 10 mm in diameter, flexible heating mats, and smoke and fire detectors. The heating rods are inserted into prepared bore holes, and the heating mats are insulated from the outside with mineral fiber boards and clamped to the wood. Temperature is controlled by way of temperature sensors which are inserted into 3 mm holes in the wood. Reliable killing of *Serpula lacrymans* mycelium requires 60°C for 1 h in the wood interior. When using the contact heating process, the temperature of the heating elements should not exceed 150°C because otherwise heating over several hours can lead to extensive thermal decomposition of the wood.

Control of wood-destroying organisms with microwaves or high frequency waves also depends on thermal effects. These methods will be discussed in Section 9.5.

Heat treatments with moisture control, as opposed to the treatments without it discussed so far, are necessary to control wood-destroying insects and fungi in sensitive museum objects in order to maintain the moisture content of the material at a constant level. This requires that the objects are portable and that the treatment is carried out in a closed system, such as a programmable, controlled climate chamber. Humidity-controlled heating

processes developed in Germany are the Thermo-Lignum and the klav-Ex processes. Treatments are based on the hygroscopic isotherms for spruce developed by W.K. Loughborough as modified and extended by R. Keylwerth (Kollmann and Côté 1968). They show the relationship between temperature, relative humidity, and wood moisture content, and in practical situations is sufficiently accurate for other wood species as long as the moisture content is below the fiber saturation point.

Objects are treated in stationary or mobile walk-in climate chambers with a volume of up to 50 m³, where they are heated to about 55°C by circulated hot air while the relative humidity is regulated such that the moisture content of the object remains constant. This requires that moisture must be added to the air during the heating phase and removed during cooling. Control of temperature and relative humidity is done by microprocessors. The temperature is slowly raised to 55°C and held there for 1 h before cooling begins. The moisture content of the object must be determined accurately before starting the treatment. In the Thermo-Lignum process the moisture content sensor must be inserted into the object to a depth of at least 5 mm. For larger objects a temperature sensor must be inserted into a 3 mm bore hole extending to the center. If objects of differing moisture contents are to be treated together, it is necessary to wait until their moisture contents have been equalized. Normally treatment extends over a cycle of 24 h before the chamber is loaded again.

In the case of valuable art objects with insect infestation, where the above temperature regime may be deemed to be too much of a strain, the hot air treatment can be combined with inert gas fumigation (nitrogen or carbon dioxide), making it possible to kill off the insects even at temperatures of 25–30°C.

Uses

Historical

- 1796 According to Meinert, wood should be dried in a baking oven or by some other means in order to prevent attack by wood borers (Clausnitzer 1990).
- 1848 Baudet recommends heating wood in an oven to 80–100°C to protect it from pests (Clausnitzer 1990).
- ca. 1900 Rathgen (1910) mentions heat as a means of controlling wood borers.
- 1908 Control of wood borers by heating in a baking oven for several hours (Haupt).
- 1931 Hot air for the control of the house longhorn beetle (Jensen).
- 1955 Jensen reports on control of house longhorn beetles with hot air in Denmark.
- 1957 Schmidt and Schneider publish results on the lethal and preventive effects of hot air in the control of house longhorn beetles.

- 1961 Extermination of the larvae of the common furniture beetle and the powder post beetle in a climate chamber at 55 °C within 30 min (Becker and Loebe).
- 1983 Discussion of hot air treatments in the presence of bats (Cymorek and Wegen).
- 1984 Becker lists advantages and disadvantages of hot air treatments in the control of house longhorn beetles. Review by Unger of physical control methods of wood pests, including hot air treatments.
- 1985 Evaluation of and bibliography on the use of heat to control insect pests in museums by Story.
Treatment of insect-infested old woods in drying chambers or by hot air (Trübswetter).
- 1986 Fundamental research on the control of *Serpula lacrymans* with heat by Hegarty et al.
- 1987 German leaflet on the control of animal wood pests with hot air (Anonymous).
Graf discusses the effect of hot air in the control of fungal and insect pests in materials such as wood and masonry.
- 1988 According to Hegarty extermination of the spores of *Serpula lacrymans* by hot air treatment is almost impossible under practical conditions.
- 1989 Overview by Brokerhof evaluating the effect of heat treatment on the pest organisms and on infested cultural property.
- 1990 Koch as well as Paul describe the use of hot air treatment against *Serpula lacrymans*.
- 1991 Further contribution by Koch to the control of *Serpula lacrymans* with hot air.
- 1993 Description of the Thermo-Lignum process and its potential applications against wood pests (Voigt).
- 1994 Ktipper, also Trübswetter and Ertelt report on the suitability of the Thermo-Lignum process for control treatments of works of art and cultural property.
- 1995 Detailed description of the use of hot air against *Serpula lacrymans* by the Danish commercial consortium VKS and by Rudolphi.
Evaluation of the use of hot air against wood-destroying insects and *Serpula lacrymans* by Grosser.
- 1996 Description of the Thermo-Lignum process for the control of insects by Nicholson and von Rotberg, and by Pinniger.
- 1997 Combination of the Thermo-Lignum process with inert gas fumigation (Piening, also von Rotberg).
- 1998 Detailed description of the control treatment by hot air of a building infested with *Serpula lacrymans* (Paul).
- 1999 Solarization of an iconostasis by placing it inside a black plastic bag to control pests (Brokerhof). The method is suitable only for undecorated wood.

Present Day

Hot air treatments are used for control of insects, and to a limited extent fungi, as an alternative to liquid wood preservatives and fumigants.

Advantages/Disadvantages

Processes Without Moisture Content Control. The hot air process without moisture content control can exterminate active infestations of wood-destroying insects and insect pests of stored materials which occasionally may be attacking wood without biocides and within a short time. In contrast to liquid wood preservatives, no residual substances remain in the wood. The process is therefore particularly well suited for control in children's day care centers, hospitals, warehouses for foodstuff and animal feed, finished attics and spaces housing bats. Removal of insect-infested portions of structural timbers prior to hot air treatment is not necessary.

Except for the exhaust gases of oil burners, the process is environmentally friendly. The mycelium, but the spores only rarely, of *Serpula lacrymans* and other wood-destroying fungi can be killed off under practical conditions by hot air treatment; however, the process is not a true alternative to traditional control methods for *Serpula lacrymans*, but rather must be considered an exception or an additional safety measure. Control of *Serpula lacrymans* in thick masonry, in basements and sometimes on the ground floor with hot air is problematic but is being used (Paul 1998). It is especially important in hot air treatments that the temperature in the wood or masonry to be treated is monitored continuously and that the formation of cold pockets is avoided. The latter danger can be ameliorated by the installation of deflector shields or by slightly elevating the pressure of the hot air in the treatment space, for example. The use of hot air does not represent any fire danger because the ignition temperature of wood is considerably greater than the air temperature. However, hot air may loosen wall paper and cause blisters in paint films. Electrical switches, outlets, distributor boxes and similar installed equipment must be either removed or insulated with heat resistant materials, in order to avoid warping. Hot air treatment will unavoidably lead to the more or less visible formation of cracks or the enlargement of existing ones in building timbers, in polychromed surfaces that may be present, and in plaster. Paint layers with poor adhesion to the wood may flake off. The resin in certain softwoods can become liquefied by the heat and ooze to the surface. Painted woods may therefore require remedial treatments. Furthermore, there is a danger that plaster of Paris and stucco become dehydrated, leading to cracks and reduced strength. Hot air treatments are not very suitable for treating purlins, beam ends set into masonry, or structural timbers protruding into the exterior because they cannot be heated sufficiently. If there is danger of renewed moisture problems after the hot air treatment, preventive treatments with chemicals such as boron salts must be added, because the hot air treatment has no preventive effect.

Contact heating methods can be good supplements to traditional methods in cases of early stages of decay or localized infestations. The proper arrangement and installation of heating rods and mats are costly, and the insertion of bore holes removes additional original substance and reduces the strength of the wood. In addition, reductions in wood moisture content during the heating phase lead to stresses and cracks or splits in the member being treated. Contact heating methods are not generally applicable, and their use has to be decided on a case-by-case basis.

Heat Treatments with Moisture Content Control. Heat treatments which maintain largely constant wood moisture content make it possible to free even valuable art objects and cultural property of wood pests without the use of biocides. Portable objects can be treated within a short time and at relatively low cost in stationary or mobile chambers. Altars, pulpits, and pipe organs can be treated in the same manner if they are provided with a temporary enclosure. The extent of damage, if any, objects might suffer during this process depends, among other factors, on accurate monitoring of core temperature and moisture content. Often it is not possible to determine these parameters directly on the object, because insertion of bore holes and electrodes would cause too much damage. Therefore representative test specimens of the same wood species as the objects to be treated must be placed into the treatment space so they can be used to monitor the process parameters.

Trübswetter and Ertelt (1994) and von Rotberg (1997) stated that the dimensional stability of objects is only marginally affected by the treatment, and that dimensional changes are barely distinguishable from those in normal ambient conditions in interior spaces. The glue shear strength is improved if the heating phase, the cooling phase, and an additional equilibration phase of 24h are made an integral part of the treatment. Also, veneered reference panels (2500 × 1500 mm) as well as old, ravaged paintings did not show any macroscopically visible changes even at patches, veneer cracks, and lifted paint layers.

Objects made of several different species of wood are probably difficult to treat. In spite of the positive aspects discussed above, the behavior under the influence of elevated temperature of polychromed or finished objects, and those combining wood with other materials such as metals is likely to be problematic. Differences in coefficients of thermal expansion can lead to stresses, cracks and warping. Softening of temperature-sensitive materials such as rubbed finishes and adhesives or consolidants on a wax/resin basis must be expected. Aging of materials caused by elevated temperatures should be negligible considering the short exposure times. Reducing the treatment temperature with simultaneous exchange of air with an inert gas can reduce the danger of damage to objects without jeopardizing the extermination of the pest.

9.2.2

Freezing Treatments

Technology

Decreasing temperatures at first slow down the metabolic processes of insects, and then lead to frozen stiffness. Depending on insect species and developmental stage, further decreases in temperature cause death by freezing. As the insect's tissues freeze, ice crystals form which probably effect irreversible damage. It is important to note that during slow cooling, some insect species, the wood-destroying Coleoptera among others, are able to extravasate water. Owing to their low moisture content, the fat tissues of the insects do not freeze and the insects can survive.

Freezing treatments can be used for portable wood objects infested with insects. The objects which, prior to treatment, were stored in room conditions must then be sealed hermetically in polyethylene film using heat sealing or special clamps. According to recent research, the formerly recommended wrapping in acid-free paper and addition of silica gel can be omitted (Strohschnieder 1998). Care must be taken to remove most of the air from the plastic bags, as for instance by vacuum suction. Once sealed, the objects should be stored at room temperature or in a refrigerator at a temperature of <5°C.

Freezer chests or chambers are suitable for treatment, but it is important to make sure that the required temperatures of -20 to -30°C can be achieved within a few hours and then held constant. Freezers with air circulation are considered advantageous, but the objects must then be loaded in such a manner that air can circulate freely between objects in order to guarantee rapid freezing. Normally, extermination of insects requires at least -20°C for 48h, not including the cooling phase. Pests living inside materials, such as the larvae of wood-destroying insects, require at least -20°C for 3-7 days or at least -18°C for 2 to 3 weeks for extermination (Brokerhof 1989). Florian (1990) has proposed a double freezing treatment of -20°C for 48h for small objects and -30°C for 72 h for large objects to make certain that no insect eggs can survive. Treatment temperatures cannot be taken simply as read inside the freezers, but must be core temperatures measured on reference specimens if the cultural property cannot be invaded. Freezing should be rapid, reaching at least 0°C after 4h to guarantee complete extermination, whereas thawing should proceed stepwise and slowly, taking 8h to reach 0°C for instance. Either the freezer is turned off or the objects are taken to a refrigerator or cold-storage room. The double freezing treatment entails renewed freezing after complete thawing. When the objects have been thawed, they should be equilibrated to the room temperature of their final destination for 1 or 2 days before they are unwrapped.

Occasionally, shock freezing has been proposed, but this represents risks for cultural property while the effect on pests living inside materials such as

wood is likely to be minor. If freezing equipment is not available, treatment can be done outdoors in countries with low winter temperatures. In Russia, icons 30–40 mm thick which were severely attacked by *Anobium punctatum* were successfully treated during the winter months at average temperatures of -5 to -10°C , and minimum temperatures of -25 to -30°C for 5 days (Toskina 1978). Wood objects such as pallets attacked by termites can be treated in freezing chambers at -19 to -22°C core temperature within 70 min, including freezing and thawing (Pearce 1997).

Preventive measures to guard against insect attack in museum objects can be achieved by storage at $<5^{\circ}\text{C}$, and even in the temperature range of 5 – 10°C the development of insect species is very slow. Low temperatures inhibit the growth of microorganisms. Freeze-drying of wood prevents or inhibits its colonization by fungi, but because of their low moisture content, spores are not killed off by freezing.

Uses

Historical

- 1896 Howard describes the use of low-temperature storage to protect rugs and furs from carpet beetles and moths.
- 1926 Investigations of insect behavior at low temperatures by Payne.
- 1936 Salt deals with the effects of freezing on insects.
- 1947 Parfentiev investigates the possibilities of controlling Anobiidae with the aid of low temperatures.
- 1977 Application of the freezing method to cultural property. At the library of Yale University 37,000 books infested with insects are treated in a freezing chamber (Nesheim 1984).
- 1978 Toskina treats icons infested with Anobiidae with the aid of cold winter temperatures.
- 1979 Detailed investigations on the lethal effects of low temperatures on insects by Mullen and Arbogast.
- 1984 Review article by Unger which includes freezing treatments.
- 1985 Bibliography on the use of low temperatures to control museum pests by Story.
- 1986 Florian characterizes the effects of freezing on insect pests and the infested cultural property.
- 1987 Further contribution by Florian discussing freezing as a method to control insect pests.
- 1989 Comprehensive discussion and evaluation of the freezing method for cultural property by Brokerhof.
- 1990 Florian summarizes control of insects found in museums by freezing.
- 1991 Gilberg and Brokerhof investigate the effect of low temperatures on *Stegobium paniceum*.

- 1992 Hansen discovers that *Anobium punctatum* eggs can survive even an exposure to -30°C for 48h.

Strang summarizes published results on the freezing method and states more precisely the lethal freezing periods proposed by Florian (1986) for some museum pests.

- 1994 A thesis by Elert on pest control in ethnographic collections, including the use of the freezing method.
- 1995 Detailed description and discussion of the use of high and low temperatures to control pests with special consideration of textile artifacts (Kneppel).
Exposition of the effects of high and low temperatures on works of art and cultural property in the control of museum pests (Strang).
- 1996 Michalski publishes results on changes by freezing in wood and parchment.
- 1997 Evaluation of freezing insect pests in heritage objects for disinfection and eradication by Florian
- 1998 Investigations on changes in wood properties by low temperatures including consideration of panel paintings (Strohschnieder).
- 1999 Physical effects (moisture fluctuations, thermal contraction) are small when wood and lacquer ware are frozen at -30°C (Ishizaki).

Present Day

The freezing method for the control of insects in museum objects continues to be used in special cases and has gained some importance, especially in the USA, Canada, Australia, England and Scandinavia. Systematic control of wood-destroying insects in works of art and cultural property by freezing of objects is done only rarely, and is usually limited to ethnographic objects and utensils made of wood.

Advantages/Disadvantages

Cold treatments, like heat treatments, make it possible to dispense with the use of biocides, and there are no residuals left in the wood. Compared with heat treatments without moisture content control, the freezing method can be considered advantageous because only minor changes in moisture content occur. Wet objects should not be treated at very low temperatures because ice crystals forming in the cell lumens might damage the cell walls. Ice crystals will not form in air-dry wood and cell wall damage will not take place (Nanassy 1978). The adsorption of water from the surrounding air during freezing and its return during thawing by properly wrapped and sealed objects will cause only minor dimensional movement. Thermal contraction and expansion of plain wood are of even less importance. Such dimensional changes as occur during the freezing and thawing cycles are reversible, and

permanent embrittlement does not take place at -20°C . In the case of painted wood, contraction and expansion of wood and paint layers will not differ significantly, and damage to the paint layers can hardly be expected (Strohschnieder 1998).

Few data are available regarding the control of wood-destroying insects by low temperatures. Systematic experiments to determine optimum temperatures and exposure times for various insect species and their developmental stages are still needed.

9.3

Changing Air Humidity and Material Moisture Content

Technology

Lowering relative humidity and material moisture content at constant temperature brings about a slowdown and inhibition of the life processes of many wood-destroying organisms. According to Pinniger (1994), extremely dry conditions of less than 10% relative humidity are disadvantageous for most insects. Extermination of insect or fungal infestations by dehumidification of objects at room temperature can hardly be realized within acceptable time periods. Dehumidification of compact, porous, organic materials like wood is almost always accompanied by reversible structural changes. The Rentokil firm has combined a fumigation bubble with a dehumidifier for the control of mites and book lice in valuable books and works of art (Smith 1988). However, detailed information on the effectiveness of the method and required treatment times are not available.

Uses

Dehumidification of objects at constant temperature for the control of wood-destroying organisms is not used in conservation practice. Attempts to freeze-dry objects infested with insects and fungal decay have been reported, but this will merely slow down the growth of the fungi, and some developmental stages of insects are able to survive. Fungal growth can be effectively inhibited if the relative humidity is significantly less than 65%. During treatments to control *Serpula lacrymans* in buildings it is important to eliminate moisture sources which might encourage fungal growth or enable renewed infestation.

Advantages/Disadvantages

Effective control of active infestations by wood-destroying organisms solely by reducing relative humidity and material moisture content is not possible within acceptable time spans.

9.4

Use of Pressure Differentials

9.4.1

Reduced Pressure

Technology

From time to time attempts have been made to control active infestations of wood-destroying insects in portable objects by placing them into vacuum chambers or airtight plastic bags and removing most of the air, but they have shown little success. Barriers to air removal inside the wood which prevent the attainment of the necessary vacuum and low oxygen requirements of insect respiratory systems are considered the cause. According to Unger (1984), exposed Anobiidae larvae and termites are killed by a vacuum of 133.3 Pa after 2 h, but house borer larvae will survive. Anobiidae larvae living in wood 7.5 and 35 mm below the wood surface were not affected by a vacuum of 133.3 Pa for 24 h. Only at 13.3 Pa and otherwise equal conditions were up to 60% of the test insects killed, but this kill rate does not suffice for acceptable control. Straub (1963) stated that extermination of the larvae of wood-destroying insects would probably require high vacuum for a full week. Exploratory experiments by Preuß (1994), however, showed that even after 5 days at 299 Pa, living Anobiidae larvae remain inside $25 \times 100 \times 200\text{ mm}$ wood samples. In contrast to insects living deep inside wood, other museum pests can be killed off up to 99% at 2 kPa in 12–56 h, depending on species (Bergh et al. 1996). The cause of death is considered to be the desiccation of larvae and imagoes during treatment.

Surface and interior mycelium cannot be controlled by vacuum treatment, but minor attacks, as for instance in books, can be largely eliminated by vacuum suction. Sealing objects in plastic films accompanied by air removal reduces the danger of rapid fungal infestation. Reduced pressure during fumigation treatments reduces the length of treatment and is necessary in some cases (cf. Chap. 8).

Uses

Historical

- 1925 Investigation of the applicability of reduced pressure to the control of insects by Back and Cotton.
- 1963 Straub rejects the potential of the reduced pressure method for the control of wood-destroying insects.
- 1984 Unger tests the effect of reduced pressure on Anobiidae and house borer larvae and on termites.

1989 Vacuum suction can remove superficial fungal growth in books (Brokerhof).

1994 Elert reviews the literature on vacuum treatments.

Anobiidae larvae survive a 5-day vacuum treatment (Preuß).

1996 Bergh et al. investigate the lethal effects of reduced pressures on museum insect pests other than wood-destroying insects.

Present Day

Reduced pressure treatments to control wood-destroying organisms are not being used in conservation practice.

Advantages/Disadvantages

Precise parameters for the extermination of wood-destroying insects by reduced pressure are not available, so that this method cannot be recommended for the elimination of active infestations. Decay fungi cannot be controlled by reduced pressure. Treatment is only possible for portable objects which can be taken to suitable vacuum chambers. Severely damaged objects are at risk of collapse during high vacuums. Since the application of vacuum is also a means of drying materials, prolonged exposure of objects to vacuum can lead to the formation of cracks in wood supports and paint layers.

9.4.2

Elevated Pressure

Technology

It can be assumed that the application of elevated pressures alone cannot effect reliable extermination of wood-destroying insects in objects. However, if the air is replaced by CO₂ (cf. Chap. 8), elevated pressure can accelerate extermination at room temperature. This procedure has been used for some time to control insect pests in stored plant products, where the material is placed into a rapid closing CO₂ pressure chamber and exposed to pressures of up to 4 MPa at ambient temperature. This method could also be applied to portable cultural property. It was tested on a wood sculpture 870 mm tall and infested with *Anobium punctatum* (Binker 1993). Following evacuation of the pressure chamber to a residual pressure of 0.02 MPa, CO₂ was introduced to a pressure of 2 MPa at an ambient temperature of 9°C. After 2.5h exposure followed by rapid pressure release the sculpture was removed. All anobiid larvae contained in a control specimen treated with the sculpture were killed. The rapid extermination of all larvae is attributed to an intensive solution of carbon dioxide in the insect blood and the irreversible mechanopneumatic damage to the insect's body by the rapid pressure release, analogous to the

bends experienced by divers. Within certain limits temperature is not an important factor. Presumably, similar effects could be achieved by using supercritical carbon dioxide.

Uses

Historical

1993 Exploratory test of CO₂ pressure fumigation of a sculpture infested with Anobiidae by Binker.

Present Day

Pressure treatments of cultural property using air or its constituent gases are not actually used in conservation.

Advantages/Disadvantages

Reliable data regarding the treatment of insect-infested wood objects with elevated pressure and air are not presently available. If the air is replaced by carbon dioxide, successful treatments should, in principle, be possible. However, the suitability of the process against different species and their various developmental stages must be investigated, with the goal of determining optimum treatment parameters. The suitability for treating heavily damaged objects must also be tested.

9.5

Utilizing Sound and Electromagnetic Waves

9.5.1

Ultrasound

Technology

In addition to its diagnostic uses for wood (cf. Chap. 6), ultrasound could theoretically also be used to kill insect larvae. This would require that the sound waves are strong enough and act long enough to inhibit feeding of the larvae, but to date all attempts have been unsuccessful.

Uses

Historical

1984 Unger rules out the use of ultrasound for control of wood-destroying insects.

- 1985 According to Story, ultrasonic equipment cannot prevent pests from entering buildings, and it also fails in their control.
- 1995 Grosser rates equipment based on ultrasonics as unsuitable for the control of the larvae of wood-destroying insects.

Present Day

Ultrasonics are not used to control insects, and there is little reason to expect future application.

Advantages/Disadvantages

Aside from the lacking or unproven effectiveness of the method there is also a danger that it will cause damage to the object. For example, veneer could separate from furniture, as might loose parts or monochrome or polychrome paint layers on works of art.

9.5.2

Microwaves/High Frequency Waves

Technology

Microwaves and high frequency waves are delimited variously in the literature. In Germany it has been proposed that microwaves would extend over the frequency range from 300 MHz to 300 GHz, at a wavelength ranging from 1 m to 1 mm, and high frequency waves from 3 kHz to 300 MHz, at a wavelength from 100 km to 1 m.

When microwaves or high frequency waves are applied to dielectric materials containing moisture such as wood, the major part of the radiated energy is converted into heat during aligning of the water molecules which will vibrate when fields of alternating current are used. The major factor governing heating is the specific absorption rate, which depends on the wavelength of the radiation and the material moisture content. Dry wood is heated less than damp wood, since bound water absorbs microwaves only weakly. The extermination of wood-destroying organisms, which contain water in their cell fluids, is effected by the heating caused by microwaves or high frequency waves (cf. Sect. 9.2.1). The waves can penetrate to the insect larvae or fungal mycelium in the interior of the wood, and will heat the organisms and the wood inside out. The energy required for the control of wood-destroying organisms is produced either by a magnetron for microwaves or a high frequency generator. Magnetrons often operate in the range of 2000–3000 MHz and produce a power of 500–3000 W. High frequency generators used so far, for example, operate at a frequency of 13.56 or 27.12 MHz at a power of 1000–1500 W. Treatment times are matters of seconds or minutes.

Uses

Historical

- 1949 Jaquiot uses high frequency waves to exterminate wood-destroying insects.
- 1959 Larvae of *Lyctus brunneus* in oak wood can be killed off in 40 s at frequencies of 76 or 37.5 MHz (Thomas and White).
- 1960 Larvae of *Hylotrupes bajulus* should be exterminated in 30 min at 2425 MHz (van den Bruel et al.).
- 1965 Bletchly (1965a,b) treats Anobiidae larvae living in birch plywood using a magnetron at 2450 MHz over a period of 3–7 min.
- 1970 German patent for the local control of pests in buildings by microwaves.
- 1975 Wälchli and Tscholl use a frequency of 13 MHz to kill larvae of *Hylotrupes bajulus* in 3–4 min.
- 1981 Experiments to use microwaves to sterilize polychrome wood with a 600-W generator (Burski and Zygmunt).
- 1984 Review of the literature on the control of wood-destroying insects by microwaves or high frequency waves by Unger.
- 1985 Development in Switzerland of a high frequency apparatus for the extermination of wood-destroying insects.
- 1986 Construction of a microwave device in Denmark to treat wood with fungal decay (Bech-Andersen and Andersen 1992).
- 1987 Report by Krajewski et al. on the control of wood-destroying insect larvae with microwaves.
- 1989 Brokerhof lists advantages and disadvantages of using microwaves on cultural property.
- 1990 Burski et al. investigate the effects of microwaves on wood-destroying organisms, on the impregnation of wood with liquids, and on the technological properties of wood.
- Krajewski uses portable microwave equipment with a frequency of 2450 MHz and a power of 600 or 1400–2400 W and a microwave chamber at 1000 W to exterminate wood-destroying insects.
- 1990–1992 Approximately 100 treatments with microwaves to control *Serpula lacrymans* in buildings in Denmark (Bech-Andersen and Andersen 1992).
- 1992 Kjerulf-Jensen and Koch treat mycelium of *Serpula lacrymans* in wood and masonry with microwave equipment. At a temperature of 39–40 °C eradication is achieved after 15 min in a wood beam 200 mm thick and after 30 min in masonry 350 mm thick.
- 1994 Elert discusses the use of microwaves on works of art and cultural property, and Pinniger mentions some disadvantages.
- Egg and adult larvae of *Hylotrupes bajulus* and *Anobium punctatum* inside pine samples are not sufficiently killed off by use of a magnetron at 2450 MHz and 1000 W (Graf et al.).

Report by Munck and Sundberg on controlling *Serpula lacrymans* in buildings using high frequency energy (13.56 MHz) in Denmark.

- 1995 Andreuccetti et al. determine that larvae of *Hylotrupes bajulus* in wood can be killed off within 3 min at 53°C.

Critical evaluation by Grosser of microwave and high frequency technology for the control of wood-destroying pests.

Description of the use of high frequency equipment for the control of wood-destroying organisms in buildings (Sauer).

- 1997 Critical commentary by Kempe on the use of microwaves against decay fungi in buildings and wood-destroying insects.

Zielonka et al. investigate the temperature distribution during heating of wood by microwaves.

- 1998 Jütterschénke and Weija advocate high frequency heating to control insects and fungi in wood.

Pohleven et al. determine lethal temperatures and exposure times for *Coniophora puteana* (4 min at 75°C), *Lentinus lepideus* (10 min at 90°C) and *Gloeophyllum trabeum* (12 min at 90°C) when using high frequency waves of 4.75 MHz.

Unger mentions serious disadvantages of the use of microwaves on works of art and cultural property, and points out the need for optimization of the technology.

Present Day

Occasionally, equipment incorporating microwaves or high frequency-energy as a heat source for wood is used to control wood-destroying organisms in small infestations. However, it is not certain that reliable and complete extermination of the pests can be guaranteed.

Advantages/Disadvantages

The lack of suitable methods for treating selected building components in historical structures without loss of original substance makes the use of microwaves or high-frequency energy appear attractive. In principle, it can be taken as a given that control of localized infestations in built-in wood members such as window frames and sills, door frames, wood stairs, pipe organ parts, column paneling, and half-timbering can be treated. As a prerequisite, suitable equipment and technology must be developed which can eradicate the wood-destroying organisms in an infested component in their entirety. Equipment used to date has repeatedly permitted occasional insects or fungi, or their developmental stages, to survive. One of the reasons may have been uneven temperature distribution, and reportedly the insects can regenerate moisture lost during the treatment.

Microwave and high-frequency technology is not suitable for large-scale applications. The rapid transport of energy into the wood to be treated, and

the consequent short treatment time and localization of heating are an advantage. The method can be – aside from the generation of stray electrical fields – considered as environmentally friendly because no toxic substances are introduced into the wood. Uneven heating and corresponding changes in moisture content can lead to drying checks and cracks, and resin exudation in certain coniferous woods. It is also possible that paint layers darken and adhesives soften. Especially dangerous are metal parts hidden inside the wood, which are heated preferentially and could lead to charring of the wood. The extent of damage would depend on such factors as the radiating power of the equipment and the length of exposure to microwave or high frequency energy.

9.5.3

X-rays

Technology

X-rays are produced with the aid of an X-ray tube and a high voltage source, and have a wavelength in the range of 10^{-7} – 10^{-10} m. A distinction is made between soft and hard X-rays depending on the wavelength. Whereas soft X-rays can be used to locate insect larvae inside wood (cf. Chap. 6), increasing hardness of the rays yield insecticidal and fungicidal effects. However, the insecticidal effect is limited to exposed eggs, larvae, and imagoes of wood-destroying insects. Larvae living inside wood are not killed, nor are termites of an active infestation.

Uses

Historical

- 1961 According to experiments by Schmidt, exposed house longhorn beetle larvae are killed immediately at a dosage of 2–3 kGy radiation for 664–1000 s. Larvae inside wood do not show any abnormal reactions after radiation at 1.8 kGy for 6 h. Termites also can only be killed if exposed.
- 1982 Exposed insects of the genera *Anobium*, *Xestobium* and *Lyctus* can be killed with a dosage of 0.08 kGy, eggs with 0.5–0.7 kGy and *Hylotrupes* larvae with 1.5–2 kGy (Raschle and Graf). If the *Hylotrupes* larvae are inside the wood at a depth of 60 mm, 1.8 kGy for 6 h is insufficient for extermination.
- 1989 Brokerhof discusses the effects of X-rays on pest organisms. The radiation reportedly prevents the emergence of the larvae from the eggs.
- 1994 Elert summarizes the state-of-the-art use of X-rays against museum pests.

Present Day

X-rays are not used for the control of wood-destroying organisms. Their use as a diagnostic tool is discussed in Chapter 6.

Advantages/Disadvantages

Aside from the lack of effectiveness in controlling insect larvae living inside wood or any mycelium substrate which may be present, X-rays can also cause material damage. According to Brokerhof (1989), a dosage of 1 kGy can lead to changes in lead pigments in painted objects (white lead turns gray), and the tensile strength of cotton decreases with increasing X-ray dosage.

9.5.4

Gamma Rays

Technology

Gamma rays are electromagnetic rays of high energy and a wavelength between 4×10^{-10} and 10^{-13} m, which are emitted by the nucleus of a radioactive substance. Synthetic radioactive materials are primary sources, and stationary irradiation facilities most often incorporate the radio nuclides ^{60}Co or ^{137}Cs . In contrast to X-rays, gamma rays have high penetrating power, so that medicinal articles, cosmetics, and foodstuff can be sterilized by irradiation and pests active inside wood can be exterminated. Penetration depends on the density of the material to be treated and the energy of the applied radiation.

Total dosage required to exterminate wood-destroying insects ranges from 0.25–3 kGy, depending on species and developmental stage. To control decay fungi in wood usually requires higher dosages, ranging from 2–18 kGy depending on species. Mycelium of *Serpula lacrymans* can be killed off with 2–3 kGy, and this can be reduced to 0.5 kGy if the temperature is raised to 50°C. To exterminate bacteria requires 3–15 kGy. Treatment time depends on the dosage capacity of the treatment facility and is usually in the order of several hours. The polymerization of monomers introduced into wood by gamma radiation will be discussed in Chapter 11.

Uses

Historical

- 1957 Experiments by Bletchly and Fisher on the extermination of various developmental stages of *Anobium punctatum*, *Xestobium rufovillosum* and *Lyctus brunneus* by gamma radiation.
- 1961 Further report by Bletchly on treating wood-destroying insects with gamma radiation.

- 1963 Straub mentions the method for the control of wood-destroying insects, but does not consider it promising.
- 1969 According to Beck et al. it is possible to eradicate wood-destroying insects and fungi in old wood and paper by ionizing radiation. Total dosage for wood-destroying insects and fungi is 2–3 kGy, but some mold fungi and spore-forming bacteria require up to 15 kGy.
Bors investigates the dependence of the required radiation dosage on temperature when treating wood infested with *Serpula lacrymans* and *Coniophora puteana*. Results show that heating the object to be treated allows a significant reduction of the dosage required to exterminate the fungi.
- 1972 Beginning of a continuing program of treatment of insect infested works of art with gamma radiation at the Nuclear Research Center in Grenoble, France.
- 1973 The sterilization of wood with gamma rays is investigated in Japan (Yamamoto et al.).
- 1978 Urban et al. publish details on the construction of a stationary facility for ^{60}Co irradiation in a museum near Prague. Plans call for the irradiation of about 2000 objects from various museums in Czechoslovakia.
- 1979 Control of wood-destroying insects in wall paneling in the Sanssouci palace near Potsdam, Germany, with portable ^{137}Cs radiation equipment (Bär et al. 1983).
- 1982 Raschle and Graf discuss the effect of gamma rays on wood-destroying organisms.
- 1984 Evaluation of the literature and details of experiments on the use of gamma rays on infested cultural property by Unger.
- 1985 Investigations by Sedláčková and Urban on the effect of gamma rays on paint layers.
Bibliography by Story on the use of gamma rays against museum pests.
- 1986 Teply et al. introduce a mobile irradiation facility for cultural property.
Urban and Justa describe the conservation of cultural property with gamma rays.
- 1989 Brokerhof discusses the use of gamma rays on works of art and cultural property.
- 1990 Verdu et al. discover that irradiation of polychrome sculptures infested with fungi and insects leads to symptoms of aging in paint consolidants.
- 1991 Caneva et al. mention treatment with gamma rays during conservation of works of art.
- 1993 Irradiation of aged paper with 10 kGy for 1 h accelerates the aging process by 50–100% (Hofenk de Graaff and Roelofs).
- 1994 Evaluation of the literature on using gamma rays by Elert.

Pinniger mentions gamma ray treatments for the control of insects in museums.

Experiments on the sterilization of microorganisms on waterlogged wood by Pointing et al.

1996 Practical aspects of waterlogged wood sterilization by gamma radiation as a novel storage method (Pointing et al. 1997).

Present Day

Gamma radiation is used occasionally on works of art and cultural property when other methods are not promising, as in the case of molds and bacteria, provided this is allowable by the radiation safety regulations of the country in question.

Advantages/Disadvantages

Gamma rays are capable of good penetration of the objects to be treated, and many objects can be irradiated in a short time. The irradiated objects do not become radioactive, there are no residuals, and further treatments can be applied immediately after irradiation. A disadvantage is that objects must be transported to a stationary radiation facility. Depending on the dosage applied, the irradiation causes formation of radicals and ionization of molecules. In wood chemical bonds are broken, cellulose chains become shortened, and functional groups are altered. The effect is cumulative, i.e., additional irradiation will increase the processes of transformation and decomposition. Acceleration of aging can lead to increased susceptibility of objects to biological attack. Gamma radiation leaves no preventive effects. Causes for the relatively rare use of gamma rays are the lack of detailed guidelines with respect to particular pests and to the objects which are infested, the high cost of safety measures to prevent dangerous radiation, and the strict regulations for radiation safety in various countries.

References

- Andreuccetti D, Bini M, Ignosti A, Gambetta A, Olmi R (1995) Feasibility of microwave disinfection of wood. IRG/WP/40051
- Anonymous (1987) Das Heißluftverfahren zur Bekämpfung tierischer Holzzerstörer in Bauwerken. WTA (Wissenschaftlich-Technischer Arbeitskreis), Merkblatt 1-87, 4pp
- Back EA, Cotton RT (1925) The use of vacuum for insect control. J Agric Res XXXI(11): 1035-1040
- Bär M, Kerner G, Köhler W, Unger W (1983) Die Bekämpfung holzerstörender Insekten mit ionisierender Strahlung. Neue Museumskd 26(4):208-215
- Bech-Andersen J, Andersen C (1992) Theoretical and practical experiments with eradication of the dry rot fungus by means of microwaves. IRG/WP/1577-92
- Beck W, Gesswagner D, Kaindl K (1969) Beiträge zur Konservierung von Holz und Papier. Die Frage des Einsatzes ionisierender Strahlen zur Sanierung alter Hölzer und Papiere. Hermann Böhlaus Nachf, Wien

- Becker G, Loebe I (1961) Hitzeempfindlichkeit holzerstörender Käferlarven. Anz Schädlingsskd (34):145-149
- Becker H (1984) Das Heißluftverfahren zur Hausbockbekämpfung - Möglichkeiten und Grenzen. Prakt Schädlingsskd 36(10):177-180
- Bergh J-E, Mourier H, Poulsen KP (1996) Lethal effects of low pressure ("vacuum") on some museum pest insects. ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland, 1-6 Sept 1996, vol I, pp 3-7
- Binker G (1993) Mit Kohlendioxid gegen Insektenbefall. Restauro 99(4):222
- Bletchly JD (1961) The effect of gamma radiation on wood-boring insects. Ann Appl Biol 49(2):362-370
- Bletchly JD (1965a) Very high frequency radio waves and wood-boring insect control. Holz-forschung 19(2):47-52
- Bletchly JD (1965b) Very high frequency radio waves and wood-boring insect control. Ind Pest Control 7(3):1-20
- Bletchly JD, Fisher RC (1957) Use of gamma radiation for the destruction of wood-boring insects. Nature 179:670
- Bors J (1969) La suppression des dommages aux bois par des radiations ionisantes. ICOMOS symposium on the weathering of wood, Ludwigsburg, 8-11 June 1969 (AATA 11-553)
- Brokerhof A (1989) Control of fungi and insects in objects and collections of cultural value "a state of the art". Central Research Laboratory for Objects of Art and Science, Amsterdam
- Brokerhof AW (1999) Low-oxygen treatment and solarisation of the *Protoplasma iconostasis*: alternative pest control methods in the field. In: Bridgeland J, Brown J (eds) ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 Aug-3 Sept 1999. Preprints, vol I, pp 14-20
- Burski Z, Zygmunt A (1981) Badanie mozliwosci sterylizacji drewna polichromowanego za pomoca energii mikrofalowej (Examination of the possibilities of microwave sterilization of polychrome wood). Chemia w Konserwacji Zabytkow, pp 39-47 (AATA 20-432)
- Burski Z, Chrzanoski A, Tomaszewski K, Zygmunt A (1990) Wstepne badania nad wplywem napromieniowania mikrofalami na niektore wisciwości drewna sosnowego (Preliminary studies of the impact of microwave radiation on selected properties of pine wood). Rocznik przedsiwiorstwa państwowego Pracownia Konserwacji Zabytkow, 1986, (1):245-258 (AATA 29-2349)
- Caneva G, Nugari MP, Salvadori O (1991) Biology in the conservation of works of art. ICCROM Rome 1991
- Clausnitzer K-D (1990) Historischer Holzschutz. ökobuch, Staufen bei Freiburg
- Cymorek S, Wegen H-W (1983) Schutz für Fledermäuse/Fledertiere. Prakt Schädlingsskd 35(6):119-120
- Elert K (1994) Schädlingsskd in Völkerkundlichen Sammlungen. Diplomarbeit, Institut für Technologie der Malerei der Staatlichen Akademie der Bildenden Künste, Stuttgart
- Florian M-L (1986) The freezing process - effects on insects and artifact materials. Leather Conserv News 3(1):1-17
- Florian M-L (1987) The effect on artifact materials of the fumigant ethylene oxide and freezing used in insect control. ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, Australia, 6-11 Sept 1987, vol I, pp 199-208
- Florian M-L (1990) Freezing for museum insect pest eradication. Collect Forum 6(1):1-7 (AATA 28-1406)
- Florian ML (1997) Heritage eaters. Insects and fungi in heritage collections. James & James, London
- Gilberg M, Brokerhof A (1991) The control of insect pests in museum collections: the effects of low temperature on *Stegobium paniceum* (Linnaeus), the drugstore beetle. J Am Inst Conserv 30(2):197-201
- Graf E (1987) Biogene Schäden an kulturhistorischen Holzbauteilen und ihre Sanierung. In: Schiessl U (ed) Bemalte Holzdecken und Tafelungen. Haupt, Bern, pp 101-105

- Graf E, Manser P, Lanz E (1994) Bekämpfung holzerstörender Insekten mit Mikrowellen. Interner Bericht der Abteilung Biologie Nr 120'500/A der EMPA, Switzerland
- Grosser D (1995) Überblick über die derzeit bestehenden Möglichkeiten bekämpfender Holzschutzmaßnahmen. In: DGfH (ed) 20. Holzschutz-Tagung, Rosenheim, 18–19 Oct 1995, Kurzfassung der Vorträge, pp 69–89
- Hansen LS (1992) Use of freeze disinfection for the control of the common furniture beetle *Anobium punctatum*. IRG/WP/1528–92
- Haupt R (1908) Vom Holzwurm. Zentralbl Bauverwalt 28:558–559
- Hegarty B (1988) Neue Erkenntnisse über den Echten Hausschwamm *Serpula lacrymans*. Holz-Zentralblatt 114(46):655, 660–666
- Hegarty B, Buchwald G, Cymorek S, Willeitner H (1986) Der Echte Hausschwamm – immer noch ein Problem? Mat Org 21(2):87–99
- Hofenk de Graaff JH, Roelofs WGTH (1993) The influence of ethylene oxide and gamma radiation on the aging of paper. ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 22–27 Aug 1993, vol II, p 896
- Howard LO (1896) Some temperature effects on household insects. In: United States Department of Agriculture, Division of Entomology (ed) Proceedings of the 8th Annual Meeting of the Association of Economic Entomologists, Bulletin 6, Washington, DC, pp 13–17
- Ishizaki T (1999) Evaluation of physical effects of thermal methods on materials of artifacts. The 23rd International Symposium on the Conservation and restoration of cultural property, 27–29 Sept 1999, Tokyo, Abstracts, p 18
- Jacquot C (1949) De l'emploi du chauffage haute fréquence pour la destruction des insectes des bois mis en oeuvre. CR Acad Agric France 36:637–638
- Jensen K (1931) Neue Wege der Hausbockbekämpfung. Techn Gemeindebl 34:32–36
- Jensen K (1955) Hausbockbekämpfung in Dänemark. Gesundheitswesen, Heft 49
- Jütterschenke F, Weijs A (1998) Hochfrequenzwärme. BauSanierung (2):49–53
- Kempe K (1997) Hausschwamm bekämpfung – ohne falsche Illusionen. Holz-Zentralblatt 123(35):518
- Kjerulf-Jensen C, Koch AP (1992) Investigation of microwave as a means of eradicating dry rot attack in buildings. IRG/WP/1545
- Kneppel B (1995) Schädlingsbekämpfung an textilem Kulturgut unter Einsatz hoher und tiefer Temperaturen. Kölner Beiträge zur Restaurierung und Konservierung von Kunst- und Kulturgut, vol 2. Anton Siegl GmbH Fachbuchhandlung, München
- Koch AP (1990) Dry rot – new methods of detection and treatment. BWPDA Record of Convention, The British Wood Preserving and Damp-proofing Association, London pp 1–13
- Koch AP (1991) The current status of dry rot in Denmark and control strategies. In: Jennings DH, Bravery AF (eds) Fundamental biology and control strategies. Wiley, Chichester
- Kollmann FFP, Côté WA Jr (1968) Principles of wood science and technology I. Solid wood. Springer, Berlin Heidelberg New York
- Krajewski A (1990) Zwalczanie owadów-szkodników technicznych drewna za pomocą mikrofal (Control of wood pests with microwaves). Ochrona Zabytków 43(1):27–34 (AATA 29-1176)
- Krajewski A, Zygmunt A, Burski Z (1988) Bekämpfung der holzerstörenden Insektenlarven mit Hilfe von Mikrowellen. In: Eri I, Sárközy G (eds) Conservation-restoration of leather and wood; training of restorers. 6th International Restorer Seminar Veszprem 1987. National Centre of Museums, Budapest, pp 67–82 (AATA 25-1803)
- Küpper R (1994) Wärmebehandlung bei schädlingsempfindlichem Holz. Holz in der restauratorischen Denkmalpflegerischen Praxis-2. Fortbildungsveranstaltung für Restauratoren, Hannover, 11 March 1994, pp 61–66
- Michalski S (1996) Freezing wood and parchment. Paper Conserv News 80:11–12
- Miric M, Willeitner H (1984) Lethal temperatures for some wood-destroying fungi with respect to eradication by heat. IRG/WP/1229
- Mullen MA, Arbogast RT (1979) Time-temperature-mortality relationships for various stored-

- product insect eggs and chilling times for selected commodities. J Econ Entomol 72(4): 476–478
- Munck O, Sundberg H (1994) Experiences from a Danish large-scale test by means of a new method of treatment by attack of true dry rot fungus (*Serpula lacrymans*) in buildings. IRG/WP/10064
- Nanassy AJ (1978) Temperature dependence of NMR measurement on moisture in wood. Wood Sci 11(2):86–90
- Nesheim K (1984) The Yale non-toxic method of eradicating book-eating insects by deep-freezing. Restaurator 6:147–164
- Nicholson M, von Rotberg W (1996) Controlled environment heat treatment as a safe and efficient method of pest control. In: Willey KB (ed) Proceedings of the 2nd International Conference on Insect pests in the urban environment. Heriot-Watt-University, Edinburgh, Scotland, 7–10 July 1996, pp 263–265
- Parventiev VYa (1947) *Anobium striatum* Ol. and possible control measures against it with the help of low temperatures (Russ.). Entomol Obozrenie 29(3/4):154–164
- Paul O (1990) Hausschwamm bekämpfung mit Heißluft. Bautenschutz Bausanierung 13:12–15
- Paul O (1998) Der Hausschwamm stirbt im Backofen. Bautenschutz Bausanierung 21(6):35–37
- Payne NM (1926) Freezing and survival of insects at low temperature. Q Rev Biol 1:270–282
- Pearce MJ (1997) Termites. Biology and pest management. CAB International, New York
- Piening H (1997) Modifizierte Inertatmosphären in der Schädlingsbekämpfung – oder: Im Zweifel für's Objekt. Dem "Zahn der Zeit" entrissen! Neue Forschungen und Verfahren zur Schädlingsbekämpfung im Museum. Landschaftsverband Rheinland, Rheinisches Archiv- und Museumsamt, Rheinland-Verlag Köln in Kommission bei Dr. R. Habelt GmbH, Bonn, pp 98–105
- Pinniger D (1994) Insect pests in museums, 3rd edn. Archtype Publications Limited, London
- Pinniger D (1996) Insect control with the thermo lignum treatment. Conserv News 59: 27–29
- Pohleven F, Resnik J, Kobe A (1998) Eradication of wood decay fungi by means of radio frequency. IRG/WP/98–10292
- Pointing SB, Jones AM, Jones EBG (1994) The potential use of gamma irradiation for improving the long-term storage of waterlogged archaeological wood. In: Hoffmann P (ed) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, pp 437–452. (AATA 32-872)
- Pointing SB, Jones AM, Jones EBG (1997) Practical considerations for gamma radiation sterilization of waterlogged archaeological wood. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 317–330
- Preuß H (1994) Versuche zur Schädlingsbekämpfung: Kälte und Vacuum. In: Landschaftsverband Stade u. Museumsverband für Niedersachsen und Bremen (ed) Bekämpfung holzerstörender Insekten in Museen und Sammlungen. Tagung im Schwedenspeichermuseum Stade, 18 Feb 1994, pp 21–23
- Raschle P, Graf E (1982) Mikroorganismen, Kryptogamen, Biozide, Konservierungsmittel und kulturhistorische Objekte. SKR Publikation, Arbeitstagung St. Gallen, 16 March 1981
- Rathgen F (1910) Über Mittel gegen Holzwurmfress. Museumkunde 6:23–27
- Rudolphi A (1995) Versuch der Schwamm bekämpfung mit Hilfe des Heißluftverfahrens. Holzschutzkonferenz des DHBV am 13.5.1995 in Berlin. Deutscher Holz- und Bautenschutzverband e.V., Köln
- Salt RW (1936) Studies on the freezing process in insects. Techn Bull 116. University of Minnesota, Agricultural Experiment Station, Minnesota
- Sauer A (1995) Hochfrequenztechnik für biozidfreie bekämpfende Holzschutzmaßnahmen. Holz-Zentralblatt 121(50):801–802

- Schmidt H (1961) Die Wirkung von Röntgenstrahlen auf holzerstörende Insekten. *Holzforsch Holzverwert* 13(1):8–11
- Schmidt H, Schneider A (1957) Abtötende und vorbeugende Wirkung bei der Hausbockbekämpfung mit Heißluft. *Holz Roh Werkst* 15:406–410
- Sedláčková J, Urban J (1985) Účinok gama žiarenia na polychrómiu (The effect of gamma radiation on polychromy). *Pamiatky Píroda* 15(2):18–20 (AATA 22–1335)
- Smith CP (1988) Fumigation – a new concept. BPCA Paper Rentokil PLC, East-Grinstead
- Story KO (1985) Approaches to pest management in museums. Smithsonian Institution, Washington, DC
- Strang TJK (1992) A review of published temperatures for the control of pest insects in museums. *Collect Forum* 8(2):42–67
- Strang TJK (1995) The effect of thermal methods of pest control on museum collections. *Biodeter Cult Prop* 3. Proceedings of the 3rd International Conference on Biodeterioration of cultural property, Bangkok, Thailand, 4–7 July 1995, pp 334–353
- Straub RE (1963) Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich
- Strohschnieder M (1998) Holztechnologische Untersuchungen zur Gefriertechnik als Möglichkeit der Schädlingsbekämpfung unter besonderer Berücksichtigung gefäster Bildwerke. Diplomarbeit, Fachhochschule Hildesheim/Holzminde
- Teichert M (1996) Untersuchungen über eine Wärmebehandlung von verbaulichem Holz zum Abtöten von Schwammbefall. Diplomarbeit, Fachbereich Biologie, Universität Hamburg
- Teply J, Franek C, Kraus R, Cervenka V (1986) Mobile irradiator and its application in the preservation of the objects of art. *Radiat Phys Chem* 28(5/6):585–588 (AATA 25–609)
- Thomas AM, White MG (1959) The sterilization of insect-infested wood by high-frequency heating. *Wood* 24:407–410, 449–451, 487–488
- Toskina IN (1978) Wood pests in articles and structures and pest control in museums. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 78/13/2/1–10 (AATA 16–460)
- Trübswetter T (1985) Probleme bei der Sanierung alter Hölzer. *Holz-Zentralblatt* 111(16):230
- Trübswetter T, Ertelt P (1994) Holzschutz mittels kontrollierter Klimatisierung. *Holz-Zentralblatt* 120(24):393–396
- Unger A (1998) Alternative Bekämpfungsmaßnahmen gegen Holzzerstörer – Möglichkeiten und Grenzen. *Prakt Schädlingsbekämpfer* (6):20–24
- Unger W (1984) Möglichkeiten der Bekämpfung holzerstörender Insekten durch physikalische Methoden. *Holztechnologie* 25(5):264–269
- Urban J, Justa P (1986) Conservation by gamma radiation. *Museum* 151:165–167
- Urban J, Santar I, Sedláčková J, Pipota J (1978) Use of gamma radiation for conservation purposes in Czechoslovakia. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 78/17/4 (AATA 16–463)
- van den Bruel WE, Pietermaat F, Bollaerts D, Stefens P (1960) Recherches sur la destruction au moyen d'un champ électrique à très haute fréquence des insectes xylophages forant les bois ouverts. *Meded Landouwhogeschool* 25(3/4):1377–1391
- Verdu J, Kleitz MO, Dijoud F, Valot H (1990) Le rayonnement gamma et la désinfection des sculptures polychromes. La conservation du bois dans le patrimoine culturel, Besançon-Vesoul, 8–10 Nov 1990, pp63–80 (AATA 30–167)
- VKS (Varmbehandlingskontrol mod svamp) (1995) Heat treatment why and how. Informations-skrift des Firmenzusammenschlusses VKS, Taastrup, Denmark
- Voigt T (1993) Mit Klimatechnik gegen Holzschädlinge. *Prakt Schädlingsbekämpfer* 11:240–242
- von Rotberg, H-W (1997) Holzschutz mittels kontrollierter Klimatisierung. Dem "Zahn der Zeit" entrissen! Neue Forschungen und Verfahren zur Schädlingsbekämpfung im Museum. Landschaftsverband Rheinland, Rheinisches Archiv- und Museumsamt, Rheinland-Verlag Köln in Kommission bei Dr. R. Habelt GmbH, Bonn, pp114–119
- Wälchli O, Tscholl P (1975) Möglichkeiten der Bekämpfung holzerstörender Insekten ohne Giftanwendung. *Holz Roh Werkst* 33(2):49–53

- Yamamoto M, Mizushina T, Miyazaki H (1973) Study for the wood sterilization by gamma ray irradiation. *Taisei Kensetsu Gijutsu Kenkyusho-ho* (6):15–39
- Zielonka P, Gierlik E, Matejak M, Dolowy K (1997) The comparison of experimental and theoretical temperature distribution during microwave wood heating. *Holz Roh Werkst* 55:395–398

10 Biological Methods

10.1

Opportunities for Biological Control of Insect Infestations and for Bioprotection

Classical biological control encompasses the use of living organisms with the goal of exterminating pest species. More broadly viewed, it would also include partially biological or biotechnological procedures and biogenous pesticides. In addition to biological control, bioprotection for wood is of interest to the industry and for safeguarding cultural property. Overviews of biological control of and bioprotection against wood-destroying organisms have been published in tabular form by Unger and Unger (1995).

For the biological control of wood-destroying beetles and termites, possible agents are insect enemies (cf. Sect. 5.1.7), microorganisms (fungi, bacteria, and viruses), nematodes and mites. The autocide method (sterilization of male insects) is another possibility. Attractants such as pheromones combined with traps are not suitable for control of wood-destroying beetles, especially when the population density is high. Termites, however, can be attracted with such substances and then exterminated. Traps with attractants are not effective over a sufficiently large radius to provide preventive protection against beetles that may fly in. The main application for pheromones is for monitoring (cf. Sect. 5.1.8). In principle, insect repellents would be ideal for preventive protection of individual objects, exhibit spaces, and storage facilities, but so far pest-specific preparations and methods are largely unavailable. Synthetic growth regulators, which intervene in the developmental cycle of insects, are not purely biological substances and have already been discussed as part of the liquid wood preservatives (Chap. 7).

For the biological control of Anobiidae and of *Hylotrupes bajulus*, the following insect enemies, whose parasitic or predatory nature has already been discussed in Section 5.1.7, are possible candidates: *Rhyssa persuasoria*, *Spathius exarator*, *Scleroderma domesticum*, *Opilo domesticus* and *Korynetes caeruleus*. *Monolexis fuscicornis* could play a role in the biological control of Lyctidae. In principle, certain mites could conceivably be used against larvae and imagoes of wood-destroying pests. However, so far almost no attempts

have been made to test the effectiveness of using insect enemies against wood-destroying members of the Coleoptera under practical conditions. Nematodes can be used against termites, but their effectiveness differs widely, depending on termite species.

According to Graf (1992), microorganisms can act directly as insect pathogens, can be indirectly toxic by means of their metabolic products (mycotoxins), or can deprive the insects of food by their own growth on the wood. Another possibility lies in disrupting the symbiosis between the host and its microorganisms which break down cellulose, as for instance in *Anobium punctatum*. *Lyctus* species avoid wood with blue stain, and some varieties of *Aspergillus flavus*, *Penicillium funiculosum*, and *Trichoderma viride* have a strongly toxic effect on larvae of the house longhorn beetle. The use of fungi as insect pathogens (mycoinsecticides) as part of integrated wood preservation appears to be most realistic against termites. The mycoinsecticides can be introduced into the termite population via infected insects or suitable bait, or spores could be blown into termite nests. The use of the fungi *Metarhizium anisopliae* and *Beauveria bassiana* as termite pathogens is the most advanced to date (Delate et al. 1995; Zoberi 1995). Isolates of *Metarhizium anisopliae* are being used particularly in Australia (Milner et al. 1996), and in the USA the fungus is used as a termite repellent in the form of dust or powder. Detailed investigations on the use of viruses on wood-destroying insects is lacking almost entirely.

Uses

Historical

- 1966 Cymorek discovers that *Lyctus* beetles avoid blue stain triggered by green-wood insects.
- 1968 Varieties of the genera *Aspergillus*, *Penicillium* and *Trichoderma* have toxic effects on larvae of the house longhorn beetle (Becker).
- 1975 Hickin describes a number of predator insects and parasites of wood-destroying insects.

Investigations by Unger on the toxic effects of metabolism products of wood-inhabiting fungi on termites.

Wälchli and Tscholl discuss the possibilities of biological control of wood-destroying insects

- 1981 Hänel investigates the virulence of the fungus *Metarhizium anisopliae* against termites.

Wälchli describes the status of biological control of wood-destroying insects and fungi

- 1982 Contributions by Hänel (1984) and Wälchli (1984) to biological control at the DESOWAG symposium 'Wood Preservation - Research and Practice'.

- 1983 Hänel and Watson publish the results of field tests with the termite pathogenic fungus *Metarhizium anisopliae*.
- 1985 Story comments on biological control of museum pests.
- 1989 A monograph by Brokerhof contains a section on biological control of museum pests.
- 1992 Graf discusses prospects and limitations of biological wood preservation.
- 1995 Investigations by Hertel of the scent orientation of the house longhorn beetle.
- 1996 Use of a *Metarhizium anisopliae* isolate on Australian termite species under field conditions (Milner et al.).
- 1997 Pearce discusses biological control of termites among other topics in his book.
- 1999 Control of drywood termite infestations in objects such as a 1929 Buick automobile with spinosad, a fermentation product of the naturally occurring soil bacterium *Saccheropolyspora spinosa* (Scheffrahn and Thoms).

Present Day

Practical methods for the biological control of wood-destroying Coleoptera are so far lacking. However, biological control of termites (Isoptera) is being used in Australia and the USA.

Advantages/Disadvantages

Biological methods of wood protection do have the advantage over chemical wood preservatives in being largely free of ecological and toxicological concerns. In most cases, the antagonists are specific to a particular pest organism. To what extent particular biological agents and methods represent a toxicological danger to humans remains to be investigated in detail. Enemy insects of wood-destroying beetles probably will not themselves attack wood supports or paint layers, leaving the original work of art intact. However, it must be expected that they will leave remains of the insect pests as well as excrement on the objects, which might serve as food for other pests and adversely affect the object's appearance. A decisive shortcoming of the use of biological control methods is the fact that the antagonists or the attractants, repellents, or inhibitors have so far been unable to completely exterminate the target pest population. The danger of recurrence of the pest infestation therefore remains. The time span required for complete extermination of insect pests can be very long, so that the damage can continue to grow. If preventive protection of wooden objects is required, long-term effects of the biological agents and methods used play a large role. In this respect bioprotectants are so far inferior to chemical preservatives.

10.2

Opportunities for Biological Control of Fungal Decay and Bioprotection

In principle, wood-destroying fungi can be controlled biologically with the aid of certain microorganisms. Antagonistic fungi, e.g., mold fungi, and bacteria as well as their metabolic products are of particular importance. The antibiotic effect of the metabolic products prevents the growth of the fungus to be controlled. The antagonists of the decay fungi must grow throughout the wood to be protected, which would require extended periods of high moisture content. Consequently, bioprotection is important primarily for green lumber. Protection of wood against attack by staining fungi, e.g., blue stain fungi, and Basidiomycetes are of principal concern. Mainly the mold fungi of the genera *Trichoderma*, *Scytalidium*, *Gliocladium* and *Ceratocystis* are used as antagonists. The LTC method uses a selected natural variety of the fungus *Trichoderma harzianum*, and subjects softwoods to pressure impregnation with spores followed by a controlled incubation period which is intended to guarantee uniform growth throughout the wood (Messner et al. 1995). Field experiments with wood so treated have not shown any sign of attack by Basidiomycetes. Possibilities of controlling *Serpula lacrymans* with various species of *Trichoderma* are being investigated intensively (Score and Palfreyman 1994).

In addition to mold fungi, bacteria can also be used as antagonists to wood-destroying fungi, where they give rise to antibiotic effects as well. Certain varieties of *Bacillus subtilis* have been shown to be suitable, for instance.

The use of fungal or bacterial preparations for the preventive protection of structural timbers and for the control of Basidiomycetes does not at present appear to be realistic. There is, for instance, the latent danger that the fungi or bacteria used, or their metabolic products, will lead to discoloration of wood or will provoke allergic reactions in humans. In the case of polychromed art objects, it would be necessary to investigate whether enzyme complexes of the mold fungi might attack and degrade the paint layers.

Uses

Historical

- 1967 Ricard and Bollen make the first attempt to inhibit infestations of the fungus *Antrodia carbonica* in Douglas-fir with mold fungi of the genus *Scytalidium*.
- 1976 Ricard tests mold fungi of the genera *Scytalidium* and *Trichoderma* for their suitability to prevent decay in creosote-treated Douglas-fir poles.

- 1983 Control of *Neolentinus lepideus* (*Lentinus lepideus*) in Scots pine with preparations from *Scytalidium* and *Trichoderma* (Bruce and King).
- 1992 Palfreyman et al. apply for a patent for the protection from infestations of *Serpula lacrymans* using species of *Trichoderma*.
Zabel and Morrell summarize results to date on the biological control of fungi with fungi.
- 1993 Discussion of biological control of wood-destroying pests by Eaton and Hale.
- 1995 Häfner et al. introduce the potential of preventive protection of wood against fungal attack with the aid of antagonistic bacteria.
Description of the biological control method LCT with *Trichoderma harzianum* as the antagonist by Messner et al.
Preservation of pine wood against blue stain with the fungus *Ophiostoma* (*Ceratocystis*) *piliferum* (trade name Cartapip 97; Müller and Schmidt).
- 1996 Proof of preventive preservation of wood against Basidiomycetes with *Trichoderma viride* isolates (Tucker et al.).
- 1997 Highley uses the biofungicide *Trichoderma* (*Gliocladium*) *virens* against white rot and brown rot fungi. Wood which has been treated with *T. virens* is not colonized by the fungus.
- 1998 An infestation of *Serpula lacrymans* in wood cannot be prevented from spreading with species of *Trichoderma* (Score et al.).
An isolate of *Trichoderma viride* effects a noticeable reduction of sapstain colonization in field tests (Brown and Bruce).

See also references to the historical development of biological control in Section 10.1.

Present Day

The development of methods for the bioprotection of wood and for the biological control of wood-destroying fungi is being pursued on a laboratory or pilot plant scale, but commercial and industrial applications are just beginning.

Advantages/Disadvantages

In contrast to the broad-band chemical fungicides, individual pest fungi have their development inhibited by specifically selected antagonists (fungi, bacteria, viruses), and in ideal cases are killed off. So far, preparations which act as preventives against fungal infestation and isolates of fungal antagonists appear to be most promising. Such bioprotectants must lend themselves to production in sufficient quantities and purity, and they must not have any toxicological side effects. The desired preservative effects for wood must also be long-term. Control of fungal decay in structural timbers

of historic buildings or in a single art object by biological means does not appear to be realizable in the near term. It is also questionable whether the preparations tested under laboratory conditions would show the same effectiveness in practical situations. It is possible that the enzyme systems of the fungal antagonists could attack the wood or its coatings in an uncontrolled manner. The technical aspects of control treatments would also appear to present difficulties in regard to short- and long-term exposure of workers or inhabitants of a building to suspensions of spores or biogenetic metabolic products.

References

- Becker G (1968) Der Einfluß von Ascomyceten und Fungi imperfecti auf Larven von *Hylotrupes bajulus* L. *Mat Org* 3(3):229–240
- Brokerhof A (1989) Control of fungi and insects in objects and collections of cultural value “a state of the art”. Central Research Laboratory for Objects of Art and Science, Amsterdam
- Brown HL, Bruce A (1998) Assessment of the biocontrol potential of a *Trichoderma viride* isolate in a field trial. *IRG/WP/98–10252*
- Bruce A, King B (1983) Biological control of wood decay by *Lentinus lepideus* (Fr.) produced by *Scytalidium* and *Trichoderma* residues. *Mat Org* 18(3):171–181
- Cymorek S (1966) Experimente mit *Lyctus*. *Mat Org, Beih 1, Holz und Organismen*, pp 391–413
- Delate KM, Grace JK, Tome CHM (1995) Potential use of pathogenic fungi in baits to control the Formosan subterranean termite (Isopt., Rhinotermitidae). *J Appl Entomol* 119:429–433
- Eaton RA, Hale MDC (1993) Wood. Decay, pests and protection. Chapman & Hall, London
- Graf E (1992) Biologischer Holzschutz – Möglichkeiten und Grenzen. 19. Holzschutz-Tagung, Rosenheim, 7–8 Oct 1992, pp 21–32
- Häfner B, Krebs B, Ockhardt A (1995) Biotechnologische Möglichkeiten im Holzschutz. Antagonistische Bakterien und deren Wirksubstanzen zum Schutz gegen holzerstörende Pilze. 20. Holzschutz-Tagung, Rosenheim, 18–19 Oct 1995, pp 121–131
- Hänel H (1981) A bioassay for measuring the virulence of the insect pathogenic fungus *Metarhizium anisopliae* (Metsch.) Sorok. (fungi imperfecti) against the termite *Nasutitermes exitiosus* (Hill) (Isoptera, Termitidae). *Z Angew Entomol* 92:9–18
- Hänel H (1984) Biologische Bekämpfung von Termiten mit dem Pilz *Metarhizium anisopliae*. Holzschutz – Forschung und Praxis, Symposium 1982 DRW, Leinfelden-Echterdingen, pp 62–63
- Hänel H, Watson JAL (1983) Preliminary field tests on the use of *Metarhizium anisopliae* for the control of *Nasutitermes exitiosus* (Hill.) (Isopt.: Termitidae). *Bull Entomol Res* 73:305–313
- Hertel H (1995) Duftorientierung des Hausbockkäfers im Nahbereich. 20. Holzschutz-Tagung, Rosenheim, 18–19 Oct 1995, pp 141–155
- Hickin NE (1975) The insect factor in wood decay, 3rd edn. Associated Business Programmes, London
- Highley TL (1997) Control of wood decay by *Trichoderma (Gliocladium) virens*. I. Antagonistic properties. *Mat Org* 31(2):79–87
- Messner K, Fleck V, Marchler A, Bürgel J, Horvath E, Schlick A (1995) Stand der technischen Entwicklung des biologischen Holzschutzverfahrens LCT. 20. Holzschutz-Tagung, Rosenheim, 18–19 Oct 1995, pp 111–119
- Milner RJ, Staples JA, Lenz M (1996) Options for termite management using the insect pathogenic fungus *Metarhizium anisopliae*. *IRG/WP 96-10142*
- Müller J, Schmidt O (1995) Biologischer Schutz von Kiefernholz gegen Verblauen. *Holz-Zentralblatt* 121(123):2017–2018, 2020
- Palfreyman JW, King B, Bruce A, Quarmby A (1992) Treatment or prevention of *Serpula lacrymans* infection. UK Patent 9000868.1
- Pearce MJ (1997) Termites. Biology and pest management. CAB International, Wallingford
- Ricard J (1976) Biological control of decay in standing creosote-treated poles. *J Inst Wood Sci* 7(4):6–9
- Ricard J, Bollen WB (1967) Inhibition of *Poria carbonica* by *Scytalidium* sp., an imperfect fungus isolated from Douglas-fir poles. *Can J Bot* 46:643–647
- Scheffrahn RH, Thoms EM (1999) A novel, localized treatment using spinosad to control structural infestations of drywood termites (Isoptera: Kalotermitidae). In: Robinson WH, Rettich F, Rambo GW (eds) Proceedings of the 3rd international conference on urban pests, Prague, 19–22 July 1999, pp 385–390
- Score AJ, Palfreyman JW (1994) Biological control of the dry rot fungus *Serpula lacrymans* by *Trichoderma* species: the effects of complex and synthetic media on interaction and hyphal extension rates. *Int Biodeter Biodegrad* 33(2):115–128
- Score AJ, Bruce A, King B, Palfreyman JW (1998) The biological control of *Serpula lacrymans* by *Trichoderma* species. *Holzforschung* 52(2):124–132
- Story KO (1985) Approaches to pest management in museums. Smithsonian Institution, Washington, DC
- Tucker EJB, Bruce A, Staines HJ (1996) Protection of wood blocks treated with *Trichoderma* isolates selected on the basis of preliminary agar screening studies. *IRG/WP 96-10154*
- Unger A, Unger W (1995) Die Bekämpfung tierischer und pilzlicher Holzschädlinge. Holzschutz, Holzfestigung, Holzergänzung. Bayer Landesamt Denkmalpflege, Arbeitsheft 73, pp 6–14
- Unger W (1975) Zur Wirkung toxischer Stoffwechselprodukte aus holzbewohnenden Pilzen und synthetischer Insektizide auf Termiten und deren Darmsymbionten. Dissertation, Ernst-Moritz-Arndt-Universität Greifswald
- Wälchli O (1981) Möglichkeiten einer biologischen Bekämpfung von Insekten und Pilzen im Holzschutz. *Holz-Zentralblatt* 108(136):1946, 1948
- Wälchli O (1984) Möglichkeiten einer biologischen Bekämpfung von Insekten und Pilzen im Holzschutz. Holzschutz – Forschung und Praxis, Symposium 1982, DRW, Leinfelden-Echterdingen, pp 57–61
- Wälchli O, Tscholl HP (1975) Möglichkeiten der Bekämpfung holzerstörender Insekten ohne Giftanwendung. *Holz Roh Werkst* 33(2):49–53
- Zabel RA, Morrell JJ (1992) Wood microbiology. Decay and its prevention. Academic Press, San Diego
- Zoberi MH (1995) *Metarhizium anisopliae*, a fungal pathogen of *Reticulitermes flavipes* (Isoptera: Rhinotermitidae). *Mycologia* 87:354–359

11 Consolidants

11.1

Objectives, Scope, and Procedures for Consolidation Treatments

Wood consolidation includes all treatments for reestablishing cohesion and for the stabilization of objects which have been damaged by biological, mechanical or chemical agents. In the ideal case the original properties of the wood should be recovered. From a conservation point of view, the primary objective of consolidation treatments is the preservation and protection of original substance. In addition, the treatment should ensure the suitability for future exhibition or use (Wermuth 1990). As a first step, it must be determined whether the object needs to be returned to being fully functional or whether it must only be stabilized to withstand later handling or transport. Often, no more than strengthening of surface layers to resist abrasion is required. Depending on the extent of the object's deterioration and its intended use, complete or partial impregnation with consolidants, or stabilization of surface areas with strengthening adhesive binders will be necessary. In every case, no more than the absolutely necessary quantity of consolidant should be introduced into or onto the object. In addition to strengthening the wood structure, the materials used may also effect some dimensional stabilization of the object and impart some resistance against biological pests.

An ideal consolidant (Grattan 1980; Unger 1988; Schniewind 1998):

1. Should effect lasting consolidation through its own long-term stability,
2. Should impart dimensional stability of the object, especially in the case of waterlogged wood finds,
3. Should not alter the appearance of the object by
 - Partial or complete dissolution of paints and finishes
 - Formation of surface films or patches
 - Changing paint layers or the texture and color (darkening) of the wood, including gloss formation,
4. Should not cause shrinkage or swelling of the object during treatment,
5. Should be compatible with wood preservatives applied earlier,
6. Should allow the use of original procedures, such as gluing, gilding, and inpainting after treatment,

7. Should permit sufficient penetration and distribution of the consolidant in the wood through small particle size and low viscosity,
8. Should be nontoxic or at most slightly toxic to humans or the environment,
9. Should not increase flammability if at all possible,
10. Should impart sufficient protection against renewed attack of the consolidated object by insects or fungi,
11. And finally, be largely reversible.

The "ideal" consolidant does not exist and will not exist in the future. Furthermore, the priority of the various requirements will vary from one application to the next. For conservators it is important to know what points should be considered when choosing a consolidant and a method of its application, and the following discussion is intended to be of assistance in this regard.

11.1.1

The Role of Wood Permeability

Wood can be consolidated by introducing liquid or gaseous media into its porous structure. The transport or movement of fluids through or into wood can be modeled in several ways, but in each case the governing factors are the geometry of the object, its permeability, the viscosity of the fluid and the pressure differential providing the driving force. Since for a given object the geometry and the permeability are fixed, the viscosity and the pressure differential are the only factors that can be manipulated to control the uptake of consolidant (Schniewind 1998). The permeability of sound wood can vary from species to species by as much as a factor of 1 million, and permeability is greater in the longitudinal than in the transverse (radial or tangential) directions (Siau 1984). Furthermore, the permeability of deteriorated wood will usually differ from that of sound wood, and is most often greater.

11.1.2

Damage Diagnosis

An object to be consolidated should first be characterized with regard to type and extent of the damage. Its permeability will depend among other factors on whether the wood has been attacked by insects, fungi, or bacteria either singly or in combination. Normally, the permeability of biologically destroyed wood will be increased, but in the case of insect damaged wood, frass can exert a wicking or filtering action depending on the viscosity of the consolidant. Wood with fungal attack may be subject to uneven penetration because of blockage of the pits. As insect damage in wood increases, the uptake of consolidants will also increase, but if a high proportion of frass is present, the retention of low viscosity consolidants is much reduced. In waterlogged wood

uneven degrees of destruction can lead to problems with the replacement of water by stabilizing substances and by their uneven distribution in the material. The degree of destruction – partial or almost total – is also decisive for the selection of the consolidation method.

11.1.3

Condition and Mobility of the Object

Prior to any consolidation treatment, it must be determined if a surface covering – paint, decorative metal, polish or varnish – is present. Objects without any surface covering can be consolidated much more easily than those with residual pigments or stains, or with complete polychrome films. If polychromed objects are to be consolidated, for example, it must first be determined if animal glue or oils and resins were used as a binder. Aqueous solutions of consolidant could swell the animal glue binder, while organic solvents might attack the oils and resins. It is also important to know what type of adhesive was used for joining individual wood parts of objects when choosing a consolidant. Consolidation of objects made of wood in combination with other materials, such as ethnographic objects or archaeological finds from soil or water environments, where the different materials cannot be separated, are especially complex problems. The choice of consolidation method also depends very much on the mobility of the object. For movable objects the range of possible treatment choices is significantly greater than for objects fixed in place or members of buildings. Whereas mobile objects might, for example, be treated by full immersion, only brushing of consolidant or injecting it into insect exit holes would be possible for fixed objects.

11.1.4

Intended Renovation and Use

It is important to decide prior to treatment whether the object should be merely stabilized or completely restored. Sometimes clients will request only a renovation. Consolidants which are to serve only for substance stabilization and protection are easier to choose than those which are to serve as a basis for additional restoration treatments. Consolidants used as part of complete restoration treatments should be as compatible as possible with the usual coloring and inpainting materials and adhesives, and should permit traditional methods of working. When adding loss compensation, it should not be necessary to first remove a part of the consolidant in order to obtain a good joint between the original and the compensation. Partial removal of consolidant is only possible if the substance is reversible.

Subsequent use of an object is also important for the choice of consolidant. Structural members of buildings, for instance, which have load-bearing functions, cannot be consolidated with synthetic resins that are either soft or brittle. Smaller finds of archaeological waterlogged wood, on the other

hand, where future use is limited to being placed on exhibit, permit the use of soft consolidants. It is important that the amount of consolidant impregnated into the wood is not so great that the mass of the consolidant could damage the object, or that the object turns into a block of synthetic resin with wood filler.

11.1.5

Physical State of Consolidants for Application

Either gaseous or liquid media can be considered for the consolidation of works of art and cultural property. Many of the substances used to stabilize cultural property trace their origins to industrial methods for modifying wood to improve its physical, mechanical and biological properties. Gaseous substances are mainly being investigated with respect to improvements of dimensional stability and resistance to biological deterioration of wood, concentrating on chemical modifications of functional groups of the polysaccharide constituents. Such chemical modification would not be acceptable for wooden works of art since it has to be considered irreversible. The use of gaseous substances for consolidation has – except for a few applications (Humphrey 1986) – not gained any importance, either in the industrial sector, or for conservation of cultural property. However, liquefied solids such as wax, polymers in solution and liquid monomers or prepolymers have already been used to a great extent for the modification of solid wood and for the consolidation of cultural property. In most cases the modifying substances are merely deposited physically within the porous structure of the wood. Grafting reactions onto the main wood constituents during the curing of monomers and prepolymers inside the object take place only to a minor extent.

Liquefied solids can be divided into natural substances, such as beeswax, and synthetics, such as paraffin and polyethylene glycol. The same division can be made for polymers in solution, which can be either true solutions or dispersions. True solutions can be aqueous or use organic solvents, while dispersions are mainly aqueous systems. The monomers, oligomers and prepolymers used for strengthening wood are usually of synthetic origin.

11.1.6

Choice of Consolidants

The wide spectrum of available consolidants can be divided into natural, traditional materials, semisynthetics, and synthetic substances (Unger and Unger 1987). The properties of natural, traditional consolidants such as proteinaceous glues, drying oils, waxes and natural resins, but also carbohydrates (sugars) for conservation of waterlogged wood with respect to their application and aging characteristics are well known because of their long period of use. Their predictable aging characteristics, their more or less pronounced

reversibility, as well as a desire to work with traditional materials and methods in a manner appropriate to the object are the reasons that many conservators will consider natural consolidants ahead of semisynthetic or synthetic materials. Nevertheless, the disadvantages of natural consolidants cannot be ignored. Particularly the poor penetration and the concomitant low degree of strengthening, the sensitivity to changes in moisture content of the treated wood and the increasing embrittlement and reduction of reversibility with age of certain consolidants are disadvantages. Additional factors will be discussed with the individual materials.

The semisynthetic cellulose derivatives form a bridge between natural and synthetic consolidants. Used almost universally at the end of the nineteenth and beginning of the twentieth centuries as consolidants for all manner of cultural property, their disadvantages such as insufficient penetration into wood, rapid embrittlement, and severe object discoloration soon became apparent. Among the reasons for the rapid aging were contaminants from production such as nitric acid residues in the case of cellulose nitrate, insufficient or excessive derivatization of the cellulose, loss of plasticizer and degradation due to thermal or UV radiation exposure.

Synthetic consolidants for wood can be divided into thermoplastic resins, elastomers, and thermosetting resins. Thermoplastic resins soften when heated and become formable, but upon cooling become solid again, a process which can be repeated. Thermosetting resins are initially soft or liquid and become irreversibly hard, and in some cases brittle, upon curing. Thermosetting resins must therefore be shaped before curing.

Whereas thermoplastic resins, due to their molecular structure, are soluble in suitable solvents, thermosetting resins form a three-dimensional network and cannot be dissolved. However, depending on the resin and the solvents used, the thermosetting resin may swell strongly. Cross-linking can also take place in thermoplastic resins in the course of hardening or due to aging processes, which leads to reduced solubility (Ciabach 1983; Bockhoff et al. 1984). Since the solubility of a given resin determines its reversibility, thermoplastic resins which do not cross-link significantly should be given preference to thermosetting resins in conservation.

Elastomers consists of sparsely cross-linked chains. At room temperature and above they are of rubbery consistency, do not melt and have limited solubility but can be caused to swell. Elastomers serve for consolidation indirectly by way of their use as gap fillers for cracks, splits, and open joints in assembled wood objects (cf. Chap. 12).

In the production of synthetic wood consolidants three types of reactions can be distinguished: chain polymerization, polycondensation and polyaddition. In each case the synthetic is built up from monomers, in contrast to the semisynthetic materials which involve a partial depolymerization of the original natural substances.

Chain polymerization reactions are of special significance to the production of wood consolidants, and the thermoplastic resins most important for

wood conservation are produced in this manner. Chain polymerization requires monomers with double bonds. If two or more different monomers are bound by double bonds it is referred to as copolymerization. The most important groups for wood consolidation are polyvinyl, polyacryl and polymethacryl compounds.

Whereas chain polymerization involves the joining of like building blocks, polycondensation represents a substitution reaction. Compounds with two like or unlike reactive groups react with each other to form low relative molecular mass byproducts such as water or alcohol. Both thermoplastic and thermosetting resins can be produced by polycondensation reactions. Polyamides, linear polyesters, and the group of various polyethers are among the thermoplastic resins, and of these the polyamides gained some significance for wood consolidation for a short period in the past. The thermosetting polycondensate resins important for wood consolidation include the alkyd resins; phenol, urea, and melamine formaldehyde resins; unsaturated polyesters and polysiloxanes.

Polyaddition processes are based on the combination of at least two bifunctional compounds without the formation of by-products, and as in the case of polycondensation, both thermoplastic and thermosetting resins can be produced. Among the thermoplastic resins are linear polyurethanes and ketone resins, and the thermosetting resins include epoxy resins and cross-linked polyurethanes. The epoxy resins have principally found application in wood conservation, while the ketone resins have been used mainly for the consolidation of paint and ground layers and for relining.

Choice of consolidant also depends on the origin and intended use of an object. Structural timbers of historic buildings, works of art in museums, and archaeological waterlogged wood finds often require special consolidants. Architectural timbers often demand consolidants which can guarantee significant improvements of the elasto-mechanical properties. In these cases reversibility is not necessarily a primary consideration, in contrast to museum objects where it plays an important role, and the consolidant may not need to do more than hold the affected wood together so that it will not collapse under its own weight. Of particular interest for waterlogged wood are water-soluble consolidants which allow an exchange of the water in the wood for the aqueous solution of consolidant. Here strengthening and dimensional stabilization take on equal importance.

Consolidation treatments use mainly organic compounds. Inorganic compounds such as water-soluble salts had some importance in the past for conservation of building timbers and waterlogged wood.

11.1.7

Criteria for the Selection of Solvents

If a given dry wooden object is to be consolidated with a soluble polymer, the choice of a suitable solvent is based not only on good solubility but also on acceptable technical aspects of the treatment process. In particular, the following factors will play a role:

1. The shrinking and swelling behavior of the wood in response to the solvent,
2. The evaporation of the solvent (evaporation number),
3. The ease of penetration,
4. Any propensity for retention,
5. Migration behavior, and
6. Possible toxicity of the solvent to humans and the environment.

Solvents can be divided into polar and nonpolar liquids. Polar solvents have a greater affinity for wood than nonpolar ones, which is based on physico-chemical interactions with the main constituents of wood. Adsorption on the internal surfaces of wood reduces the mobility of polar solvents, and they do not penetrate air-dry wood as well (Nicholas 1972). Swelling of wood generally increases as solvent polarity increases (cf. Chap. 3; Table 3.3). Polymer solutions in polar and nonpolar solvents show the same tendency after impregnation, but the swelling of wood when polar solvents are used is only temporary (Schniewind 1998). In general, nonpolar solvents should be preferred over polar solvents for wood consolidation, but this recommendation does not apply to waterlogged wood finds. In addition to the swelling capacity of solvents for dry wood, their evaporation is important in regard to the transport of an adequate quantity of consolidant into the material, as well as their retention propensity and their migration behavior. The evaporation of solvents is indicated approximately by their boiling points, but can be characterized better with the evaporation number (Table 11.1). Depending on the method of application, solvents with a low evaporation number may not transport the solute sufficiently deep into the wood so that only surface layers are consolidated, whereas a high evaporation number may allow deeper penetration of polymer into the wood. During evaporation, solvents with high evaporation numbers can cause reverse migration of polymer back toward the surface (Payton 1984) or they may even be retained in the polymer over an extended period. Solvents retained in the polymer will reduce the glass transition temperature T_g of the polymer with detrimental effects on its elasto-mechanical properties (Carlson and Schniewind 1990).

The rate of evaporation can be regulated by controlling temperature and ventilation, e.g., by covering treated portions or the entire object. Fast drying of wood saturated with consolidant solution results in uneven distribution of the polymer and a tendency for reverse migration toward the surface layers (Wang and Schniewind 1985; Schniewind and Eastman 1994). In general, solvents with medium evaporation numbers such as toluene or petroleum ether should be given preference over solvents with low evaporation numbers such as *n*-hexane or acetone.

It is imperative that conservators who work with solvents be cognizant of possible health threats. In every case solvents of the lowest possible toxicity should be used. Such solvent vapors as may develop can then be more easily removed, and there is less danger to people and the environment.

Table 11.1. Boiling points and evaporation numbers of selected solvents

Solvent	Boiling point (°C)	Evaporation number (diethyl ether = 1)
<i>n</i> -Hexane	69	1.4
Acetone	56	2.1
Chloroform	61	2.5
Ethyl acetate	78	2.9
Benzene	80	3.0
<i>n</i> -Heptane	98	3.3
Cyclohexane	81	3.5
Tetrachloromethane	76	4.0
Petroleum ether	50–115	4.5
Toluene	111	6.1
Methanol	65	6.3
Ethanol	78	8.3
2-Propanol	82	11.0
Xylene	144	13.5
1-Propanol	97	16.0
1-Butanol	117	33.0
Ethylene glycol monoethyl ether (ethyl glycol)	135	43.0
Water	100	~80
Ethylene glycol monobutyl ether (butyl glycol)	171	160
Turpentine	150	~170
Ethylene glycol	198	600

When a solvent has been selected as suitable for the polymer and the object, giving consideration to such factors as solubility of paint layers, the question arises as to the best concentration of the treating solution. Two requirements must be considered, namely (1) that the consolidant should penetrate into the wood as deeply as possible, and (2) that the amount of consolidant introduced into the wood is large enough to provide for adequate stabilization of the wood. Low concentrations of consolidant result in low viscosity of the solutions and good penetration. At higher concentrations the solutions are more viscous and do not penetrate as well, but effect better strengthening of the surface layers. The maximum amount of consolidant that can be introduced into wood can be estimated based on Kellogg's (1989) equation for the pore volume of sound wood (Schniewind 1998). In wood damaged by insects or fungi the relative density decreases and the pore volume increases, making possible higher loading of consolidant.

11.1.8

Choice of Treatment Method

The amount of consolidant taken up by wood depends in great measure on the treatment procedure used. Consolidants can be introduced into wood in

almost the same manner as liquid wood preservatives (cf. Chap.7). For individual works of art such as sculptures or panel paintings, brushing and injecting consolidant solution are the most common methods, but in most cases this leads only to partial strengthening, especially in the surface zones. Sculptures heavily damaged by insects are often treated by infusion with polymer solutions of as low a viscosity as possible (Aberle and Koller 1989), which leads to fuller penetration of the attacked wood. If complete impregnation can be tolerated by the object or is necessary because of heavy damage, it can be done either with or without application of pressure. Common procedures are soaking in a tank at atmospheric pressure, or vacuum impregnation. For heavily damaged objects soaking is often sufficient, especially if solutions of low viscosity lead to good loading. Less damaged objects should be treated by vacuum impregnation, in order to guarantee adequate loading and a reasonably even distribution of consolidant. Vacuum impregnation generally achieves the greatest consolidant loading. Full impregnation requires that the object is mobile and of an acceptable size. Very large objects, which cannot be taken apart, must be treated by spraying, preferably in a closed system. Typical examples are canoes, boats, and ships such as the *Wasa*.

Attempts to improve on the strengthening effects of consolidation, which can be only moderate for some objects, include the following measures:

1. Prewetting the object with the same solvent used to prepare the consolidant solution, with the intent of reducing surface tension during brushing of the consolidant solution and increasing penetration into the wood.
2. Unlike methods used to date, attempts are being made to use mixtures of solvents rather than a single solvent, which should increase the depth of penetration of the consolidant into the wood.
3. Because in certain objects, such as historic parquet strips, soaking treatments do not achieve sufficient loading, impregnation with the application of ultrasound has been proposed. For sensitive and already heavily damaged cultural property such a procedure would hardly be appropriate.
4. To prevent migration of the consolidant toward the surface during the drying phase as much as possible, slow fixation can be carried out in an atmosphere saturated with solvent vapor.
5. In certain cases, the often time-consuming drying process can be circumvented if reactive rather than neutral solvents are used, as for instance with some epoxy resin formulations.
6. The use of a combination of different but if possible related consolidants may be a means to improving the elasto-mechanical properties of the consolidated wood, but this is used only rarely.

Further details on consolidation processes will be discussed in Section 11.4.

11.2 Inorganic Compounds

11.2.1 Aluminum Compounds

11.2.1.1 Aluminum Sulfate

Formula: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Properties: Colorless, needle-shaped crystals with a sour taste; m.p. 86.5°C (decomposition); readily soluble in water

Analysis: AES for the cation; after leaching from the wood followed by evaporation of the solution by X-ray diffraction, for example

Uses with Waterlogged Wood

Historical

1913 Gustafson boils parts of the *Oseberg* Ship (Norway) with aluminum sulfate, and after drying impregnates them with linseed oil (Anonymous 1935).

Present Day

Aluminum sulfate is no longer used for waterlogged wood conservation.

Advantages/Disadvantages

According to Gustafson (1913) most treated parts did not shrink nor change color. However, the objects are sensitive to changes in air relative humidity. Deposits appear on the surface. Some parts do not tolerate the treatment.

11.2.1.2 Aluminum Potassium Sulfate (Potassium Aluminum Sulfate, Alum)

Trade name: Alum

Formula: $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Properties: Colorless, clear octahedrons or colorless crystal powder; m.p. 92.5°C; with acid reaction readily soluble in water; not soluble in alcohol

Analysis: AES for the cation; after leaching from the wood followed by evaporation of the solution by X-ray diffraction, for example

Uses with Dry Wood

Historical

ca. 484–424 B.C. Herodotus describes the use of alum to protect wood against fire. (Anonymous 1935).

83 B.C. The Greek general Archeolos has a wooden tower in Piraeus near Athens coated with alum, and the Roman army under Sulla is unable to set fire to the tower (after Aulus Gellius, as cited by Grattan and Clarke 1987).

1740 Fagot recommends dipping wood into alum or wood vinegar (Clausnitzer 1990).

1770 A mixture of alum, sea salt, green vitriol, and staining gallnut to protect wood from fire (Troschel 1916).

1848 Treatment of wood with alum solution followed by oil saturated with iron oxide (Clausnitzer 1990).

1891 Impregnation of the so-called Dürer Cabinet with alum solution and brushing with petroleum ether. The wood turns whitish and is rubbed down with cloth, followed by brushing with oil of turpentine (Michaelsen 1984).

1909 Insect damaged wood is impregnated with a warm to hot solution of 1 l of water, 4 g thymol, 16 g alum, and a tablespoon of glue water (Anonymous).

1950 Seekamp lists alum as a component of fire retardants.

Present Day

Aluminum potassium sulfate is not used as a wood preservative or fire retardant.

Uses with Waterlogged Wood

Historical

1858–1860 The Dane C.F. Herbst (1861) is the first to describe the alum method in detail. Objects are boiled for 2 h at 95–100°C in supersaturated alum solution and after drying are dipped into linseed oil. Speerschneider also describes the method at the same time but does not use linseed oil.

1859 Jørgensen mentions alum as a conservation material (Brorson Christensen 1970a).

1858–1958 The method is used in the Danish National Museum. More than 80% of all waterlogged wood finds (about 100,000 pieces) are conserved by this method (Brorson Christensen 1970a).

ca. 1890 Attempts by Rosenberg to improve the alum method (Brorson Christensen 1970a).

- 1904 Gustafson (1913) boils soft oak parts of the *Oseberg* Ship (Norway) in the salt solution, but the wood becomes heavy and brittle.
- ca. 1910 Rosenberg attempts to combine the alum treatment with glycerol (Brorson Christensen 1970a).
- 1921 Conservation of the *Hjortespring* Boat (Denmark) with a mixture of 4 parts alum, 1 part glycerol and 1 part water by mass (Brorson Christensen 1970a).
- 1924 Detailed description by Rathgen of the method of Herbst, Gustafson and Rosenberg.
- 1933/1934 Rosenberg recognizes the danger of moisture fluctuations to alum-treated objects (Brorson Christensen 1970a).
- 1939 Periodic blooming of the salt in treated bog woods. Objects treated 20 years earlier have to be boiled again in alum solution (von Stockar).
- 1952 Conservation of the staves of a wooden pail with a mixture of 3–4 parts alum/potash (potassium carbonate), 1 part glycerol, and 1 part water by mass (Moss).
- Two large wooden troughs are soaked for 5 days in a 30% alum solution at a temperature of 90°C (Pittioni).
- 1952/1953 Electrokinetic method using alum (Zurowski; cf. Sect. 11.2.4.1).
- 1956 Plenderleith describes the alum method in detail. Strengthening reportedly is better in hardwoods than in softwoods.
- 1959 Werner reports on the alum treatment.
- Change-over from the alum method to freeze-drying for the treatment of parts of the *Oseberg* Ship (Rosenqvist).
- 1964 Alum and glycerol found as a suitable variation for the conservation of a boat (Wojciechowska).
- 1969 Reviews of waterlogged wood conservation, including the alum method, by Ankner (1969a,b), Mühlethaler (1969a,b) and Rosenqvist (1969a,b).
- 1970 Very detailed review of the history of alum conservation treatments by Brorson Christensen (1970a).
- 1977 De Jong mentions the alum method (1977a).
- 1980 Hu Jigao applies the alum method to Chinese lacquer objects. Szalay combines poly(ethylene glycol) with alum and achieves an advantageous change in the appearance and gluability of waterlogged wood.
- 1981 Šimůnková et al. publish on the alum method.
- 1983 Discussion of various conservation treatments for waterlogged wood by Xu, including mention of the advantages and disadvantages of the alum method.
- 1986 Jespersen presents an historic overview of waterlogged wood conservation with alum at the Denmark National Museum from 1859 to 1984.
- 1987 Detailed contribution on the conservation of waterlogged wood by Grattan and Clarke, including the alum method.

- 1989 Jensen et al. remove the alum from the *Hjortespring* Boat with hot water and then impregnate it with poly(ethylene glycol). Ringgaard describes the alum method and various surface treatments on the *Hjortespring* Boat.
- 1990 Review by Sawada with methods for the substitution of old stabilizing substances such as alum.
- 1995 According to Kaye, the stabilization of waterlogged wood with materials such as alum depends on the removal of iron sulfide or sea salts.

Present Day

The alum method is not longer used for waterlogged wood.

Advantages/Disadvantages

For dry wood alum does not offer sufficient protection against fire. In waterlogged wood alum is exchanged for the contained water. The crystalline mass prevents wood shrinkage but ruptures some of the cells. The treated wood is brittle and fractures easily. Incompletely impregnated objects develop cracks and become deformed. The surface texture of the wood becomes hazy, and moisture fluctuations cause blooming of alum crystals on the wood surface. Iron parts must be removed before the alum treatment.

11.2.2

Boron Compounds

11.2.2.1

Borax (Sodium Tetraborate-Decahydrate)

For properties and other details see Chapter 7.

Uses with Waterlogged Wood

Historical

- 1978 Borgin presents the so-called Thessaloniki process for moderately degraded waterlogged wood. The wood is soaked in a concentrated solution of sodium tetraborate which contains small amounts of sodium silicate and a water-soluble organic polymer. The object is dried until the moisture content in the surface layers reaches 24–28%, and is then placed into a concentrated solution of barium hydroxide where barium borate and barium silicate are precipitated inside the wood.

Present Day

Boron compounds are not used for waterlogged wood conservation.

Advantages/Disadvantages

The details of the Thessaloniki process for waterlogged wood are in part rather vague. Strength and aesthetic appearance of the treated wood are not likely to be always satisfactory.

11.2.3

Chromium Compounds

11.2.3.1

Sodium Dichromate (Sodium Bichromate) and Chromium(VI) Oxide (Chromic Anhydride, Chromium Trioxide)

For properties and other details see Chapter 7.

Uses with Waterlogged Wood

Historical

- 1965 French patent by Garrouste for the stabilization of waterlogged wood by exchange of water for a 2–10% solution of chromium(VI) oxide to which 10–20% sodium dichromate can be added.
- 1975 Method of Bouis: the water in the wood is exchanged for a solution of 1000g water, 250g sodium dichromate and 150g chromium(VI) oxide. The impregnated wood is dried under vacuum and then dipped into linseed oil. The chromium compounds effect a hardening of the linseed oil.
- 1985 Conservation of an antique shipwreck by Bouis.
- 1995 Schaudy mentions conservation with chromium salts.

Present Day

Chromium compounds are hardly used for waterlogged wood conservation.

Advantages/Disadvantages

Objects treated by the method of Garrouste (1965) reportedly are light, porous, largely dimensionally stable, but brittle and changed in color. Bouis (1975) reported that the objects that he treated are dimensionally stable, dry, and can be worked and glued with common adhesives. The treated wood is fire-resistant and protected against fungi, but not very elastic and changed in color. Use of chromium compounds is questionable because of their toxicity.

11.2.4

Silicon Compounds

11.2.4.1

Alkali Silicates (Sodium Silicate, Potassium Silicate)

Trade name: Water glass

Formula: 1 mol alkali oxide to 2–4 mol SiO₂

Properties: Colorless, glue-like solutions with strong alkaline reactions; can be thinned with water; the solutions are gradually decomposed by the CO₂ of the air, to produce salt solutions, gels, or precipitates of silicic acid.

Analysis: By AES of the alkali metals or the silicon

Uses with Dry Wood

Historical

- 1825 According to Fuchs wood can be made incombustible with sodium silicate (Troschel 1916).
- 1837 Wood is placed into a water glass solution for 30 days, and thereafter in dilute hydrochloric acid. It is then washed, dried, and rubbed with oil (Clausnitzer 1990).
- 1844 According to Burkes, steamed wood is impregnated first with green vitriol [iron(II) sulfate], then with water glass (Clausnitzer 1990).
- 1846 Precipitation of silicic acid by volatile acids from alkali silicates (Clausnitzer 1990).
- 1851 Impregnation of wood with (1) water glass solution and boric acid, and (2) water glass and borax (Clausnitzer 1990).
- 1859–1864 Netherlands Academy of Science: water glass and calcium chloride as an impregnation material (Clausnitzer 1990).
- 1972 Water glass to protect wood shingles against fire (Šujanova).
- 1983 Reproduction of “Renaissance” violins with wood that has first been impregnated with a solution of silicic acid and potassium tartrate to improve its response to moisture (Anonymous 1983b).

Present Day

Occasional impregnation of wood with aqueous or alcohol sols of SiO₂ against wood pests and fire, to improve dimensional stability, and to increase the strength of damaged objects, and also as a masking material (cf. Sect. 7.7).

Uses with Waterlogged Wood

Historical

- 1921–1926 Scott (1921, 1923, 1926) uses water glass for the restoration of museum objects.
- 1951 Cebertowicz and Jasienski apply the so-called electrokinetic method to structural wood members during excavations in Biskupin (Poland).
According to Filip, the objects are sprinkled with a special solution which, among other substances, also contains water glass. This is followed by the application of direct current by way of aluminum electrodes.
- 1953 Zurowski describes the electrokinetic method. Hardening and mineralization of wood is done with a direct current and different electrolytes, namely (1) alum solution, and (2) water glass solution of 15–25°Be, to which a solution of calcium chloride is added as the reactive component.
- 1956 Conservation of a dugout canoe by slow drying and brushing with a solution of sodium silicate (Plenderleith).
- 1959/1960 Wielicka mentions the electrokinetic method.
- 1973 Mühlethaler et al. describe the electrokinetic method used in Poland.
- 1977 Water glass conservation reportedly increases the strength and hardness of objects considerably (De Jong 1977a).

Present Day

Alkali silicates or water glass are not used to treat waterlogged wood.

Advantages/Disadvantages

For dry wood alkali silicates are suitable as fire retardants, as they melt at high temperatures to form a protective coating. The strongly alkaline solutions can cause cell collapse and produce a negative anti-shrink efficiency (ASE). In waterlogged wood strength and hardness are improved, and cracks can close. The appearance of the wood does not meet aesthetic requirements, and the alkali silicates introduced into the wood are fixed irreversibly. The information on the electrokinetic method includes few details.

11.3

Organic Compounds

11.3.1

Animal Glues

11.3.1.1

Protein Glues (Bone, Hide, Leather and Fish Glues, and Gelatins)

Composition: Animal proteins, with main constituents for hide and bone glue approximately 37% glycine, 15–16% proline, 13–14%

hydroxyproline, 11% glutamic acid, 11% alanine, and 9% arginine, and secondary constituents valine, leucine, isoleucine, serine, threonine, aspartic acid, lysine, methionine containing sulfur, phenylalanine, tyrosine, and histidine

- Production:** The raw materials are degreased and then treated with hot water or steam. This causes partial hydrolysis of the collagen contained in the animal tissues and produces glue solutions which solidify into jellies upon cooling and become horny, transparent masses when dried. Gelatin is produced by further extraction and purification of bone and hide glues
- Properties:** The dried glue jellies swell only slowly in cold water. Following the swelling they are prepared as a 15% solution in a water bath, producing a liquid of high adhesive strength. However, additional boiling will destroy the glue. Gelatins are colorless, glassy products with a low germ count and without pathogenic bacteria. They swell strongly at first and form viscous solutions. Gelatins are not soluble in ethanol, ethers or ketones
- Toxicology:** Protein glues are a food source for fungi and bacteria, and therefore biocides are often added to increase durability
- Analysis:** IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

- Eighteenth/nineteenth centuries Glue impregnation for wood consolidation.
- ca. 1900 Consolidation of wood with warm glue with added decay inhibitors (Aberle and Koller 1968).
- ca. 1909 Use of a mixture of animal glue and Venice turpentine in denatured ethanol, with formalin or mercury(II) chloride. The presence of formalin effects a chemical hardening of the glue. Alum or thymol are added as a preservative (Aberle and Koller 1989).
Glue is used to impregnate altars via bore holes, and to close insect exit holes (Anonymous).
- 1910 Rathgen questions the suitability of consolidation with animal glue.
- 1924 Aqueous gelatin solutions are used to consolidate objects severely damaged by insects (Rathgen).
- 1952 The impregnation of wood panels with cabinet maker's glue is rejected in Germany (Wolters 1998).
- 1954 Augusti consolidates wood panel paintings and sculptures with a glue solution containing NaF, with tannin added to effect hardening.
- 1969 Consolidation of wooden body of a serpent with animal glue (Farrington).

- 1971 Glue with alum added as a stabilizer for wooden works of art (Becker).
Warm glue, Venice turpentine, and formalin used to consolidate wood sculptures (Munnikendam).
- 1984 Evaluation of consolidation with glue by Schiessl.
- 1986 Kadry uses a gap filler made of wood flour, animal glue, and an insecticide for the Solar Boat of Cheops.
- 1987 Restoration of a chest with a solution of protein glue with chloramine derivatives and alum added (Stadler).
- 1989 Impregnation of wood destroyed by insects and fungi with a solution of protein glue and characterization of its properties (Cuaný et al. and Schiessl).
- 1990 Data on the aging characteristics of gelatin for the consolidation of paint layers on ethnographic objects (Hansen et al.).
- 1996 Tests of the insect resistance of wood damaged by insects and consolidated with protein glue (Unger et al.).

Present Day

Protein glues are used to consolidate smaller areas of wood damaged by insects or fungi, often prior to gilding, and are a component of chalk and glue gap fillers. Also used to consolidate paint and ground layers and for gluing.

Uses with Waterlogged Wood

Historical

- 1850/1900 Conservation of dugout canoes with glue solutions in Switzerland (Ramseyer and Vonlanthen 1987).
- 1924 Rathgen gives methods for consolidation with glue, namely (1) impregnating wet wood with aqueous glue solution, drying in a cool location, and then impregnating with a resin solution, and (2) pouring warm glue solution over the wood at the excavation and bandaging it. The bandages are removed in the laboratory and the wood is coated daily with sturgeon bladder solution, later with glue solution (Baum's method).
- 1950–1960 Use of animal glue for waterlogged wood conservation in Hungary (Morgós 1993a).
- 1959 Treatment of the surface of wood impregnated with alum with dilute glue solution which is subsequently hardened with a tannin solution (Augusti).

Present Day

Waterlogged wood finds are no longer stabilized with glue solutions.

Advantages/Disadvantages

For dry and waterlogged wood animal glues are not moisture resistant, they shrink a lot, and become brittle. Their adhesion decreases with increasing age.

Glue solutions do not penetrate very far into wood so that strengthening is only moderate. Water used as the solvent causes much wood swelling, and the glue introduces stresses in the wood upon drying. The glue reacts continuously to climate changes, and without biocides it is susceptible to attack by insects and fungi. The glue solutions often cause a significant darkening of the wood.

11.3.1.2

Casein

Casein is another type of animal glue which has been used for gluing wood (cf. Chap. 12) but is not commonly used as a wood consolidant. It has been used to stabilize paint layers.

11.3.2

Oils

11.3.2.1

Linseed Oil

Composition: Complex mixture of glycerol esters, mainly unsaturated fatty acids, including approximately 52% linolenic acid, 22% oleic acid, 17% linoleic acid, 5% palmitic acid and 4% stearic acid

Production: Comminuted linseeds which contain up to 30% oil are cold pressed

Properties: Golden yellow oil; m.p. about -20°C ; readily soluble in ether, petroleum ether, benzene, carbon disulfide and chlorinated hydrocarbons. Linosyn (dried linseed oil) is soluble in pyridine, morpholine, and triethanolamine, and partially soluble in methanol, acetone, ether, and ethyl acetate. In water it swells slowly

Toxicology: No danger

Analysis: IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

- Serbian icon painting: the wood panels are boiled in linseed oil before being painted (Brkić 1967).
- 1737 English privilege to Emerson: boiling of wood in oil with poisonous substances added (Troschel 1916).
- 1822 Coating of wood with linseed oil varnish (Clausnitzer 1990).
- 1826 Boiling of wood for 3–4h in a mixture of linseed oil, green vitriol [iron(II) sulfate], verdigris, arsenic and alum (Clausnitzer 1990).

- 1838 Glanz treats a high altar, after cleaning, with a pigmented oil against insect attack (Aberle and Koller 1968).
- Prior to 1900 In Dresden (Saxony) wooden objects are bathed in kettles with hot linseed oil varnish (Bachmann 1926/1927; Aberle and Koller 1968).
- 1911 Impregnation of a panel painting by Vivarini with linseed oil varnish (Aberle and Koller 1968).
- 1912 Soaking of wood in hot linseed oil with carbolic acid added (Aberle and Koller 1968).
- 1926/1927 Treatment of damaged wood objects by soaking or brushing with linseed oil varnish, amber lacquer, and camphor oil in various proportions (Bachmann).
- 1956 Linseed oil is used as a preventive measure against moisture and fungi (Plenderleith).
- 1963 Linseed oil varnish sometimes discolors panel paintings (Weihs).
- 1971 Varnish as a stabilizer for works of art made of wood (Becker).
- 1972 Linseed oil to prevent fungal attack in damp rooms (Majewski).
- 1983 Koch describes the treatment of the backs of panel paintings with hot linseed oil.
Linseed oil among materials used to conserve a church door (Werner).
- 1984 Report by Michaelsen on the conservation and restoration of the Dürer cabinet. Veneered surfaces and carvings are impregnated with hot linseed oil varnish. They are then coated with a linseed oil and mastic varnish (1 part mastic boiled with 3 parts linseed oil).
Historic overview of the use of linseed oil for art work consolidation by Schiessl.
- 1989 Cuany et al. and Schiessl report on results of linseed oil consolidation of wood damaged by insects and fungi.
- 1996 Impregnation of insect-damaged wood with linseed oil does not provide sufficient protection against a new insect attack (Unger et al.).

Present Day

Linseed oil is used as a surface coating for wood in the form of oil and resin varnishes, but it has no importance as a consolidant.

Uses with Waterlogged Wood

Historical

- Since 1904 Treatment of the *Oseberg* Ship with creosote and linseed oil (a part of the funerary objects is only treated with alum!; Rosenqvist 1959).
- Since 1908 A Celtic monumental sculpture was stored underwater for 3 years and then dried slowly in air. It was then impregnated with linseed oil, wax or paraffin, and resin/glycerol. After 65 years tar-like exudations and other indicators of decomposition become apparent (Bill 1979).

- 1913 Gustafson describes the conservation of the woods and the funerary objects of the *Oseberg* Ship.
- 1924 Wavre method (according to Rathgen): objects are soaked in alcohol for 2 months and then soaked for 10 min in linseed oil.
- 1957 Treatment of the wood of the *Oseberg* Ship with linseed oil and white spirit (Rosenqvist 1959).
- 1958 Conservation of a boat with an 80°C mixture of 75% turpentine and 25% linseed oil with colophony and Carbolineum added (Garczyński).
- 1985 After treating a shipwreck with chromium compounds, Bouis used linseed oil (cf. Sect. 11.2.3.1).
- 1995 After natural freeze-drying of a boat, the wood is sprayed with a mixture of linseed oil and 1-butanol (1:10; Zhang Lan).

Present Day

Linseed oil no longer has any importance in the conservation of waterlogged wood.

Advantages/Disadvantages

For dry wood, during full impregnation of wood damaged by insects or fungi, especially with hot linseed oil, high loading is obtained and the distribution within the wood is satisfactory to good. However, in spite of addition of siccatives, the linseed oil will not harden completely even after decades. Climate changes bring about exudation of linseed oil, e.g. in the form of drops. The linseed oil can turn rancid and will smell accordingly. Many impregnated objects darken considerably and absorb dust on the surface. Satisfactory biological resistance to wood pests is not obtained. For waterlogged wood, stabilizing effects are often insufficient.

11.3.2.2

Tung Oil

Composition: Mainly glycerides of unsaturated fatty acids, about 80% α -eleostearic, 8% oleic, 4% linoleic, 3% linolenic, 4% palmitic, and 1% stearic acid

Production: By cold pressing or extraction of comminuted seed shells and kernels of *Aleurites* species native to China, Japan, and South-east Asia

Properties: Light yellow to dark brown, viscous liquid of characteristic odor; m.p. a few degrees below 0°C; readily soluble in almost all organic solvents

Toxicology: The oil contains strongly laxative and nauseous, if not poisonous, substances. It can cause inflammation of the skin (tung oil disease)

Analysis: IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

Since 1890 Tung oil gains importance in the coating technology in Europe (Schiessl 1984).

Since 1900 Impregnation materials containing tung oil are being mentioned for wooden art objects (Schiessl 1984; Aberle and Koller 1989).

1924 Rathgen uses Chinese tung oil for the consolidation of objects severely damaged by insects. Heating the treated wood improves its hardness.

1934 Conservation of insect damaged wood objects with tung oil dissolved in French turpentine, whereby the frass is reportedly also consolidated (Aberle and Koller 1968).

1952 Busts of a Baroque choir stall without polychromy are treated with tung oil (Aberle and Koller 1968).

1962 Tung oil as the main constituent of a strengthening material for wood (Schiessl 1984).

1966 Manková impregnates linden and oak wood samples with tung oil in turpentine.

Present Day

Tung oil is of no importance as a consolidant.

Uses with Waterlogged Wood

Historical

1921 The surface of parts of the *Hjortespring* Find (Denmark) impregnated with alum were treated with tung oil (Brorson Christensen 1970a).

Present Day

Tung oil is not used to conserve waterlogged wood.

Advantages/Disadvantages

For dry and waterlogged wood, the strengthening effect of tung oil is generally small. Most of the time the oil is merely absorbed and will not harden completely in cold conditions. Moisture has a negative effect on the drying of the oil, and there is a danger of spotting on the surface. Surfaces coated with tung oil tend to brown strongly.

Additional vegetable oils: poppy seed oil, rapeseed oil, castor oil, oil of turpentine, and camphor oil. These oils were used occasionally in the past as solvents, alone or in combination with other solvents, for natural resins in wood consolidation. Oil of turpentine is used now and then even today as a solvent for beeswax and dammar mixtures for the consolidation of smaller areas or objects damaged by insects or fungi. The oils are of no importance to waterlogged wood conservation.

11.3.3

Fats

11.3.3.1

Lanolin (Wool Fat, Wool Grease)

Composition: A mixture of various esters of fatty acids, such as palmitic acid, cerotic acid, caproic acid, oleic acid, with cholesterol, lanosterol, and agnosterol

Production: Sheep's wool is treated with soap solutions and sodium hydroxide. The raw wool grease is then precipitated with calcium chloride or magnesium sulfate and purified by oxidation

Properties: Raw lanolin is a greasy, ill-smelling, yellow brown mass; water-free wool wax is a yellowish, translucent, salve-like mass with a faint odor, which does not easily turn rancid; m.p. 36–41 °C; readily soluble in ether and chloroform, not very soluble in ethanol. Pure wool wax can take up large quantities of water, resulting in emulsions

Toxicology: Lanolin has a certain potential as an irritant and can trigger allergies

Analysis: GC/MS

Uses with Dry Wood

None found for dry wood.

Uses with Waterlogged Wood

Historical

1982/1983 Vynckier publishes the lanolin method. The water in waterlogged wood is successively exchanged for alcohol, ether, and water-free lanolin, followed by drying of the wood.

Present Day

The method does not have much importance.

Advantages/Disadvantages

For waterlogged wood, according to Vynckier, the method is especially suitable for smaller wood objects which still have a more or less hard core. Shrinkage and deformation of the objects are reduced. As a particular advantage the preservation of color and a natural appearance of the wood is emphasized.

11.3.4

Waxes

11.3.4.1

Beeswax

Composition: Main components are cerin, a mixture of cerotic and melissic acids, which is readily soluble in ethanol; and myricin, an ester mixture of higher fatty acids such as palmitic acid and higher alcohols

Production: The honeycomb is separated from the honey by centrifuging, and is melted. Solid contaminants are separated from the melt. The raw wax is termed *cera flava*. The white wax, *cera alba*, is obtained by bleaching the raw wax with sunlight, podzol, hydrogen peroxide or chromium compounds

Properties: Yellowish to white, easily formable mass; m.p. 61–68°C; insoluble in water and cold ethanol, soluble in hot alcohol, ether, benzene, chloroform, tetrachloromethane, gasoline, turpentine, oil of turpentine, hot fats and etheric oils

Toxicology: There are no health threats

Analysis: IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

1902 C. Gurlitt (Aberle and Koller 1968) dips damaged wood objects into hot wax-resin solutions.

Since 1935 The American D. Rosen (1950/1951) develops the wax immersion method. For full impregnation of panel paintings and wood carvings with and without polychromy he at first uses beeswax with 25% gum elemi, later a mixture of paraffin and beeswax (cf. paraffin).

1939 A panel painting of the Prague National Gallery is “petrified” with a solution of beeswax and mastic (Slánský 1956). Aberle and Koller (1968) reject the recommendation of Slánský to plane off parts of the paintings’ backs to facilitate penetration of the solution.

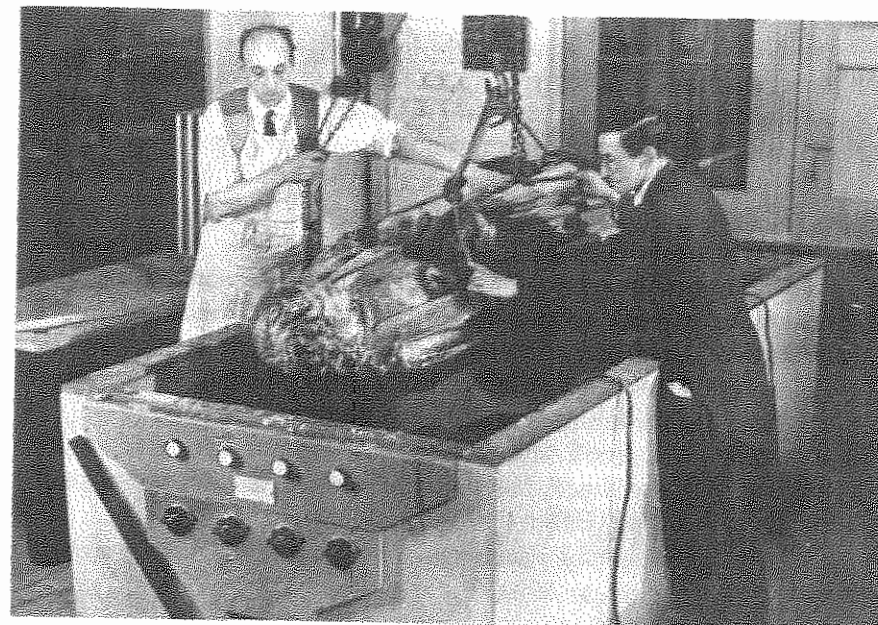


Fig. 11.1. The wax immersion method for consolidation of sculptures and panel paintings. (Plenderleith 1956)

1950/1951 Detailed description of the wax immersion method by Rosen (Fig. 11.1).

1956 Plenderleith lists the following possible applications of beeswax in conservation: consolidation of objects with beeswax-resin mixtures, impregnation of the wood as a preventive measure against moisture gain, and filling of insect exit holes with beeswax containing DDT.

1958 According to Losos, beeswax is suitable for consolidating sculptures and panel paintings, but the strengthening effect is small.

1962 Lehmann describes the wax immersion method.

1963 Wax is suitable for the consolidation of the backs of decayed wood panels and for loss compensation (Straub).

1963/1964 Cleaning of a polychromed Christ figure with turpentine and an ammonia-wax paste. The object is impregnated with a wax-resin mixture and covered with a protective wax polish (Loeken 1967).

1966 Impregnation of a fourteenth century painting with a wax-resin mixture (Ballestrem), and a wood carving with wax using infrared lamps (Boustead).

1970 An angel figure and a figurehead are soaked for 6h in a mixture of 50% beeswax, 40% paraffin and 10% gum elemi by Packard.

1971 Becker cites beeswax dissolved in gasoline and a mixture of wax and resin in petroleum ether for the consolidation of wooden works of art.

- 1972 Soaking of sculptures in a bath of beeswax at 76°C after first safeguarding cracks with carnauba wax (Majewski; cf. carnauba wax).
- 1984 Peters stabilizes dendroglyphs (bark carvings on trees) with a mixture of beeswax, paraffin, dammar, and carnauba wax.
- 1987 Consolidation of sculptures and wood panel paintings by dipping into a mixture of dammar and beeswax in turpentine with added insecticides (Bernatova et al.; Dalorova et al.).
- 1988/1989 Šimůnková and Josef investigate the uptake of a beeswax-colophony mixture by wood as a function of the solvents used.
- 1989 According to Aberle and Koller, beeswax is still being used in the 1960s as a consolidant.
- Cuany et al. investigate the stabilization of wood damaged by insects and fungi with a hot mixture of beeswax and hard paraffin (9:1).
- 1996 Insect damaged wood consolidated with beeswax and hard paraffin mixture (9:1) was almost completely penetrated, but soft and not sufficiently bioresistant (Unger et al.).

Present Day

Full impregnation of objects with hot beeswax-paraffin mixtures is no longer customary. However, mixtures of beeswax and other waxes or resins such as colophony or dammar, in solvents such as turpentine, are now and then used to consolidate smaller areas or objects damaged by insects or fungi. The wax is also used in the form of wax polishes to seal and improve wood surfaces, for loss compensation, to fasten ground and paint layers, and for relining paintings. Beeswax is also a component of intermediate and final varnishes.

Uses with Waterlogged Wood

Historical

- 1858–1860 Speerschneider (1861) heats small wood objects for 2 h in a mixture of 8 parts rapeseed oil, 1 part wax, 1 part spruce resin, and 2 parts benzene.
- 1924 Wet wood is protected from drying by pouring molten wax over it (Rathgen).
- 1949/1956 Beeswax as a component of a consolidant (cf. carnauba wax).
- 1962/1969 Brorson Christensen (1970b) makes experiments to improve waterlogged wood conservation. Among others he impregnates waterlogged wood with beeswax dissolved in tert-butanol (2-methyl-2-propanol) followed by sublimation (tert-butanol dissolved the wax at 50°C). The method fails for oak heartwood.
- 1979 The surface of waterlogged wood that has been treated by the alcohol-ether-resin method received a protective coating of molten beeswax (Kramer).

- 1987 Ramseyer and Vonlanthen state that beeswax is unsuitable for waterlogged wood conservation.

Present Day

Beeswax consolidation is not a traditional conservation method for waterlogged wood, but is used occasionally for small, very fragile finds.

Advantages/Disadvantages

For dry wood, in its pure form beeswax is suitable only for the consolidation of very small objects or areas with minor insect or fungal damage, but the stabilizing effect is better in combination with resins. The wax is easily worked, inert, and sufficiently stable with age. It is considered water repellent and reversible. However, with full impregnation the strengthening effect is small in spite of sometimes high wax uptake. Wood damaged by fungi will especially darken considerably. According to Cuany et al. (1989), damaged wood impregnated with wax-paraffin shows clearly increased water uptake and swelling. After a period of years, beeswax can bloom out and becomes brittle. At elevated temperatures, as when exposed to sunlight, the wax or wax-resin mixtures can run out of the treated objects. The surfaces of such objects are sticky and attract dust.

Full impregnation with hot wax places objects under severe temperature stress, and glue joints may separate.

Beeswax effects only insufficient stabilization of waterlogged wood, and it should also be avoided as a protective coating for wood consolidated by another method.

11.3.4.2

Carnauba Wax

Composition: 85% esters of fatty acids, ω -hydroxycarbon acids and cinnamic acids with waxy alcohols and diols, 3–5% free fatty acids (carnaubic and cerotic acids), ca. 11% alcohols and diols, and also hydrocarbons and mineral nutrients

Production: Wax dust is brushed from the wilted fronds of the Brazilian carnauba palm *Copernicia prunifera*, melted, filtered, and after solidification broken into pieces

Properties: In purified form a light yellow, hard and brittle wax; m.p. 80–90 °C; barely soluble in water, ethanol and ether; soluble in boiling ethanol, turpentine, and petroleum ether

Toxicology: No danger to health

Analysis: IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

- 1968 Aberle and Koller list the wax as a consolidant.
 1972 Safeguarding of cracks in the paint layer of polychromed sculptures with silk cloth and carnauba wax prior to beeswax impregnation (Majewski). After the beeswax treatment the silk cloth and carnauba wax are removed with petroleum ether.
 1984 Consolidation of dendroglyphs (Peters; cf. beeswax).
 1989 Carnauba wax is mentioned as a historic consolidant by Aberle and Koller.

Present Day

Carnauba wax is not used as a consolidant, but finds application as a component of wax polishes for furniture.

Uses with Waterlogged Wood

Historical

- 1949/1956 Brorson Christensen (1970a) embeds very soft objects in a hard wax mixture. The wood is dewatered with ethanol, followed by exchange with toluene or xylene. The object is submerged in molten paraffin wax at 60°C, then in a mixture of 1 part dammar, 1 part carnauba wax 1 part paraffin, and 3 parts beeswax, by mass, at 80°C

Present Day

Carnauba wax is not used for stabilization.

Advantages/Disadvantages

For dry wood, strengthening is greater but penetration less compared with beeswax. The color of the wood surface changes, and further treatment of the object is sometimes difficult.

For waterlogged wood, according to Brorson Christensen (1970a), the mixture he uses is durable even under unfavorable climatic conditions. Objects undergo only minor dimensional changes.

11.3.4.3

Paraffin

Composition: Solid or liquid mixture of purified, saturated aliphatic hydrocarbons

Properties: Hard paraffin is a solid, colorless, odorless mass without taste. m.p. 50–62°C; insoluble in water and 90% ethanol;

soluble in ether, chloroform, tetrachloromethane, benzene and turpentine

Toxicology: In its pure form there are no health dangers

Analysis: IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

- ca. 1890ff. Paraffin waxes are used in the conservation of works of art (Schiessl 1984).
 1902 First full impregnations with wax-resin melts (Aberle and Koller 1968).
 1924 For the consolidation of insect-damaged objects Rathgen recommends heating the wood to 50–60°C followed by soaking in molten paraffin at 100°C. Bast can also be conserved with paraffin.
 Since 1935 Rosen's detailed descriptions of the wax immersion method (cf. beeswax).
 1958 Paraffin reported unsuitable for impregnation (Losos).
 1962 Lehmann gives the following variations of paraffin conservation: (1) treating wood attacked by fungi with Cuprinol, then with paraffin, (2) vacuum impregnation with a mixture of paraffin and natural resins, and (3) tank immersion with hot paraffin at an initial temperature of 70°C, elevating the temperature to 105°C, and removal of the objects at 90°C after soaking for at least 2h.
 1967 Marijnissen rejects the treatment of polychromed and gilded objects by heating to 100–110°C in molten paraffin.
 1968 Aberle and Koller criticize the shallow penetration of paraffin and the complete change of the wood surface.
 Lodewijks also discovers that decayed wood carvings and sculptures can be impregnated only superficially with paraffin. The appearance is also disfigured by a thick surface coating.
 1970 Consolidation of wood sculptures with a mixture containing paraffin by Packard (cf. beeswax).
 1972 Large charred carvings are impregnated first with paraffin wax, then with a wax-resin mixture (1:1; Gagen et al.).
 1976 Emile-Male recommends paraffin, wax, or wax-resin mixtures to consolidate wooden painting supports.
 1984 Consolidation of dendroglyphs by Peters (cf. beeswax).
 1986 Parts of ancient furniture stabilized with paraffin have the wax removed with toluene followed by new consolidation with Butvar B98 [cf. poly(vinylbutyral)] in equal parts of toluene and ethanol and with Rütapox R1210 (cf. epoxy resins; Simpson and Payton).
 1987 Hatchfield and Koestler study archaeological wood consolidated with paraffin under the scanning electron microscope.
 1989 Aberle and Koller mention paraffin wax consolidation.

Paraffin wax is used in mixture with beeswax to consolidate wood damaged by biological agents (Cuany et al.; cf. beeswax).

1996 Biological testing of wood samples impregnated with beeswax and paraffin (Unger et al.; cf. beeswax).

Present Day

Occasional use in mixture with other waxes or resins to consolidate small areas or objects. Also used as a component of polishes.

Uses with Waterlogged Wood

Historical

- 1924 According to Rathgen waterlogged wood can be kept from drying by dripping or pouring molten paraffin over it. Storage in liquid paraffin is also a possibility.
- 1929 Leechman (1931) dewateres waterlogged wood in a series of methanol baths of increasing concentration, exchanges the methanol for toluene and submerges the wood for several hours in molten paraffin wax.
- 1935 Waterlogged wood is dewatered with ethanol and then impregnated with paraffin (Kisser and Pittioni).
- 1949/1956 Brorson Christensen (1970a) embeds objects in a hard wax mixture (cf. carnauba wax).
- 1950/1960 The paraffin method is used in Hungary (Morgós 1993a).
- 1955 Gebser dewateres waterlogged wood in ethanol baths of increasing concentration and 1-propanol, the first bath consisting of 50% ethanol and 3% formalin. Subsequently, the wood is bleached for 12 h at 48–52°C in 1-propanol with 5% of 30% H₂O₂ before placing it for 6–12 h in hot paraffin at 60°C.
- 1962 Kislov and Čistáková exchange the water in waterlogged wood for ethanol or acetone, a benzene-ethanol or benzene-acetone mixture, then for benzene, and finally a benzene-paraffin wax mixture (1:1). The benzene is evaporated at 60°C. For objects with a volume of 150 cm³ the treatment takes 30 days. Good results are obtained for maple and ash, but birch and pine develop cracks. Because of flammability and toxicity of the solvents, the method is judged to be of limited applicability.
- Impregnation of the wood with warm paraffin at 60°C after ethanol, ethanol/1-pentanol and glycerol exchange (Lehmann).
- 1962/1969 Impregnation of wood with paraffin in tert-butanol and sublimation (Brorson Christensen 1970b; cf. beeswax).
- 1976 Barkman et al. describe various methods of waterlogged wood conservation including the acetone-paraffin method.
- 1987 Overview including the wax-resin impregnation by Grattan and Clarke.
- 1994 Objects can safely be dewatered and stabilized by boiling in Cellosolve (1-ethoxy-2-propanol) and petroleum, followed by a wax/petroleum

impregnation and vacuum drying (Cellosolve-petroleum-method; Jensen et al.). The conservation process takes 4–60 days.

Present Day

Paraffin wax conservation is occasionally used for small, heavily damaged objects and for wood/metal composites.

Advantages/Disadvantages

For dry wood, paraffin usually does not penetrate deeply into wood, so that the strengthening effect is small. The heat of the paraffin bath can cause flaking of paint layers, joints made with hide or bone glues can open up, and regluing of the joints is made difficult. The appearance of wood and matte paint coatings is changed considerably. Treated objects attract dust and become unsightly. According to Bruder (1987), it is virtually impossible to completely remove paraffin from porous materials.

For waterlogged wood, according to Brorson Christensen (1970a) very soft objects are suitable for embedding in hard wax mixtures. Jensen et al. (1994) report that objects consolidated by the Cellosolve-petroleum method with a wax loading of 10–25% do not collapse, shrink little, and have a light color. The lower the density, the less the shrinkage.

11.3.4.4

Microcrystalline Wax

Trade name: Cosmolloid (Great Britain)

Composition: Microcrystalline paraffins with fine crystalline structure

Properties: Black-brown, yellowish, or white in color; sticky, soft or hard mass elastic under pressure; m.p. 60–90°C; soluble in benzene, toluene and turpentine

Toxicology: No acute or chronic health dangers

Analysis: GC/MS

Uses with Dry Wood

Historical

- 1968 Agrawal and Bisht consolidate a wood carving from Nepal with a mixture of microcrystalline wax and resin (3 : 2).
- 1972 Microcrystalline wax is mentioned as a consolidant (Majewski). Šujanova uses the wax, dissolved in benzene or toluene, for surface stabilization of objects.

Present Day

The wax is rarely used in wood conservation.

Uses with Waterlogged Wood**Historical**

Microcrystalline wax is mentioned briefly by Werner (1959) and Šujanová (1972) as a consolidant.

Present Day

Microcrystalline wax is not used for stabilization.

Advantages/Disadvantages

For dry and waterlogged wood, the strengthening effect of microcrystalline wax is generally small.

11.3.5**Resins****11.3.5.1****Dammar**

Trade name: Dammar, damar

Composition: 40% alcohol soluble α -dammarresen, 22.5% alcohol insoluble β -dammarresen, 20–25% dammarol acid (a triterpene acid), 2.5% water, and about 0.5–1% essential oil

Production: Living trees of the genera *Hopea* or *Shorea* (Dipterocarpaceae) in Southeast Asia are wounded and the solidified resin is collected 3 months later (Lange 1996)

Properties: Light yellow, drop-shaped, transparent pieces with a faint aromatic odor which softens at about 90°C; m.p. ca. 120°C, also reported as 150–170°C; soluble in chloroform, benzene, toluene, xylene, petroleum ether, oil of turpentine; partially soluble in ethanol and ether

Toxicology: Can cause skin irritation

Analysis: GC/MS

Uses with Dry Wood**Historical**

1894 Small, very fragile objects are dipped into a solution of dammar in benzene, with poppy-seed oil and turpentine added (Anonymous).

ca. 1900 Rathgen recommends a solution of dammar in carbon tetrachloride for wood consolidation (Schiessl 1984).

1924 Objects severely damaged by insects can be consolidated with 25% and 40% solutions of dammar in xylene (Rathgen).

1966 Manková investigates water uptake and swelling of wood samples impregnated with solutions of 10% dammar in turpentine or toluene.

1972 A mixture of beeswax and dammar (2:1) in warm oil of turpentine is used for wood consolidation, using vacuum impregnation with a 10%, later 15–18% solution, with 0.1% of an insecticide added. The mixture is reported to be chemically stable and water-repellent, and should not attack the wood substance (Šujanová).

1981 Description of the effects of impregnation with dammar and changes of the properties of the impregnated wood (Šimůnková and Zelinger).

1984 Stabilization of dendroglyphs (Peters; cf. beeswax).

1987 Dammar as a component of a consolidant mixture for sculptures and wood panel paintings (cf. beeswax).

Present Day

Generally the resin, either alone or in mixture with other materials, is only rarely used for wood consolidation.

Uses with Waterlogged Wood**Historical**

1949/1956 Dammar as a component of a conservation material (Brorson Christensen 1970a; cf. carnauba wax).

1956 Plenderleith describes the alcohol-ether-dammar method. The object is bleached in a 5% solution of hydrogen peroxide, water is exchanged for ethanol and the latter for ether, followed by vacuum impregnation of the object with dammar in ether.

1959 Werner mentions the alcohol-ether-dammar method.

1967/1968 Kramer and Mühlethaler report on their experience with the alcohol-ether-dammar method.

1970/1973 Further reports on the alcohol-ether-dammar method by Brongers and Wijnman (1970/1971), Ankner (1972) and Mühlethaler (1973).

1974 Conservation of wooden writing tablets after water-methanol-ether exchange with dammar (Blackshaw).

1975 Gregson uses the method of Blackshaw (1974) to treat a treenail.

1976/1977 Reviews by Blackshaw (1976 and 1977) and De Jong (1977a), which also deal with the alcohol-ether-dammar method.

1979 Comprehensive exposition of the method by Kramer. The ether in the dewatered wood is replaced by a mixture of 250g dammar, 100g colophony, 50g castor oil, and 50g "English oil varnish" (sic) in 1 l

diethyl ether, either within 4 weeks or accelerated by vacuum impregnation which may, however, be risky for some objects. The impregnated objects are dried in vacuum.

- 1987 Summary of wax or resin impregnation using nonaqueous solvents, by Grattan and Clarke.
- 1988 According to Grattan, the alcohol-ether-dammar method presents a serious safety risk.
- 1989 The alcohol-xylene-dammar method reduces dimensional changes of treated waterlogged wood exposed to cyclic moisture changes (60–90–60–35% relative humidity, 12 h per cycle; Nishiura and Imazu).

Present Day

Methods based on dammar are not very important in waterlogged wood conservation.

Advantages/Disadvantages

For dry wood, dammar is very stable with age, and water repellent. Since it has little coloring of its own and is transparent, the color and texture of the treated wood are satisfactory.

For waterlogged wood, small objects can be well consolidated by the alcohol-ether-dammar method, and conservation is more effective for severely destroyed rather than less damaged areas. According to Grattan and Clarke (1987), the microscopic identification of the treated wood, the depth of penetration of the resin, the mending of fractures and the stability of the treated objects can be classified as good. However, strengthening with respect to compression and bending and shrinkage behavior must be considered only as satisfactory. The alcohol-ether-resin method presents explosion and fire risks. ^{14}C dating of treated objects is very difficult.

11.3.5.2

Colophony

Trade name: Rosin (USA); Xylamon LX Härtend (Germany; until 1964 with colophony as a consolidant and chloronaphthalene or PCP as a biocide, from 1964 to 1985 coumarone resin)

Composition: Mixture of 90% resin acids and 10% neutral substances (esters of fatty acids, terpene alcohols, and hydrocarbons). The most important resin acids are unsaturated carbon acids such as palustric, abietic, neoabietic, pimaric, isopimaric and levopimaric acids (percentages can be found in Lange 1997)

Production: Wounding of living trees (resin balsam), steam distillation of tree stumps, or from tall oil, a byproduct of the sulfate pulping process. Distillation of the resin balsam yields about 80% crystalline colophony and 20% turpentine

Properties: Light yellow to dark brown, transparent, and brittle resin, which softens at 70–80 °C; m.p. 100–130 °C; insoluble in water; soluble in (chlorinated) aliphatic and aromatic hydrocarbons, esters, ethers, and ketones; partially soluble in methanol and ethanol; soluble in vegetable oils such as oil of turpentine and mineral oils

Toxicology: No danger to health

Analysis: GC/MS

Uses with Dry Wood

Historical

Late nineteenth, early twentieth centuries Colophony used as a consolidant (Aberle and Koller 1989).

1924 Rathgen mentions colophony for the conservation of objects severely damaged by insects.

Since 1934 At the Institute for Technology and Conservation of the Vienna Academy of Art, resin emulsions consisting of methyl cellulose, Alkydal and colophony are used for wood consolidation (Aberle and Koller 1968).

Since 1935 In Berlin, large-scale vacuum impregnations of furniture from Prussian palaces were carried out with “resin solution Sommerfeld” which contains resin of *Pinus pinaster* (syn. *P. maritima*) in 1,2-dichloromethane (Weidner et al. 1999).

1956 Colophony in gasoline with pentachlorophenol for wood consolidation (Slánský).

1958 According to Losos, colophony in benzene can be used to impregnate wood, but the strengthening is low and aging characteristics are poor.

1968 Colophony can continue to be used as a consolidant with glycerol, or better with Alkydal as a plasticizer (Aberle and Koller).

1971 Becker refers to a mixture of beeswax and colophony or only colophony in benzene as a stabilizer. A combined impregnant is a mixture of 41% colophony as consolidant, 45% Tersilven as solvent, 10% Chlorkogasin as plasticizer, and 3.3% DDT and 0.7% γ -HCH as insecticides.

1986 Stabilization of parts of the Solar Boat of Cheops and of statues from the Old Kingdom, Egypt, with a mixture of colophony and wax in 1,1,2-trichloroethene (trichloroethylene; Kadry, also Nakhla).

1988/1989 Investigations of the effect of solvent polarity on the uptake of a colophony-beeswax mixture by linden wood and the resulting sorption and strength characteristics [Šimůnková and Josef 1988, 1989; cf. poly(butyl methacrylate)].

Present Day

Colophony is only rarely used for wood consolidation, usually in mixture with wax.

Uses with Waterlogged Wood

Historical

- 1972 McKerrell et al. publish the acetone-rosin method. The waterlogged wood is pretreated with 3.5% hydrochloric acid, and dewatered with acetone to a moisture content of <0.1%. The object is then impregnated with a 67% colophony solution in acetone at 52°C and air dried.
- 1975 New report on the acetone-rosin method by Bryce et al.
- 1976/1977 Blackshaw (1976, 1977) and De Jong (1977a) describe the method.
- 1979 Colophony as a component of the alcohol-ether-resin method (Kramer; cf. dammar).
- 1981 Waterlogged wood after alcohol-ether exchange can also be stabilized with a solution of colophony in diethylether (Šimůnková et al.).
- 1982 Grattan (1982a,b) compares different conservation methods for waterlogged wood. Results with the acetone-rosin method are not satisfactory.

In the Parks Canada Conservation Laboratory objects are dewatered in four acetone baths over a period of 6 months. The consolidation solution contains 66% rosin by mass in acetone. The impregnation can be done at 55°C or at room temperature and takes up to 7 months (Grattan and Clarke 1987). Excess rosin clinging to the wood surface can be removed with cotton soaked in acetone or with acetone vapors.

Masuzawa et al. investigate changes in the physical properties of wood and its dimensional stability when using the alcohol-xylene-rosin method. PEG 4000 is better than rosin.

- 1987 Fox (1989) treats hardwood objects such as dead eyes, pulley blocks, and other ship's fittings by the acetone-rosin method; for safety reasons this is done at room temperature.

Detailed evaluation of the acetone-rosin method by Grattan and Clarke.

Payton conserves inlays of wood and ivory of a sword handle by the same method. The consolidated parts fit into their previous locations in the handle.

- 1988 Review by Bhatia of waterlogged wood conservation, including the acetone-rosin method.

According to Grattan, colophony tends to oxidize and the wood becomes brittle, but corresponding aging tests are lacking.

- 1989 Giachi and Tordi obtain satisfactory results from the consolidation of underwater finds (wooden combs from the Middle Ages) with the acetone-rosin method.

- 1990 A writing tablet is treated with the acetone-rosin method by Ganiaris. Use of the method required strict safety measures.

Present Day

The acetone-rosin method is occasionally used for small wood finds with relatively light damage.

Advantages/Disadvantages

For dry wood, colophony is considered resistant to heat and is water repellent. Consolidant loading and the corresponding strengthening are low. Colophony has an irregularly strong acid content, ages poorly without the addition of a plasticizer, and the wood becomes brittle.

For waterlogged wood, according to McKerrell et al. (1972) and Bryce et al. (1975), during the application of the acetone-rosin method crack formation is absent and dimensional changes are minimal after pretreatment with hydrochloric acid and dewatering with acetone. Grain and color correspond to those of recent wood. The resin can be readily removed by extraction. The method is especially suitable for hardwoods of low permeability.

Grattan and Clarke (1987) give the advantages of the method as (1) the cleaning effect of the acetone and the resulting improved penetration into the wood, (2) the low viscosity of the acetone which increases penetration and the rate of diffusion, (3) low surface tension of the solvent, and (4) the rapid strengthening of the resin upon drying. Disadvantages are the flammability of the acetone and some minor shrinkage of the wood by the solvent. The stabilized wood is heavy and very brittle. Because of the rapid drying, large void spaces can form inside the objects. Many conservators will not use the pretreatment with hydrochloric acid on wood and metal combinations.

11.3.5.3

Shellac

Trade names: Lemon, TN, Ivory, Orange, Honey; dewaxed orange shellac; stick lac

Composition: Hydroxycarbon acids, in part unsaturated, which contain aldehyde groups and are present in the form of esters or lactones. Main components are aleuritic and shellol acids. Wax content is 4–6%

Production: Natural resin of animal origin, which is secreted by the females of the lac insect, *Kerria lacca*, infecting trees and bushes in India, Thailand, South China, and other countries of Southeast Asia. The branches covered with secretions are scraped or cut off, and the resin is obtained by extraction and purification

Properties: Red kernels or yellow plates or sheets, white after bleaching; a hard, tough resin; m.p. 100–120°C; dewaxed orange shellac

65–85°C; soluble in methanol, ethanol; ethyl acetate, diacetone alcohol (4-hydroxy-4-methyl-2-pentanone), Methylcellosolve and Cellosolve; not very soluble in ether; insoluble in hydrocarbons such as benzene and gasoline, and in water

Toxicology: Unbleached shellac is considered toxicologically and physiologically safe

Analysis: IR spectroscopy, GC/MS

Uses with Dry Wood

Historical

- Early twentieth century Shellac is used as a consolidant (Aberle and Koller 1989).
- 1934 Shellac is used to consolidate Gothic altar panels (Aberle and Koller 1968).
- 1937 Shellac is rejected because it browns the wood and increases its mass (Lill).
- 1953 The altars of Gampern and Waldburg, Austria, are treated with shellac (Tripp).
- 1956 The high altar dating to the early Baroque of the Gurk Cathedral, Austria, is consolidated with 1500l shellac solution. The fecal pellets are not consolidated but removed (Hartwagner).
Slánský opposes the use of shellac because of the large swelling effect of the solvent ethanol.
- 1961 Wolters mentions the use of solutions of shellac in alcohol to straighten warped wood panels.
- 1963 Shellac is used to repair damaged corners or edges in mixture with chalk or sawdust (Straub).
- 1976 Consolidation of the back of wood panel paintings with shellac (Emile-Male).
- 1981 Šimůnková and Zelinger describe the effects of impregnating wood with shellac.
- 1983 Impregnation of the backs of wood panels with shellac solutions as a climatic barrier to retard moisture exchange (Koch).
- 1989 Cuany et al. and Schiessl investigate strength increases of previously damaged wood samples after full impregnation with a 40% shellac solution in ethanol. Penetration and strength increases were moderate.
- 1994 Description of the shellac method to straighten wood panels with alcoholic swelling agents (Zillich).
- 1996 Egg larvae of the house longhorn beetle invade the shellac impregnated samples prepared by Cuany et al. (1989) and survive in the untreated areas in the interior (Unger et al.).

Present Day

Shellac is occasionally used to consolidate small parts which can still support themselves. It is mainly used in the form of French polishes to seal the surface of wood.

Uses with Waterlogged Wood

Historical

- 1858/1860 Objects impregnated with alum are coated with shellac after they have been dried and brushed with linseed oil (procedure of Herbst).
- 1924 Rathgen cites the procedure of Baum, in which an object impregnated with glue and linseed oil varnish is treated with a shellac solution at the end.
- 1956 Heavy waterlogged wood objects such as canoes can be dewatered with glycerol, and after drying for 1 year are coated with a solution of shellac in ethanol (Plenderleith).
Wood can also be dewatered with tert-butanol. It then is placed for a few days in an 8–10% solution of shellac before it is freeze-dried (Brorson Christensen).
- 1989 As part of a retreatment of the *Hjortespring* Boat, Ringgaard refers to the alum impregnation and subsequent surface treatment with shellac, tung oil, and beeswax by G. Rosenberg.

Present Day

Shellac is of practically no importance in waterlogged wood conservation.

Advantages/Disadvantages

For dry wood, shellac is suitable for the stabilization of small, self-supporting objects. The treated elements are resistant against mechanical stress, but the strengthening effect is not very large. Shellac coatings are water resistant in the short term, hard and brittle. The lower alcohols used as solvents are swelling agents. As a binding medium shellac can become cloudy, make white spots on the objects, and be incompatible with certain other materials (Koob 1984).

For waterlogged wood, objects conserved according to the method of Brorson Christensen (1956) are relatively light, and there is little shrinkage.

11.3.6

Polyols and Sugars

11.3.6.1

Ethylene Glycol (1,2-Ethanediol, 1,2-Glycol) and Other Alkylene Glycols

Formula: $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$

Properties: Colorless, viscous, sweet-tasting, highly hygroscopic liquid; m.p. -11.5°C , b.p. 198°C ; miscible with water, alcohols and acetone, immiscible with diethyl ether, chloroform, aliphatic and aromatic hydrocarbons

Toxicology: The vapors irritate eyes and the respiratory tract. Danger of narcotic effects. Damage to heart, lung and kidneys

Analysis: GC, iodine test to distinguish glycerol: ethylene glycol dissolves iodine with a red-brown color; glycerol only produces a weak light yellow color with iodine

Uses with Dry Wood

Historical

- 1935 Stamm and Hansen develop the Cellosolve method (ethylene glycol monoethyl ether, ethyl glycol) for the dimensional stabilization of wood (Kollmann 1955).
- 1961 Improved swelling behavior of wood panels by Wolters (cf. shellac).
- 1988 Reduction of warping in wood objects with dipropylene glycol (Howlett).
- 1990 Further contribution by Howlett on the use of low relative molecular mass alkylene glycols to correct warping.
- 1991 Thesis by Zillich on straightening of warped panel paintings, including the use of alcoholic swelling agents.
- 1992 Experiments to straighten a warped wood panel with dipropylene glycol, PEG 200 and sugar (Hopp).
- 1994 Zillich publishes thesis results (cf. Zillich 1991).

Present Day

Glycols are occasionally used to straighten, and in combination with consolidants like shellac for the stabilization of warped wood panels.

Uses with Waterlogged Wood

Historical

- 1969 Mühlethaler (1969a,b) recommends that waterlogged wood objects in very dry climates should be soaked in ethylene glycol or glycerol until the final conservation treatment.

- 1970 Brorson Christensen (1970a) investigates the possibility of consolidating the wood with ethylene glycol. It can be converted to a glyptal resin in the wood with phthalic anhydride at temperatures of about 200°C . Because of the high temperature and the irreversibility of the resin this method cannot be considered suitable.
- 1977 According to De Jong (1977a), ethylene glycol can be used to swell dried and shrunken waterlogged wood. Reportedly the method is well suited except for waterlogged oak with minor damage. The surface of the object is finally treated with PEG 4000.
- 1978 Borgin uses glycols as anti-shrink substance in the Thessaloniki process which he developed (cf. Sect. 11.2.2.1).
- 1986 Pretreatment of Neolithic spruce and also recent wood species with ethylene glycol, 1,4-butanediol, 1,5-pentanediol, glycerol and PEG prior to freeze-drying (Schaudy and Slais).
- 1988 Ethylene glycol and diethylene glycol are not suitable for stabilizing waterlogged oak with minor damage; in that case PEG 200 is optimal (Hoffmann 1988a).

Present Day

Ethylene glycol and other low-molecular glycols are rarely used in waterlogged wood stabilization.

Advantages/Disadvantages

For dry wood, the results of straightening and reforming of wood objects with ethylene glycol and other alkylene glycols are not always satisfactory.

For waterlogged wood, the low relative molecular mass glycols have insufficient swelling and stabilizing effects.

11.3.6.2

Glycerol (1,2,3-Propanetriol)

Formula: $\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$

Properties: Viscous, sweet-tasting, hygroscopic, colorless and odorless liquid; m.p. 18.6°C ; b.p. 290°C (decomposition); infinitely miscible with water and lower alcohols, somewhat soluble in diethyl ether, insoluble in gasoline, benzene, chloroform, and fatty oils

Toxicology: The undiluted liquid can cause some skin irritation. Swallowing larger amounts can lead to intoxication with headaches, kidney pain, and bloody diarrhea

Analysis: When heated with potassium hydrogen sulfate acrolein is formed, whose vapors blacken filter paper impregnated with Nessler reagent

Uses with Dry Wood

Historical

1968 Colophony with glycerol as a plasticizer for wood consolidation (Aberle and Koller).

Present Day

Not used for wood stabilization.

Uses with Waterlogged Wood

Historical

About 1900 Storing and soaking objects in glycerol.

ca. 1910 Alum-glycerol combinations for wood consolidation (Brorson Christensen 1970a; cf. aluminum potassium sulfate).

After 1911 Impregnation of a Celtic monumental sculpture with rosin/glycerol (Bill 1979).

1921 Use of glycerol to treat parts of the *Hjortespring* Boat (Brorson Christensen 1970a; cf. aluminum potassium sulfate). Development of the method by Rosenberg.

1924 Rathgen cites the method of Rosenberg.

1952 Waterlogged wood objects up to 50 mm in diameter are treated with glycerol (Madajski).

The staves of a wooden pail are treated using glycerol (Moss; cf. aluminum potassium sulfate).

1956 Plenderleith returns to use of the Rosenberg method.

1958 Stabilization of waterlogged wood finds with a mixture of poly(vinyl alcohol) and glycerol [Rumâncev; cf. poly(vinyl alcohol)].

1962 Lehmann describes various methods for waterlogged wood stabilization including the use of glycerol (cf. paraffin).

1969 Storage of objects in glycerol in dry climatic conditions (Mühlethaler 1969a,b).

Treatment of wood with glycerol and poly(vinyl alcohol) or glycerol and glyptal resins (Tomashevich).

1976 Stabilization of basketry with PEG 600/glycerol in 75% ethanol (Schaffer).

1977 De Jong (1977a) mentions the historic alum/glycerol method.

1981 Šimůnková et al. report on the alum-glycerol method.

1986 Glycerol for pretreatment of waterlogged wood prior to freeze-drying (Schaudy and Slais; cf. ethylene glycol).

1987 Review by Grattan and Clarke including historic waterlogged wood conservation methods using glycerol.

1994 Dewatering charred, waterlogged oak wood by pretreatment with glycerol followed by controlled drying (Caple and Murray).

Present Day

Glycerol is of no importance in waterlogged wood conservation.

Advantages/Disadvantages

For dry wood, glycerol serves merely as a plasticizer for the rosin consolidation of wood.

Waterlogged wood finds pretreated with glycerol and then either freeze dried or dried with thermal control are inferior to those pretreated with PEG because of crack formation and some warping.

11.3.6.3

Poly(ethylene glycol)s [Poly(ethylene oxide)s]

Short designation: PEG

Trade names: Polyglycol, Polywachs (Germany); Carbowax (USA); Modopeg, Modolog antiqua (PEG, boric acid/borax, methylpolysiloxane; Sweden)

Formula:
$$\text{H} \left[\text{O}-\text{CH}_2-\text{CH}_2 \right]_n \text{OH}$$

Properties: Liquid or waxy to solid products which are colorless, white, or yellowish and are hygroscopic.

Most important types of PEG:

Liquid, like glycerol	Like soft wax	Like hard wax
200	1000	2000
300	1500(1450)	4000(3350)
400		6000
600		

Soluble in water, ethanol, benzene, 1,3-dioxolane and other organic solvents; insoluble in gasoline, turpentine, linseed oil, mineral oils

Toxicology: PEG is not considered dangerous to health

Analysis: The concentration of PEG solutions by refractive index or colorimetrically (Anonymous 1981); in wood, qualitatively: by a rapid method according to Hoffmann (1983), using a transfer print method and ammonium cobalt(II) thiocyanate as the reagent; in wood, quantitatively: after extraction from the wood with potassium hexacyanoferrate(II) and back titration of the excess precipitating agent with ammonium cer(IV) sulfate as reagent and

ferroin as indicator (De Jong 1977a); IR spectroscopy (Pang 1981), HPLC (Barka and Hoffmann 1987; Hoffmann 1989)

Uses with Dry Wood

Historical

- 1859 Synthesis of PEG (Grattan and Clarke 1987).
 1939 Production of PEG by Union Carbide, USA (Grattan and Clarke 1987).
 1948/1949 Presumed first use of PEG for wood and wood-based materials (Grattan and Clarke 1987).
 1949 US patent for treating fiberboard with PEG (Ericks and Upson Chemical Co.).
 1952 Swedish patent for improving the dimensional stability of fresh wood with PEG (Mo och Domsjö and Centerwall).
 1956 Stamm publishes his results on using Carbowax together with water-soluble phenol-formaldehyde resins for the dimensional stabilization of wood.
 1959 Further report by Stamm on dimensional stabilization of wood with PEG.
 1969 Schneider describes the time dependence of PEG uptake by beech wood.
 1982 Baumgartner and Lanooy present the "falling acetone series" for the PEG impregnation of already dried bones, teeth, and wood. The objects are first soaked in pure acetone, followed by gradual addition of water. Finally they are treated with PEG at 60°C in a heating chamber.
 1992 PEG 200 is used to treat a warped wood panel (Hopp; cf. ethylene glycol). Niedzielska reattaches paint layers of a wood sculpture with PEG 2000 and poly(vinyl alcohol).
 1998 According to Boucher (1999), warped marquetry wood panels and veneered furniture parts can be straightened using an aqueous solution of PEG 1500 of about 30%. This method makes possible reshaping in furniture conservation, returning the objects to up to 80% of their original shape.
 Triboulot lists the best conditions for reshaping with PEG in furniture conservation, and shows PEG to be compatible with animal glues.

Present Day

Only a few methodical attempts have been made to use PEG treatments for such purposes as dimensional stabilization and straightening of works of art.

Uses with Waterlogged Wood

Historical

- 1950–1956 Morén and Centerwall (1961) and Stamm (1956) recognize the suitability of PEG for waterlogged wood conservation

- 1957/1958 Brorson Christensen (1970a) begins experiments with PEG 4000
 1958 According to Tamer, PEG treatment of waterlogged wood gives satisfactory results.
 1959 Organ successfully places paleolithic waterlogged wood into an aqueous solution of PEG 4000 of 12 and 24% concentration, and heats it slowly to 65°C, allowing the water to evaporate.
 Rosenqvist soaks sample specimens from the *Oseberg* Ship in molten PEG 4000 at 65°C for a few days, but the results are unsatisfactory.
 Organ and also Rosenqvist experience unsatisfactory results from freeze-drying objects without prior treatment with PEG.
 1960/1961 Morén and Centerwall publish the standard method for treating waterlogged wood objects in tanks with aqueous PEG 4000 solution. Temperature and concentration are increased while the water evaporates. The initial concentration is at 10% (w/v) PEG; at 70°C the objects are in molten wax. As a biocide, 1% (w/v) Na-PCP is added. As the PEG solutions age, the pH value decreases and the Na-PCP is precipitated.
 Wooden implements (a club, spades, paddles), for thicknesses up to 40 mm, do not show any changes in shape, color, or size after a PEG 4000 treatment (Schuldt).
 1961 The conservation of the Swedish warship *Wasa* with PEG begins (Birkner et al.).
 Lefèvre undertakes the surface treatment of the staves of a wooden pail (Fig. 11.2) with Carbowax 4000, but the wood collapses.
 1962 Barkman reports on the conservation of the *Wasa*. During the next few years the following typical impregnation technology is developed for movable wood objects: tanks are filled with pure water and the temperature is raised to 60°C. As a fungicide, 2% of a mixture of boric acid and borax (7:3) are added. The PEG 1500 concentration (in the initial stages of conservation, PEG 4000) is adjusted to 15 or 30%. During the first 12 months, the concentration is increased by 1/12% per day, bringing the concentration at the end of this period to 45%. During the next 5 months, the concentration is increased 1/5% per day, leading to a 90% concentration at the end of this period. After the treatment the objects are dried for about 6 months at 65–70% relative humidity. Finally, the surface of the finds is sprayed with a 35% (w/v) PEG solution. The PEG loading of the objects is about 40%. Later, the initial concentration of the PEG solution is reduced to 5% to reduce the danger of cell collapse.
 The hull of the *Wasa* is sprayed intermittently for 5h/day with PEG 1500 in an enclosure maintained at 95% relative humidity.
 In the fall of 1962 conservation begins of the five Viking ships from the Roskilde Fjord (Skuldelev find) in Denmark with PEG 4000 at 60–65°C by Brorson Christensen (1970b). He divides oak wood on the basis of the proportion of its core of sound wood into three categories: I, no or little sound core; II, somewhat more sound core; and III, considerable sound core. PEG 4000 is suitable only for categories I and II. Wood of category III is first almost completely dewatered with tert-

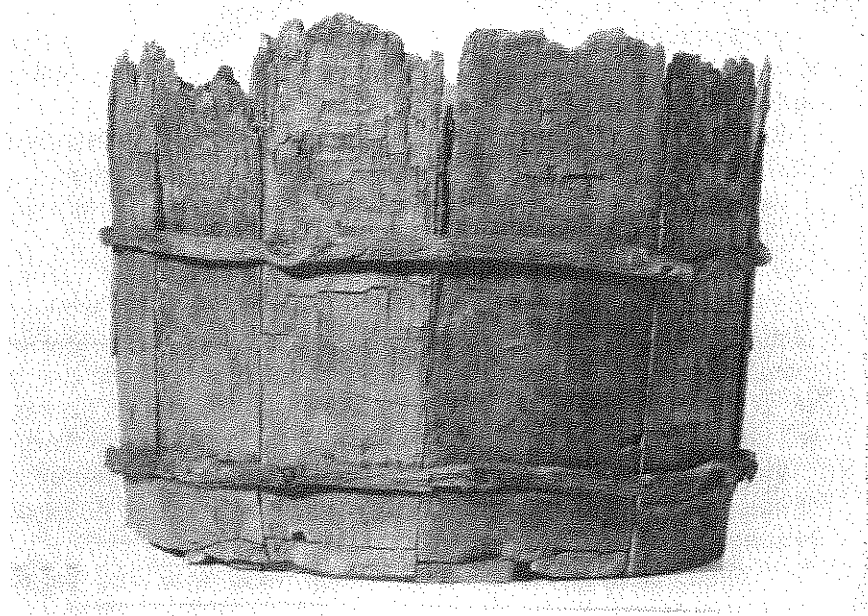


Fig. 11.2. A wooden pail impregnated with PEG 3000. (Photograph courtesy of D. Sommer)

butanol, PEG 4000 is then added and the concentration raised to 60%. This is followed by freeze-drying, during which the tert-butanol is sublimated and the PEG 4000 remains in the wood. Methanol can be used instead of tert-butanol.

Seborg and Inverarity stabilize 200-year-old boats with PEG 1000. Parts of planks are soaked for 4h to 3 weeks in a 50% aqueous solution of PEG 1000 at 20°C. The parts are dried at 35°C and 30% relative humidity. The boats are soaked in the PEG and air-dried for 3 months.

- 1963 Gaudel reports in detail on the polyglycol process and treats a well box made of oak planks. The planks are soaked for 2 months in a tank of galvanized steel with a 30% aqueous solution of PEG 4000, and the solution is then heated to 30°C, later to 65°C. Excess PEG on the wood surface and wax residuals are removed with hot water or 50% ethanol after cooling. The drying is done with IR lamps. The entire treatment takes 5 months.

- 1965 Program-controlled system for spraying the hull of the *Wasa* (Barkman). The system consists of 175 nozzles on both sides of the hull and 96 sprinklers with a total of 192 nozzles inside the hull. Periodically, 4 t each of a 15% PEG 1500 solution (Modolog antiqua) are sprayed, for a total of 128t over a period of 24h.

Noack recommends an impregnation by soaking in 5–10% solutions of PEG 1000 for the *Bremen Cog*. The concentration of PEG should

be raised to 60–70% over a period of ca. 25 years. Because of the hygroscopicity of the PEG, treatment of the wood surface with a 25% solution of toluene diisocyanate in ethyl acetate to form urethanes is recommended.

- 1966 Albright reports on experiments to shorten conservation treatments using PEG 4000.

Lefève and Vynckier stabilize oak samples with a 40% aqueous solution of Carbowax 4000 initially at 21°C. Later the temperature is raised in stages to 50 or 60°C. The treatment takes 56–72 days.

- 1968 Parts of the *Sjøvollen* Ship, Norway, are treated with PEG (Christensen, jr.).

- 1969 Barkman, and also Noack present a detailed overview on the status of the conservation of the *Wasa* and the *Bremen Cog* at a conference in Ludwigsburg, Germany. It is planned to impregnate the latter with PEG in its assembled form in a large tank. To make it possible for visitors to follow the conservation treatment through portholes in the tank, continuous cleaning of the solution is necessary to remove colored extractives and suspended debris. Results obtained with an experimental setup are reported.

When freeze-drying wood writing tablets, crack formation can be prevented by submerging them for 15 min in a 50% solution of PEG 6000 followed by freeze-drying (Iwasaki and Higuchi).

- 1970 Freeze-drying of swamp wood using PEG 400 by Ambrose. The objects are impregnated for 1–6 months in a 10% aqueous solution of PEG 400, frozen with carbon dioxide, and wrapped in perforated aluminum foil. Freeze drying begins at –60°C, and the wood is dry when the temperature reaches 0°C.

Brorson Christensen publishes the standard-setting *The conservation of waterlogged wood in the National Museum of Denmark* (1970a), and an additional report on the extensive experiments of waterlogged wood conservation carried out from 1962–1969 (1970b).

- 1971 Urbon introduces equipment for the impregnation of waterlogged wood with PEG.

- 1972 Contribution by Ambrose on the freeze-drying of waterlogged wood after pretreatment with PEG.

Impregnation of wood artifacts from the *Machault* Shipwreck, in Canada, with Carbowax 4000 (Arthur).

- 1973 Freeze-drying of wood objects using Carbowax 400 by Elmer.

Jenssen and Murdock (1982) treat large oak timbers from the *Machault* Shipwreck by spraying with a PEG 540 blend for nearly 10 years, but the depth of penetration is unsatisfactory.

Waterlogged wood conservation with PEG in Japan (Masuzawa and Nishiyama).

Conservation techniques for small and large objects of waterlogged wood using Polydiol 1000 and 6000 (Mühlethaler).

Freeze-drying of wood with rune inscriptions impregnated with PEG 400 by Rosenqvist.

- 1974 Impregnation of parts of the *Kyrenia* Shipwreck, Cyprus, with PEG (Katzev and Katzev).

Pirling and Buchwald propose impregnating a barge from the Carolingian age with PEG 1000–1500.

A Roman barge is first brushed with a 20% solution of PEG, and then impregnated, by Weidman and Kaenel.

- 1975 Ambrose describes the stabilization of boomerangs with a 7% PEG 400 solution containing an antioxidant and a biocide. The objects are soaked in PEG at 20°C for 6 months. The concentration is then raised to 10% over a period of 3 months followed by freeze-drying. Surface appearance, color, and shape are preserved well.

Report by De Jong (1975a,b) on the conservation of the wood parts of six Roman shipwrecks found at Zwammerdam, Netherlands, and two ships recovered near Utrecht, Netherlands, in cold and warm baths of a 50% solution of PEG 400.

Gerasimova and Nikitina cite formulas for calculating the degree of substitution of water in wood by PEG.

Experiments on the conservation of the *Graveney* Boat, Great Britain, with PEG 4000 by Gregson.

Treatment of waterlogged wood finds with 3–15% solutions of PEG 4000 in a mixture with dichloromethane or 1,2-dichloroethane and tetrachloromethane (Mihailov).

PEG impregnation of oak parts of the *Ferriby* Boat III, Great Britain, by Suthers.

- 1976 Pacific Northwest Conference on the conservation of waterlogged wood. Ambrose (1976, 1977) reports on sublimation drying. Barkman et al. (1976) and Barkman (1977), also Blackshaw (1976, 1977) present overviews on waterlogged wood conservation. Grosso (1976, 1977) recommends PEG as the standard impregnation material. Murdock (1977) presents construction details of a PEG impregnation tank.

Basketry can be preserved by treating with PEG 600 and glycerol, dissolved in 75% ethanol (Schaffer).

Parts of a wooden bowl with portions of stucco painting are impregnated with a 70% solution of Carbowax 1540 at 28°C (Stark).

- 1977 Alagna describes details of the facilities for conservation treatment with PEG of the Punic ship of *Marsala*, Italy.

Detailed and comprehensive contributions on waterlogged wood conservation, including his own investigations, by De Jong (1977a,b).

Freeze-drying of writing tablets after exchange of the water with tert-butanol and impregnation with 20 or 40% solutions of PEG 4000 in tert-butanol (Sawada 1978).

- 1978 ICOM contribution by De Jong on the conservation of oak wood from shipwrecks with varying moisture content. Objects with a moisture content >400% are impregnated with PEG 4000 at 60°C. The concen-

tration of the solution is raised from 0 to 90% in 18 months, and the final concentration maintained for an additional 6 months. Wood with a moisture content of 185–400% is impregnated with PEG 4000 at 30°C. The concentration of the solution should be raised from 10 to 50% over 12 months, maintaining the final concentration for another 12 months. If the moisture content is <185%, the objects are dewatered in tert-butanol at 20°C up to the formation of the tert-butanol-water azeotrope, followed by impregnation of the wood with PEG 4000 dissolved in the azeotrope at 55°C. The concentration of the solution is raised from 0 to 50% in 10 weeks and the final concentration is maintained at 55°C for a further 8 weeks. The tert-butanol is then allowed to evaporate for 2–3 weeks, followed by heating to 60–80°C for 1 or 2 weeks.

Treatment of a Thracian dugout canoe with aqueous solutions of PEG 4000 and 1500 with an addition of glycerol (Mihailov).

Investigation of the reversibility of various impregnation materials after exposure to UV radiation (Schaffer). All PEG types tested maintained their water solubility.

Objects from the *Mombasa* Shipwreck, Kenya, are treated with PEG 4000 (Turner).

- 1979 Comparative exposition of the methods of waterlogged wood conservation by Bräker in cooperation with other authors. Among others, Hug (1979b) describes the Carbowax/freeze-drying method. The well-cleaned and bleached objects are first placed into water at 60°C, then in water at 80°C, and while still warm, the wood is submerged in a 15% aqueous solution of PEG 400 at 50–60°C with 1% boric acid/borax (7:3) added. Soaking is continued for at least 1 month, and the objects are then placed into a freezer chest at –25°C. Freeze-drying is started after 24h at a working pressure of 26.7–160Pa and a condenser temperature of –50°C. Freeze-drying is interrupted after 12h, the wood is allowed to thaw and is then impregnated with 15% PEG 400 solution under vacuum, before being subjected again to freeze-drying. The thawing and freeze-drying cycles are continued until the objects reach constant mass. The wood surface then receives a protective coating of microcrystalline wax.

The water in the staves of a Franconian pail is exchanged with PEG 4000, which is then replaced by alum (Bucsányi).

- 1980 Impregnation of a hurdle with PEG (Bryce).

Objects from excavations in Novgorod, Russia, are first dewatered with acetone and then impregnated with PEG (Bulatov).

Natural freeze-drying of objects in the Canadian winter climate after pretreatment with a 15% solution of PEG 400 (Grattan et al.).

Conservation of three 1600-year-old Balanghais (canoe-like outriggers) with PEG in the Philippines (Peralta).

Japanese patent for PEG treatment of wood in the presence of oxalic acid, which is added to prevent discoloration by wood extractives (Takano).

The use of the PEG-alum method results in an advantageous change in the appearance and the gluability of the wood (Szalay).

- 1981 Freeze-drying of parts of the shipwrecks *Solen* and *W-1*, Poland, after impregnation with 5–15% solutions of PEG 400 (Dyrkova and Jagielska).

Impregnation of a canoe with a 10 and 15% solution of PEG 400 followed by natural freeze-drying in the Canadian winter climate for 66 days (Grattan et al.).

Masuzawa et al. (1982) determine the physical properties and dimensional stability of waterlogged wood impregnated with PEG 4000 or natural or acrylic resins.

Contribution by Murray (1982) on the preparations for the conservation of artifacts from the *Mary Rose*, Great Britain. The hull will be sprayed with PEG.

The Netherlands National Commission for UNESCO publishes conference proceedings on the conservation of large waterlogged wood objects, including a comprehensive bibliography for publications from 1946 to 1979.

Pang treats parts of the shipwreck *Batavia*, Australia, with PEG 1500. The impregnation tanks are filled with wood and water containing a biocide, the water is heated to 60°C, and PEG 1500 is added. The PEG concentration is then raised to 90% over 2–3 years. At 6-month intervals sample cores are removed to determine the content of PEG and water. The surface of the treated objects is brushed with PEG 6000.

Sawada (1981a) attempts to improve the PEG/freeze-drying method by submerging the wood successively into 60°C solutions of 40, 60 and 80% tert-butanol in water, pure tert-butanol, and 20, 40 and 60% PEG 4000 in tert-butanol, the treatment extending over 6 months or more. The PEG concentration in the last impregnation bath is adjusted in accordance with the moisture content of the wood. After removal of excess PEG 4000 the objects are placed into the freeze-drying chamber.

Singley introduces the planned PEG treatment facility for *Brown's Ferry Vessel*, USA. Impregnation with PEG 1450 (1300–1600) and an additional stabilization with PEG 4000 are planned.

Reviews by Šimůnková et al. and Unger et al. (1981b) with reference to PEG.

Young and Wainwright (1982) determine the penetration into the wood cell wall by PEG.

- 1982 The *Mary Rose*, Great Britain, is raised and conservation with PEG begun (Grattan 1984). The main part of the hull is sprayed with a solution of PEG, and the concentration of the solution is slowly raised to 70%. Individual objects are impregnated with PEG, followed by freeze-drying. The conservation of the ship planks will take approximately 15 years.

Grattan (1982a,b) treats waterlogged wood of various species and degrees of deterioration with a series of conservation materials. Among

others he uses PEG 4000 in water, methanol and tert-butanol; PEG 540 in water and PEG 400 in tert-butanol. In regard to appearance and shrinkage, satisfactory results are obtained by pretreatment of the samples with PEG 400 in tert-butanol and freeze-drying, and by PEG 540 in water.

- 1983 Detection of PEG in wood by the formation of colored complex compounds (Hoffmann).

Xu reports on the conservation of waterlogged lacquer objects, using PEG among other materials.

- 1984 De Witte et al. publish the results of the conservation of three Gallo-Roman boats with PEG 4000 at 65°C.

Staves of spruce can be stabilized by 25–30% solutions of PEG 200 and subsequent freeze-drying (Hoffmann).

Laures describes a method for the fast drying of antique wood. Objects are desalted for 1 year and then impregnated with PEG 4000 at a temperature of between 5 and 20°C for 18 months or longer. Drying of the wood is then done in molten PEG 4000 at 120–130°C, until bubbles appear. Excess PEG is removed before the object cools.

Conservation of ship's timbers from the *Batavia*, Australia, with PEG (Reid et al.). The depth of penetration is determined by IR spectroscopy on cores. A proposal is made for gravimetric determination of PEG after extraction of the wood with benzene.

Second meeting of the Waterlogged Wood Working Group in Grenoble, at which Cook et al. (1985) consider the problem of the simultaneous conservation of wood and metal in aqueous solutions. They use poly(propylene glycol) substituted melamine and other commercial amino derivatives because PEG solutions attack metal. Cook and Grattan (1985) report on pretreatments for freeze-drying where, among others, various PEG types and PEG mixtures are used. According to Ginier-Gillet et al. (1985), waterlogged wood can be conserved by preimpregnation with PEG 400 and freeze-drying, and Håfors (1985) reports on her observations of the drying process of the outer planks of the *Wasa* hull. According to Hoffmann (1985), slightly decomposed waterlogged oak wood can be stabilized best with PEG 200, and Hug (1985) recommends wrapping objects impregnated with PEG with damp paper prior to vacuum drying, in order to prevent surface cracks. Jespersen (1985) discusses the problems of prolonged storage of waterlogged wood in its natural environment with reference to large shipwrecks and their conservation with PEG 4000. Nielsen (1985a) explains the conservation of waterlogged wood finds from the excavation of the Viking ship of *Haithabu*, Germany, with PEG 4000 or vacuum freeze-drying. Saeterhaug (1985) states that for pretreatment of waterlogged wood prior to freeze-drying, PEG 4000 is suitable for severely damaged material, while for moderately decomposed wood PEG 400 is suitable. Sawada (1985) commented on morphological changes during freeze-drying of wood impregnated with PEG 4000, and

Seifert and Jagels used PEG 400 and 540 in combination with thermal vacuum drying for the conservation of ship timber. Watson (1985) discussed the problems of absorbed iron salts and the effect of different PEG types and concentrations on the freeze-drying process of severely decomposed hardwoods.

- 1985 Contribution by Nielsen (1985b) on the conservation of the Viking ship and waterlogged wood finds of Haithabu, Germany, with PEG 4000, explaining the construction of the impregnation tank and its use.

Dewatering of a medieval climbing stem from a mine with a PEG solution containing borax and boric acid and subsequent freeze-drying (Schaudy et al.). The freeze-dried object is impregnated with an unsaturated polyester resin (cf. Sect. 11.3.10).

Thunell proposes that wood treated with PEG should be kept at 20°C and 60% relative humidity.

According to Yin, PEG 4000 is better suited than PEG 1000, 6000 and 12000 for the conservation of wood samples of *Cunninghamia lanceolata* and *Pinus massoniana* from old shipwrecks.

- 1986 Hoffmann (1986a,b) discovers that waterlogged oak wood with uneven levels of decomposition cannot be stabilized satisfactorily with a single PEG type. He proposes a two-step impregnation, first with PEG 200 and then with PEG 3000, by which wood of all levels of damage can be stabilized equally well. Optimum amounts of PEG uptake depend on the degree of deterioration of the wood, and are about 50 and 66% of the maximum moisture content of the wood for low relative molecular mass and high relative molecular mass PEG, respectively. Based on good results with this approach, the treatment of the *Bremen Cog*, Germany, is changed to the two-step process.

Jespersen describes the freeze-drying method used at the National Museum of Denmark since 1972. The wood is dewatered with tert-butanol, partially impregnated with PEG 4000, and frozen to -10°C before vacuum freeze-drying is begun. Shipwrecks and bridges are sprayed with aqueous solutions of PEG 400 and PEG 4000.

Further contribution by Laures on fast drying ("frying") after saturating the wood with PEG.

Pretreating neolithic spruce, but also recent spruce, beech, linden, and cherry with tert-butanol, ethylene glycol, 1,4-butanediol, 1,5-pentanediol, glycerol and PEG and subsequently freeze-drying these led to the formation of cracks (Schaudy and Slais), but among the substances tested PEG performed best.

- 1987 Natural freeze-drying of the six Québec boats in winter climate after pretreatment with PEG 400 (Bergeron).

Clark and Gregson describe the PEG impregnation equipment at the National Maritime Museum Greenwich, UK.

Comprehensive report by Grattan and Clarke on the status of waterlogged wood conservation and developments in conservation methods using PEG.

Gilberg et al. (1989) treat wood/iron composite materials with a mixture of PEG 400 and a corrosion inhibitor (Hostacor KS 1).

Mass changes in storage of archaeological wood samples treated with PEG by different laboratories are examined by MacLeod (1989) who concludes that the hygroscopic behavior of the treated wood depends on the relative molecular mass of the PEG impregnated. The relative molecular mass of PEG at which zero mass change would occur can be predicted from linear regression equations.

MacLeod et al. (1989) investigated the effect of concentration and relative molecular mass of aqueous PEG solutions on the extraction of chloride ions associated with iron corrosion products. The optimum PEG concentration is generally in the range of 5–10% (w/v).

Five to 40% solutions of PEG 1000, 1500, 3400 and 4000 in ethanol, sometimes with the addition of 1% Na-PCP, in combination with 1–8% Primal AC 33 in ethanol, effect a better waterlogged wood stabilization than PEG alone (Mihailov and Ivanova).

Review by Ramseyer and Vonlanthen with reference to PEG.

Starling (1987) undertakes a two-stage treatment with PEG and freeze-drying of medieval woods from the harbor of London.

In a further report, Starling (1989) treats wood/metal archaeological artifacts with PEG solutions which contain corrosion inhibitors such as Hostacor KS 1 and Pluracol 824. The conservation of composites of wood, metal and leather is also described.

- 1988 Choi uses PEG 400 for lightly damaged wood and PEG 4000 for the severely decomposed woods of the *Shinan* Shipwreck, South Korea.

Review of waterlogged wood conservation methods and comparison of their advantages and disadvantages by Grattan, who also presents an equation to calculate PEG uptake by wood.

Hoffmann (1988a) investigates the effectiveness of oligomers in waterlogged wood conservation (cf. ethylene glycol).

Hoffmann (1988b,c) treats deformed bowls and goblets with, among others, boiling PEG 200 or tert-butanol and PEG to obtain correction of their shapes. Boxes with shrinkage damage are impregnated with 10 and 20% solutions of PEG 200 and PEG 400 at 60°C followed by freeze-drying, but the obtained swelling was not permanent.

Imazu attempts to overcome the disadvantages of PEG conservation – long duration and complex procedures – by a combined treatment with mannitol and PEG 4000 followed by freeze-drying.

Kawagoe and Ishigaki use a diffusion model to make theoretical predictions for the impregnation of waterlogged wood with PEG.

Ramière removes iron salts with oxalic acid or Na-EDTA and bleaches the waterlogged wood with H₂O₂ and ammonia prior to impregnation with a 10–20% solution of PEG 400 with boron salts or quaternary ammonium compounds added, followed by lyophilization.

Riens investigates the effect of concentration of solutions of PEG 200, 400, 2000 and 4000 after impregnation of the wood on subsequent freeze-drying. Low concentrations bring about better stabilization than high ones.

Schaudy and Knoll also test the influence of the concentration of the PEG pretreatment solution on stabilization of the wood when followed by freeze-drying. They did not observe any effect of pretreatment on deformation and crack formation.

- 1989 Conservation of parts of a 6000-year-old walkway with PEG over a period of 9 months (Coles).

Jensen et al. undertake a new conservation treatment of the *Hjortespring* Boat, Denmark. The alum is leached out with hot water and the wood is then impregnated with PEG.

According to Nishiura and Imazu, dimensional changes of waterlogged wood exposed to short-term cyclic moisture changes (60–90–60–35% relative humidity, 12h per cycle) are reduced after impregnation of the wood with PEG 4000, tert-butanol and PEG 4000 (plus freeze-drying), mannitol (plus freeze-drying) or mannitol and PEG 4000 (plus freeze-drying).

Preißler describes the conservation of waterlogged wood finds with PEG or a PEG and ethanol process, where deformed objects must be shaped and fragile parts must be mounted on a wood core prior to consolidation.

- 1990 Ambrose presents a comprehensive report on vacuum freeze-drying of small objects after pretreatment with low relative molecular mass PEG types and on the natural freeze-drying of larger objects in the Antarctic climate.

Baron and Wright impregnate fragments of basketry with PEG and freeze-dry them.

PEGCON, a computer program developed at the Canadian Conservation Institute, can be used as a guide for selecting the grade and concentration of PEG to be used on wood (Cook and Grattan 1991).

Håfors summarizes the conservation of the *Wasa* and the development of the PEG method with special reference to PEG uptake and distribution in the wood.

Hoffmann (1990a) stabilizes a medieval ship from the river Rhine by the two-step process with PEG 200 and PEG 3000, where it is necessary to insert a partial extraction before the second step in order to improve the surface hardness of the wood. An additional report (Hoffmann 1990b) deals with PEG stabilization of softwoods from China and Korea.

Imazu and Nishiura report on their combined mannitol and PEG pretreatment when freeze-drying objects.

In connection with the conservation of the wood from the *Batavia* Shipwreck, Australia, with PEG 1500, MacLeod refers to degradation of wood by iron corrosion products such as pyrite.

Nishiura and Imazu note that under moist conditions PEG runs out of impregnated wood even though the wood swells, and that under dry conditions the wood containing PEG shrinks severely.

Padfield et al. melt off excess PEG after treatment and observe the formation of three different phases. Whereas dry PEG is decomposed oxidatively at 75°C within 4h, water imparts protection against that.

In a detailed contribution on the gluing of archaeological wood Rice also discusses the gluing of wood treated with PEG.

Richards describes the deacidification of the ship timbers of the *Batavia*, Australia, which contain iron salts by gaseous ammonia, and discusses the search for corrosion inhibitors.

Sawada reviews waterlogged wood conservation with reference to the PEG/freeze-drying method.

By soaking waterlogged wood to be conserved in a 5% solution of laurylamine acetate (a cationic surfactant) followed by PEG 4000 impregnation at 60°C, Ueda et al. achieve a much more rapid stabilization than with the customary PEG method.

Verdu et al. describe the aging of PEG 3400 when exposed to gamma radiation.

- 1991 Grattan treats remains of a fossil forest, which were not petrified, with PEG 200 and follows this with freeze-drying.

Investigations by Hoffmann et al. show that the two-step PEG process is not suitable for the Chinese softwoods from the *Shinan* Ship, South Korea. However, PEG 400 and PEG 4000 appear to be well suited.

- 1992 Lu Heng and Zheng Youming state that large building timbers can be stabilized after pretreatment with PEG 1000 by natural freeze-drying during one winter season.

- 1993 Astrup (1994) treats remains of softwoods of a medieval log house with an aqueous solution of 50–55% PEG.

Bilz et al. (1994a) investigate the aging of PEG 400 and PEG 3350 as a function of high temperature, exclusion of air, PEG concentration, and the presence of iron salts, wood blocks, and antioxidants. PEG extracted from wood treated 10 years earlier did not show any decrease of relative molecular mass, indicating that there had been no degradation.

A sample of an oak stockade post from Biskupin, Poland, is treated by Bilz et al. (1994b) experimentally by PEG/freeze-drying, the two-step process of Hoffmann, and by sucrose impregnation, where the first method was the most effective and the last one the least.

According to Brown et al. (1994) Great Britain had 15 facilities in 1989 and 25 in 1993 for freeze-drying of waterlogged wood objects, including those equipped for PEG pretreatment.

Cooke et al. (1994) extract waterlogged wood previously stabilized with PEG 540 and undertake a new conservation treatment with PEG 200 and PEG 3350 followed by freeze-drying. The appearance of the wood is thereby clearly improved and its hygroscopicity is decreased.

Dean et al. (1994) use BREOX 50W poly(alkylene glycol)s (PAG) 200 and 600 because of their lower hygroscopicity and low biodegradability, as well as because of their good stabilizing effects compared with PEG 600, for slightly degraded oak and in combination with PEG 4000 (two-step treatment) for oak of all states of degradation.

Håfors (1994) reports on improvements in the treatment of waterlogged wood by the tank immersion process.

Further contribution by Hoffmann on the restoring of turned objects with deformations by waterlogging again and reshaping followed by stabilization with PEG.

Kaenel (1994) also uses PEG 4000 for the conservation of a 10-m-long Gallo-Roman barge.

A shura, a wooden sledge for transporting large rocks, is conserved by Masuzawa et al. by impregnation with PEG without formation of cracks and splits.

Morgós (1993a) mentions the use of PEG for waterlogged wood conservation in Hungary.

Investigation of corrosion inhibitors for PEG conservation with freeze-drying of wood/metal composites by Selwyn, who found that aqueous organic amines are the most suitable.

Watson conserves the Dover Bronze-Age Boat, Great Britain, with PEG and freeze-drying.

- 1994 Caple and Murray treat charred oak wood by dewatering followed by treatment with the PEG 400/freezing-drying method, and also use controlled drying after pretreatment with PEG 400, glycol or PEG 4000.

Paleolithic wood artifacts are stabilized by Jover with PEG 4000.

Investigation of bacterial and fungal attack on PEG 400 solutions during the conservation of a dugout canoe of camphor wood, and the use of isothiazolones as biocides (cf. Chap. 7) by Kigawa.

Ueda and Inoue report on the effect of concentration, temperature and treatment duration during PEG 4000 impregnation of waterlogged wood and recommend alternative methods.

- 1995 Hoffmann describes the use of sugar instead of PEG 200 for the conservation of a medieval shipwreck. The PEG already in the wood is washed out, and residual PEG does not hinder the sugar crystallization.

Jiang discusses simple possibilities for improving PEG impregnation.

Reviews by Kaye and by Schaudy of waterlogged wood conservation with reference to PEG methods.

- 1996 WOAM Conference in York, UK. Bilz and Grattan (1997) report on butylated hydroxy anisole (BHA) as an antioxidant for PEG. Review by Glas-trup (1997) on oxygen as the cause of PEG degradation. Consolidation of cedar basketry and cordage after PEG treatment followed by vacuum freeze-drying with Parylene (Grant et al. 1997). Parylene is a cyclic dimer of p-xylylene and forms an irreversible polymer film on the surface of the substrate after polymerization. Hoffmann (1997a) dis-

cusses new results on the conservation of the *Bremen Cog*. Comparison of the effectiveness of treating waterlogged wood with sugar alcohols, sucrose, or PEG 4000 (Imazu and Morgós 1997). Meyer (1997) reports on the impregnation and freeze-drying of a 3550-year-old Swiss dugout boat at the National Museum of Denmark. Two papers on freeze-drying highly degraded waterlogged wood and on progress in the conservation of the Bronze Age Boat from Dover by Watson (1997a,b).

Grattan et al. conserve the remains of a fossil forest by the PEG/freezing-drying method, among others.

Description of the customary PEG methods for shipwrecks – impregnation with high relative molecular mass PEG, pretreatment with low relative molecular mass PEG followed by freeze-drying – and impregnation with sugar solutions by Hoffmann (1996a).

- 1997 Hoffmann (1997b) publishes a progress report on the status of the conservation of the *Bremen Cog*, Germany, with the two-step process he developed. The second stage with PEG 3000, begun in 1995, is scheduled to be completed 1998/1999.

Hoffmann, together with Blanchette, reports on the impregnation of a fossil log with a 25% solution of PEG 300.

- 1998 WOAM Conference in Grenoble, France. Trials to recover all or part of the initial volume of collapsed objects by using the mechanical swelling produced by impregnation and rapid decompression of supercritical carbon dioxide fluid and PEG solutions (Chaumat et al. 1999). Ancient boats were treated with PEG by Cohen (1999) and Lan (1999). Pretreatment with aqueous PEG solutions followed by vacuum freeze-drying is the most suitable method of conserving waterlogged *urushi* objects and lacquered wooden sculptures (Masuzawa et al. 1999; O'Guinness Carlson et al. 1999). Pournou et al. (1999) test poly(alkylene glycol)s (PAGs) for treating waterlogged wood prior to freeze-drying. Tran et al. (1999) describe the reshaping of a Carolingian boat by pressure after impregnation. Use of a copper-silver electrode system for the sterilization of waterlogged wood in PEG solution by Vere-Stevens et al. (1999). The 1000ppm concentration at a Cu:Ag ratio of 7:3 has the best biocidal effect.

Experiments to improve and accelerate the PEG impregnation of waterlogged wood using supercritical carbon dioxide as the solvent (Coeuré et al.).

- 1999 Stabilization of dugout canoes with the two-step PEG treatment (Babiński) and the PEG/freezing-drying method (Barthez et al. 1999b).

Reshaping PEG-impregnated timbers of a medieval river craft by local reheating (Hoffmann).

- 2000 Official presentation of the *Bremen Cog*, its conservation treatment completed, on May 17/18.

Present Day

The stabilization of smaller objects with moderate deterioration by pretreatment with low relative molecular mass PEG followed by freeze-drying, the impregnation of larger waterlogged wood finds such as shipwrecks with an uneven degree of deterioration by the two-step PEG process, and the consolidation of severely deteriorated artifacts with high relative molecular mass PEG in impregnation tanks are, as ever, the standard methods which have not lost any of their importance to the alternative sucrose impregnation. Existing PEG procedures can probably be optimized further, at least for smaller objects, by combining PEG with various water-soluble substances such as other poly(alkylene glycol)s and sugar alcohols, or by improvements in process conditions such as the use of supercritical carbon dioxide for dewatering and as a PEG solvent.

Advantages/Disadvantages

For dry wood, the straightening of warped wood panels with low relative molecular mass PEG types has not been investigated sufficiently, and it harbors the danger that the panels will continually shrink and swell because of the hygroscopicity of the PEG, and that the hoped-for permanent stabilization cannot be guaranteed. The PEG may also be exuded from the wood when the temperature of the surroundings becomes elevated. The low relative molecular mass PEG has to be adsorbed into the cell wall in order to maintain the wood in a permanently swollen condition.

For waterlogged wood, a direct exchange of water for the reversible PEG is possible. Present knowledge indicates that PEG has fairly long-term stability. Necessary PEG types and technologies for stabilizing waterlogged wood of differing degrees of deterioration are available (Fig. 11.3). Even with large objects such as shipwrecks, good to very good dimensional stabilization can be obtained. The heating of the impregnation tanks over months and years entails high energy costs.

PEG treatments darken the wood somewhat, but this occurs with other conservation materials as well. Color and surface condition of the wood can vary from dark brown to gray and dry to black and wax-like.

The strength of the stabilized wood depends on the original condition of the waterlogged wood, the types of PEG used, and the penetration. In general, it will be sufficient to reassemble the original object from its parts or to allow objects maintained in their entirety to support themselves.

In order to make certain that the required penetration can be achieved, the initial concentration of the PEG impregnation tank or spray solution must be low, and the concentration can be raised only slowly. Sometimes the process has to be done in two steps with different PEG types, so that PEG treatments, especially of large objects, are very time consuming.

The PEG solutions used for treatments are susceptible to biological deterioration at room temperature and will be colonized by algae and bacteria. Bio-



Fig. 11.3. A Slavic cult figure stabilized with PEG 1500 and 3000. (Photograph courtesy of S. Brather)

cides must therefore be added to the solutions, which makes their disposal more difficult.

Aqueous PEG solutions can be corrosive to metals such as iron, lead, copper, brass, and aluminum, so that impregnation tanks should preferably be constructed of stainless steel. In order to avoid oxidation processes it is advisable to add antioxidants to aqueous treatment solutions. Because of the corrosive effects of PEG, corrosion inhibitors should be added to the solutions when treating wood/iron composites. Iron compounds that are already present, such as iron sulfides, hinder the conservation process, and it is advisable to remove them first with dilute hydrochloric acid, Na-EDTA, thioglycolic acid with or without added ammonia, or oxalic acid. The latter is also used to bleach PEG solutions that have been made cloudy by wood extractives.

Wood treated with PEG is difficult to glue; PEG should therefore be removed from the surface layers of parts to be glued. Larger parts can be glued

with PVA emulsions (white wood-working glue), isocyanates, epoxy and acrylic resins. Smaller pieces can be joined with high relative molecular mass PEG or with mixtures of beeswax and dammar.

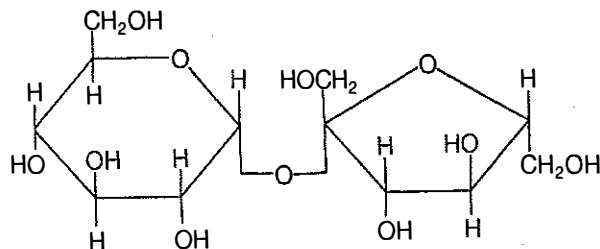
After leaching PEG from a treated object it is possible to make dendrochronological investigations, but ^{14}C dating is no longer possible once the wood has been treated with PEG.

11.3.6.4

Sucrose

Trade names: Cane sugar, beet sugar

Formula:



Properties: White, sweet-tasting crystals; m.p. 185–188°C; readily soluble in water, difficult to dissolve in ethanol, insoluble in diethyl ether; maximum solubility at 25°C and in boiling water is 66 and 83%, respectively.

Analysis: DC, IR spectroscopy

Uses with Dry Wood

Historical

- 1904 Powell receives a patent for treating wood with sugar to protect it from fungi and insects. The wood shrinks less.
- 1937 Research by Stamm on the dimensional stabilization of wood with sucrose and invert sugar, a mixture of equal parts of glucose and fructose, of which the latter is more effective.
- 1951 Tiemann uses a 42% (w/v) solution of cane sugar for the dimensional stabilization of wood.
- 1955 Kollmann cites results of the impregnation of wood with 9–30% solutions of sucrose and with molasses.
- 1960 Reports on the dimensional stabilization of wood with 40–50% solutions of invert sugar, and with mixtures of invert sugar and urea, or of invert sugar, sodium chloride and urea (Seifert).
- 1975 Chemically modified sugar, in the form of an aqueous resin solution is used to impregnate wood after addition of a catalyst. The resin is cured by heating and becomes water-insoluble and can no longer be extracted. The treated wood can be painted (Anonymous).

Present Day

No known uses.

Uses with Waterlogged Wood

Historical

- 1965 Noack mentions sugar as a possible conservation material for the *Bremen Cog*, Germany
- 1969 Mühlethaler (1969a,b) refers to sugar as a consolidant for waterlogged wood.
- 1970–1972 Franguelli and Loda (1970), also Franguelli (1971–1972) investigate conservation of waterlogged wood with sucrose in Italy.
- 1973 Waterlogged wood is first dipped into a sugar solution, followed by exchange with phenol alcohol (cf. phenol-formaldehyde resins, Sect. 11.3.8.1) which is fixed in the wood by heat. Reportedly no deformations occurred in the treated object (Kolčín).
- 1974 Smaller waterlogged wood objects are boiled for some time in a sugar solution and then dried (Vichrov et al.).
- 1976 Report on conservation with sugar by Håfors.
- 1976/1977 Report on experiments of sugar impregnation of oak wood samples by Barkman et al. (1976) and Barkman (1977). At a sucrose concentration of 43% an anti-shrink efficiency (ASE) of 85% can be obtained.
- 1977 Comments on the use of sugar to stabilize waterlogged wood by McCawley.
- 1981 Grosso impregnates many wood samples for 136 days with a 40% solution of sucrose. He also tests a series of biocides for keeping the sucrose solutions free of microorganisms. He is of the opinion that sucrose impregnation is suitable for conservation under field conditions.
- 1983 Investigations of the use of sucrose as a stabilizing material and for treating waterlogged wood prior to freeze-drying by Parrent (1983a,b).
Waterlogged wood conservation in Jamaica in a container with sugar solution which is warmed by the sun (Anonymous 1983a).
- 1984 Cook and Grattan (1985) determine that cane sugar and sorbitol bring the best results when treating waterlogged wood prior to freeze-drying.
According to Kazanskaya and Nikitina (1985), waterlogged wood can be consolidated by repeated treatment with a cold 50% phenol alcohol solution and a hot 50% aqueous solution of sugar with lactic acid added. The objects are stored at 14–25°C and 50–55% relative humidity.
- 1985 Detailed description of sucrose impregnation of archaeological wood and of recent wood treated with alkali by Parrent. According to his data, on average, 87% ASE can be obtained.
- 1987 Details on sucrose conservation by De la Baume.

Summary and evaluation of results to date on sucrose impregnation by Grattan and Clarke, and by Morgós et al. The latter propose the conservation of waterlogged wood with cold sucrose solutions.

- 1988 Use of X-ray computer tomography and nuclear magnetic resonance tomography to evaluate penetration of sucrose in impregnated waterlogged wood (Unger et al.; cf. Chap. 6).
- 1990 Dunkow and Preuss determine the ASE of small and large waterlogged wood samples and cite a cyclic treatment of boiling for 3 h and soaking for 24 h in a sugar solution at temperatures between 30 and 90°C for optimization of the process.

Fourth ICOM Group on Wet Organic Archaeological Materials Conference in Bremerhaven, Germany. Hoffmann (1991) presents detailed research results on ASE and penetration of waterlogged wood treated with sucrose. Kazanskaya and Nikitina (1991) report on improvements in the method of Minsk. Nishiura and Imazu (1991) deal with dimensional changes of wood impregnated with sucrose under changing air relative humidity. Wróblewska et al. (1991) compare the sugar method with other methods of waterlogged wood conservation.

Further contribution on conservation with cold sugar solutions by Morgós and Glattfelder-McQuirk.

Sanchez Ledesma et al. investigate the susceptibility to microorganisms of wood impregnated with cane sugar.

- 1991 Conference on the conservation of archaeological waterlogged wood with sugar in Stade, Germany. Presentations were made on the following topics:

Continuous determination of concentration of a sugar solution (Arhelger and Hilbrich 1992).

Waterlogged wood conservation with beet sugar (Becker et al. 1992).

Experiences with sugar conservation (Cott 1992).

Conservation of a dugout canoe (Ficke 1992).

Penetration of sugar into water saturated woods (Hoffmann 1992).

Variations in the use of sugar in the Minsk method (Kazanskaya 1992).

Conservation of water-saturated wood boxes with sugar solutions (Koesling 1992a).

Experiences with the stabilization of waterlogged wood in Hungary (Morgós 1992).

Noninvasive testing of waterlogged wood with X-ray computer tomography and nuclear magnetic resonance tomography (Morgós and Unger 1992).

Suitability of sugar for the conservation of waterlogged wood (Preuss 1992).

Sucrose/acetone method, use of other sugars, and conservation of the sugar solution (Strigazzi 1992).

Determination of sugar distribution in impregnated waterlogged wood (Weidner 1992).

Conservation of waterlogged wood from the excavation at Pultusk by various methods (Wieczorek 1992).

Cott and Unger document the penetration of sugar solutions into a wooden idol using X-ray computer tomography and nuclear magnetic resonance tomography.

- 1992 Using hot sugar solutions, Koesling (1992b) obtains an ASE of 80–96%.

- 1993 Fifth ICOM Group on Wet Organic Archaeological Materials Conference in Portland, Maine. The following presentations are concerned with sugar conservation:

Comparison of test results of sugar stabilization with the PEG/freeze-drying method and the two-step method with archaeological wood from Biskupin, Poland (Bilz et al. 1994b).

Investigation of the stabilizing effect of sugar as a function of the degree of deterioration of the waterlogged wood (Hoffmann 1994).

Results of a Europe-wide comparative laboratory study on the suitability of sucrose for waterlogged wood (Hoffmann et al. 1994).

Bibliography of sugar conservation (Morgós 1994).

Comparison of conservation methods using sucrose, mannitol, and their mixtures (Morgós and Imazu 1994).

Biocides in sugar conservation (Morgós et al. 1994; cf. Sect. 7.3.13).

Tests of the termite resistance of waterlogged wood impregnated with sucrose (Noldt 1994).

SEM studies on sugar impregnation of waterlogged wood (Schmitt and Noldt 1994).

Koesling (1993b) stabilizes ash pulley blocks from barges with cold sugar solution (initial concentration 5%, final concentration 61%). Shrinkage ranges from 0.2 to 5%.

Contribution by Morgós (1993 a) on the history of waterlogged wood conservation in Hungary, including reference to the sugar method.

According to Morgós and Imazu, ASE values of over 90% can be obtained in moderately to severely deteriorated waterlogged wood by using a sucrose/mannitol mixture at a temperature of 80°C.

- 1994 Chen Jinliang and Cui Zhanhua impregnate painted wooden vessels with a moisture content of up to 1562% with a sugar solution, where attack of the solution by microorganisms created serious problems.

Conservation of parts of ship's planking with hot sugar solutions followed by controlled air drying (Koesling).

Weber and Rosenthaler use cold sucrose solutions for the stabilization of archaeological waterlogged wood finds.

- 1995 Beck's Ship, Germany, is treated by Hoffmann at first with PEG 200, but the PEG is then washed out again and the object treated with a cold

sugar solution, increasing from 30 to 74% concentration. Isothiazolones are added as biocides (cf. Chap. 7).

Schaudy mentions the sugar method.

Contrary to Noldt (1994), Unger and Unger (1995a) find that wood impregnated with sugar is attacked by termites. It will also be attacked more severely by soft rot than by brown rot fungi.

- 1996 Three reports by Hoffmann (1996a,b,c) with an evaluation of results to date with stabilization of waterlogged wood with sugar compared with the various PEG methods.

A dugout boat which had been treated with PEG and then stored in water for 7 years was immersed in a (stock) 65% solution of sucrose (Hutchings 1997).

Imazu and Morgós (1997) compare the effectiveness of sucrose, lactitol and PEG stabilization of waterlogged wood.

CT studies of sugar-impregnated waterlogged wood by Potthast.

Schiweck reports on the process-related characteristics of sucrose and its solutions and recommends improvements for the conservation of waterlogged wood.

Experiments on the use of nonionic surfactants to improve and accelerate waterlogged wood conservation with sucrose (Strigazzi and Koberstein 1997).

Weber and Rosenthaler test various biocides to prevent attack of sugar solutions by microorganisms.

- 1997 Strigazzi describes the conservation of a dugout canoe.

- 1998 Hoffmann and Kühn (1999) treat the 12-m *Friesland Ship* with sucrose.

Mietke and Martin (1999) isolate two kinds of xerophytic molds and one osmotolerant yeast as biochemically active microorganisms in a saturated sugar solution, making repeated addition of 0.1% Kathon WTE necessary.

Further contribution by Strigazzi on the suitability of various surfactants and syrup types for the stabilization of waterlogged wood.

- 1999 Comprehensive report by Morgós (1999b) on the conservation of archaeological wood finds with sucrose and lactitol.

Present Day

Sucrose conservation is of increasing importance to wood artifacts whose exemplary preservation does not seem to be absolutely necessary from a historical perspective, where PEG treatment would be too time-consuming and expensive.

Advantages/Disadvantages

For dry wood, as a strengthening treatment for art objects and cultural property, sucrose should be rejected because of the high swelling capacity of the

aqueous sucrose solutions and the changed hygroscopic behavior of treated objects.

For waterlogged wood, evaluation from a conservation point of view shows that good ASE can be obtained, especially with wood having low levels of deterioration. With respect to stability of shape, the more severely decomposed woods in particular can undergo large changes, such as concave sunken faces and a washboard-like structure due to density differences between earlywood and latewood. PEG/freeze-drying or PEG impregnation methods therefore would seem to be safer for valuable objects. Nevertheless, the sucrose method offers an alternative, especially for objects of large dimensions. The strengthening effect of sucrose impregnation is sufficient for safe handling of the objects.

The treated wood has a largely natural appearance and is not very hygroscopic at low air humidity (Fig. 11.4). The surface of sucrose-impregnated wood becomes wet at high relative humidity (above 85%) and stays wet for a long time. Sucrose solutions are not corrosive, so that impregnation tanks do not have to be constructed of special materials, nor are there problems when treating wood/metal composites. Owing to the reversibility of the sucrose,

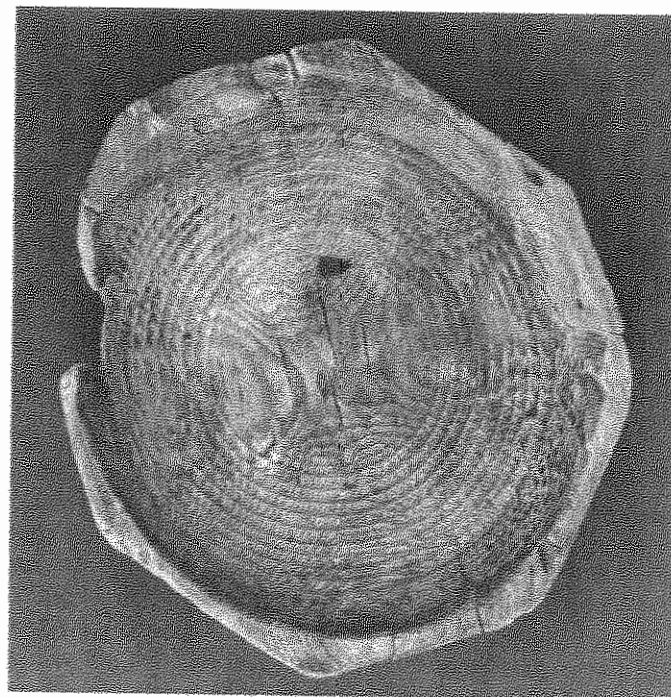


Fig. 11.4 A wooden bowl impregnated with sucrose. (Photograph courtesy of D. Sommer)

wood surfaces can be cleaned easily after impregnation. Wood containing sucrose can be worked and glued according to traditional methods, and does not represent any health dangers. The conservation treatment is relatively simple and can be applied under field conditions.

A disadvantage is the time required for treatment, as it is for PEG conservation. Biocides must therefore be added to the sucrose solutions to avoid attack by microorganisms, but odor problems can still arise and disposal of the solution becomes more difficult. Results to date on termite resistance of treated wood is contradictory (Noldt 1994; Unger and Unger 1995a; Imazu and Morgós 1997), but appear to suggest a biological susceptibility. Treated wood is, for instance, also attacked by brown-rot and soft-rot fungi. Very little is known to date of the long-term behavior of objects treated with sucrose.

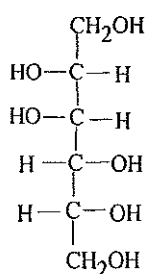
Evaluation from an economic point of view:

Sucrose is inexpensive and readily available, and complicated equipment is not required for treating objects. Sucrose can be dissolved without application of energy, nor is any required for conservation with cold sugar solutions. The solutions can be stored, and their disposal presents fewer problems than PEG. Trained personnel are necessary to supervise the process, especially in regard to undesired fermentation processes. Exchanging water and sucrose at elevated temperatures requires expenditures of energy. When large objects are impregnated with sucrose, increased demands must be expected on climate control and exhibition technology.

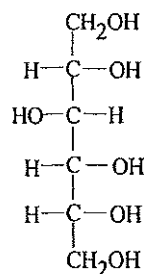
11.3.6.5

Sugar Alcohols

Formulas:



D-Mannitol



D-Sorbitol (D-Glucitol)

Properties: D-mannitol consists of colorless, sweet-tasting crystals which are not hygroscopic; m.p. 166–168 °C; soluble in water to 11.5% at 14 °C and to 41% at 70 °C. D-sorbitol consists of colorless, moderately hygroscopic needle crystals with a sweet taste; m.p. 110–112 °C when water-free; very soluble in water (83% at 25 °C), not very soluble in cold ethanol, soluble in pyridine, methanol, acetic acid, and phenol

Toxicology: D-mannitol, as well as D-sorbitol act as laxatives in larger quantities

Analysis: Alkaline copper(II) citrate solutions to determine reducing sugars; DC

Other sugar alcohols: pentaerythritol, xylitol, maltitol, and lactitol (an artificial disaccharide consisting of a glucose and a galactose unit).

Uses with Dry Wood

Historical

1936–1939 Bateson (1936, 1938, 1939) investigates dimensional stabilization of oak and beech samples with sorbitol and obtains an ASE of 80% for oak.

Present Day

No known uses.

Uses with Waterlogged Wood

1982 Barbour, also Murray (Grattan 1984) investigates the suitability of mannitol and sorbitol for waterlogged wood conservation.

1984 Sorbitol can be used for pretreatment of waterlogged wood prior to freeze-drying (Cook and Grattan 1985; cf. sucrose).

Grattan investigates dimensional stabilization with mannitol and sorbitol.

1985 Use of mannitol for pretreatment prior to freeze-drying by Murray.

1987 Grattan and Clarke review the literature to date on waterlogged wood conservation with sugar alcohols.

1988 Two-stage impregnation with mannitol and PEG as pretreatment prior to freeze-drying (Imazu). The required dimensional stability is obtained in a short time and in a simple manner.

1989 Measurements of dimensional changes of small waterlogged wood samples which had been treated with mannitol or a mannitol/PEG 4000 mixture (Nishiura and Imazu 1989 and 1991).

1990 Further contribution on mannitol/PEG pretreatment followed by freeze-drying of waterlogged wood (Imazu and Nishiura).

1993 Combined mannitol/sugar pretreatment at 80 °C of various Japanese wood species with minor to severe degrees of deterioration prior to freeze-drying by Morgós and Imazu (1993, 1994). The ASE is more than 90% and, in contrast to the two-step PEG method, woods of all levels of decomposition can be stabilized in one step.

1996 Imazu and Morgós (1997) discover that waterlogged wood samples treated with lactitol at 70 °C have a higher ASE (more than 99%) and greater resistance to termites and ants than sucrose. The final concen-

tration of the lactitol solutions must be 50–70% for softwoods and 80–90% for hardwoods. A small amount of lactitol monohydrate crystals must be dusted on the surface of the impregnated samples prior to air-drying, in order to generate the crystallization of the lactitol in the wood.

1998 Treatment of a 6-m-long waterlogged timber coffin with lactitol (Imazu and Morgós 1999a).

1999 Further lactitol conservation of a dugout pipeline (Imazu and Morgós 1999b).

Present Day

Sugar alcohols are being used for waterlogged wood stabilization only for a limited number of archaeological finds.

Advantages/Disadvantages

For dry and waterlogged wood, whereas treatment of waterlogged wood with mannitol alone results in insufficient stabilization and white deposits on the wood surface, these negative effects can be avoided by stepwise impregnation with mannitol and sucrose for woods with unequal degrees of decomposition. The heat resistant, readily soluble, slightly hygroscopic and microbiologically stable lactitol results in a natural color, high ASE and extensive termite and ant resistance of the waterlogged wood.

However, process execution and duration using sugar alcohols are not reduced significantly compared with sucrose and PEG treatment, and prices for the materials generally are above those for sucrose. As for sucrose, highly effective biocides have to be added to the solutions of sugar alcohols, which makes their disposal difficult.

11.3.7

Cellulose Derivatives

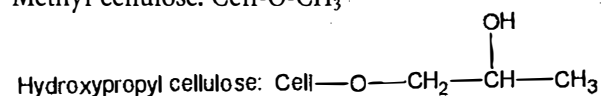
11.3.7.1

Cellulose Ethers: Methyl Cellulose, Hydroxypropyl Cellulose

Short designation: MC (methyl cellulose), HPC (hydroxypropyl cellulose)

Trade names: Methyl cellulose: Tylose, Glutolin, Methocel
Hydroxypropyl cellulose: Klucel

Formula (simplified): Methyl cellulose: Cell-O-CH₃



Properties: Methyl cellulose: white powder or granules; depending on degree of molecular substitution (MS) soluble in aqueous alkali (MS 0.7–1.4), cold water and aqueous organic solvents such as ethanol (MS 1.4–2.3) or organic solvents (MS 2.3–3); hydroxypropyl cellulose: yellowish white powder (MS 4–4.5); soluble in water and many organic solvents

Toxicology: Cellulose ethers are physiologically inert and do not irritate skin

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

1912 The Bayer company, Germany, applies for patents for the production of cellulose ethers (Koesling 1993a).

1936 Conservation of a carved altar with a resin emulsion consisting of MC, Alkydal and colophony (Aberle and Koller 1968).

Since 1945 MC in ethanol as adhesive.

1969 The Hercules Company begins production of HPC (Koesling 1993a).

1978 Schaffer tests various cellulose ethers in regard to their reversibility after exposure to UV radiation, and finds that after exposure of impregnated wood the ethers remain water-soluble.

1984 Schiessl discusses the use of cellulose ethers for wood consolidation.

1990 Comprehensive discussion of the use of cellulose ethers in the conservation of cultural property by Feller.

According to Hansen et al., who divide consolidants with respect to stability of their significant properties into Class A (>100 years) Class B (20–100 years) and Class C (<20 years), cellulose ethers fall into Class C.

1995 Johnson et al. use a 3% (w/v) solution of Klucel G in industrial methylated spirits (IMS) to consolidate the weakened wood surface of an ancient Egyptian polychrome coffin. IMS also serves to prewet the wood surface.

1996 Klucel E is attacked by various bacteria, fungi, and yeasts and its biological resistance is lower than that of Paraloid B72 and Primal AC 33 (Heyn et al.).

Egg larvae of the house longhorn beetle bore through layers of Klucel E and destroy the wood underneath (Unger et al.).

1997 Döll discusses gluing of wood using MC (cf. Chap. 12).

Present Day

Almost no use of cellulose ethers as wood consolidants.

Uses with Waterlogged Wood

Historical

- 1961 Conservation of a wood coffin with aqueous MC solution (Schlabow).
- 1963 Van der Heide reports (Noack 1965) that spraying or brushing objects with 10% aqueous MC solution is not successful with severely decomposed wood.
- 1969 Impregnation of waterlogged wood with MC does not lead to satisfactory results (Ankner 1969a).
- 1994 Caple and Murray use a 5% aqueous Klucel G solution for the consolidation of charred oak remains. However, the wood remains fragile and exhibits cracks and warping.

Present Day

Cellulose ethers are of no significance to waterlogged wood conservation.

Advantages/Disadvantages

For dry and waterlogged wood; although reversible, cellulose ethers are not suitable as consolidants because of their poor penetration into wood and their biological susceptibility to attack by fungi, bacteria, and insects.

11.3.7.2

Cellulose Esters: Cellulose Nitrate, Cellulose Acetate

Cellulose Nitrate (Nitrocellulose)

Short designation:	CN
Trade names:	Celluloid, collodion, collodion wool; in USA: Agateen, Duco cement; in Great Britain: Durofix, Ercolene, Frigilene; in Germany: Zellhorn, Zaponlack, Geiseltal-lack, Simplex-Holzkitt
Formula (simplified):	Cell-O-NO ₂
Properties:	White, fibrous, odorless and tasteless mass; insoluble in water, depending on MS soluble in alcohols, diethyl ether, esters and ketones
Toxicology:	There is no danger to health, but direct contact with food should be avoided
Analysis:	IR spectroscopy

Uses with Dry Wood

Historical

- 1865 Parkes is awarded British Patent 1313 for nitrated cellulose (Parkesin process; Domininghaus 1998).
- 1869 Hyatt is first to produce CN on a technical scale (Domininghaus 1998).
- 1892 The American Crane is awarded British Patent 6542 for zapon varnishes (Ullmann 1919).
- ca. 1900 Rathgen (1904) prefers zapon varnishes to consolidate "severely eaten wood things."
- After 1945 Intensive use of celluloid for wood consolidation (Aberle and Koller 1968).
- 1952 CN solutions are rejected for the consolidation of wood panels because of their flammability and tendency to yellow (Wolters 1998).
- 1956 Plenderleith lists celluloid syrup with sawdust to fill depressions and to clean polished veneer. The surface of basketry impregnated with beeswax is sealed with celluloid in acetone.
Conservation of a wood sculpture damaged by "dry rot" with a mixture of 100 parts collodion wool and 10 parts AP resin (ketonic resin) dissolved in acetone (Sachse).
- 1958 Nitro lacquers are not suitable for impregnation (Losos).
- 1959 Vacuum impregnation of wood with CN lacquer by Schröder, who expresses concerns regarding unsatisfactory aging characteristics and the great danger of explosion.
- 1963 Impregnation of a Madonna figure with a celluloid/alkyd resin solution in acetone (Arndt).
Zapon varnish is not very suitable for the restoration of wood carvings because the solvent evaporates too fast and the material becomes brittle (Weihs).
- 1966 A 15% CN solution in a mixture of camphor, arylphosphates and aliphatic phthalates is not suitable for wood consolidation (Manková).
- 1970 Morse discusses the use of CN in furniture conservation.
- 1978 Stabilization of a Dacian hurdle of woven wood with a mixture of CN lacquer and acetone (1:1) by Igna.
- 1984 Overview by Schiessl on the history and disadvantages of using cellulose nitrates in wood consolidation.
- 1988 Detailed report by Selwitz on the properties and use of CN for the conservation of cultural property.
- 1989 Aberle and Koller, and also Schiessl mention CN as having been used in wood conservation in the past.

Present Day

CN is not used for wood consolidation because of its disadvantageous properties.

Uses with Waterlogged Wood

Historical

- 1921 Sealing of the surface of alum-impregnated parts of the *Hjortespring* Find, Denmark, with CN varnish (Brorson Christensen 1970a).
 1954 After exchanging the water with ethanol and amyl acetate, a scabbard is treated with a 5% solution of celluloid in amyl acetate and acetone (1:1, Plenderleith).

Advantages/Disadvantages

For dry and waterlogged wood, the low penetration of the dissolved substance leads to shell formation and insufficient strengthening. The acetone and amyl acetate solvents can swell, soften, and dissolve binder systems of paint layers based on oils and resins. Fast evaporation of the solvents can lead to drying cracks in the wood. Since CN is highly flammable, objects impregnated with it are also more flammable. Consolidation with CN can lead to embrittlement, clouding and yellowing of the material, and its reversibility becomes diminished. Earlier CN preparations contain secondary components which lead to greater decomposition than in more recent products.

Cellulose Acetate (Acetyl Cellulose)

- Short designation: CA
 Trade names: In USA: Tenite; in Germany: Cellon, Cellit (T, F, K, L), Zellodyl
 Formula (simplified): $\text{Cell}-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$
 Properties: Secondary cellulose acetate is as clear as glass, light as water, and horn-like; soluble in acetone, acetone and ethanol mixtures, dioxane, and methyl acetate
 Toxicology: Does not represent any direct health danger, but is not allowed as packaging for certain foodstuffs
 Analysis: IR spectroscopy, NMR spectroscopy

Uses with Dry Wood

Historical

- 1905 Eichengrün and Becker produce acetone soluble CA (Cellit) (Koesling 1993a).

Consolidation of severely insect-damaged objects with Cellon (Schiessl 1984).

- 1952 According to a survey by Wolters (1998) Zellodyl, Cellon and Cellit L are the most often-used materials to consolidate wooden painting supports in Germany.
 1953 Tripp stabilizes the wood of an altar first with shellac, then with CA (Zellodyl).
 1955 The strengthening effect of Zellodyl is not satisfactory. Using a cellulose ether and polyacrylates (Xylamon LX Härtend) achieves better stabilization of structural timbers (Anonymous).
 1958 Lefève questions the use of cellulose lacquers for wood consolidation.
 1963 During consolidation with CA, the solvent evaporates too fast, and the consolidant turns brittle over time (Weihs).
 1968 Aberle and Koller demonstrate the advantages and disadvantages of CA.
 1984 Comprehensive report by Schiessl on the use of CA as a wood consolidant in German-speaking countries.
 1989 Schiessl mentions CA as a historic wood consolidant

Present Day

CA has no importance for wood consolidation, but is still used as a component of gap fillers.

Advantages/Disadvantages

For dry wood, CA has a strengthening effect, but because of volatile solvents such as acetone, does not penetrate deeply into wood, resulting in shell formation. CA is not very durable and does not weather well. Moisture gain results in dimensional changes of the wood. The flammability of CA is much less than CN. Surfaces of objects treated with CA incur only minor electrostatic charges.

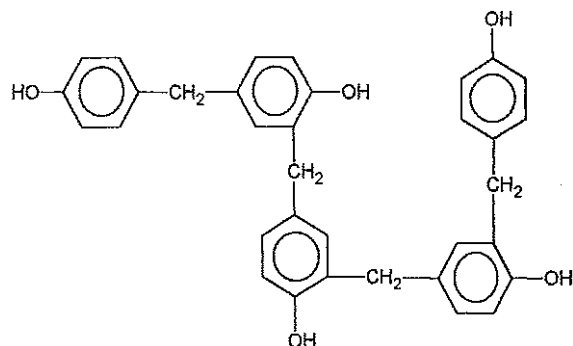
11.3.8 Formaldehyde Resins

11.3.8.1 Phenol-Formaldehyde Resins

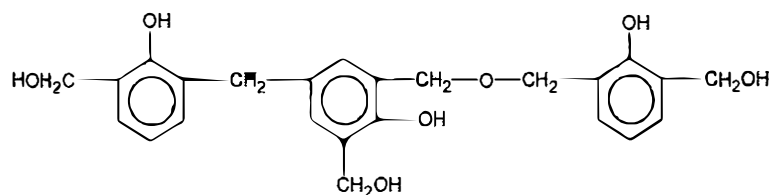
Short designation: PF

Trade names: In USA: Bakelite, Durex; in Germany: Resinol, Kauresin

Formulas:



Novolak



Resol

Properties:

Novolaks and resols are soluble and fusible substances. Novolaks are formed from phenol and formaldehyde (molar ratio 1 : 0.8) under acid conditions. The addition of hardeners such as hexamethylene diamine or para-formaldehyde effect cross-linking when heated. Resols are formed when the proportion of aldehyde exceeds that of phenol and the reaction is carried out under alkaline conditions. The first formed phenol alcohols are converted through condensation to polyalcohols by the application of heat. Resols are self-hardening. In their hardened form, the resins are insoluble in alcohols, esters, ketones, diethyl ether, chlorinated hydrocarbons, benzene, and mineral oils. Depending on the type, they can be attacked by boiling water, and strong acids and bases

Toxicology:

When processing the resins, allergic eczema, especially on hands and forearms, can be caused by unconverted formaldehyde (cf. Chap.8). Formaldehyde can also be liberated by incomplete conversion and decomposition reactions during hardening. Particleboard may emit formaldehyde as it ages

Analysis:

IR spectroscopy

Uses with Dry Wood**Historical**

- 1872 A. v. Bayer observes the ability of phenol and formaldehyde mixtures to be hardened with acids (Domininghaus 1998).
- 1907 Patent No. AP 942 699 of L.H. Baekeland for the production of PF compression molding materials (Bakelite, Domininghaus 1998).
- 1956 Plenderleith lists PF resins and resorcinol-formaldehyde (RF) resins for consolidation and surface treatment of works of art.
- 1970 Wooden elements of Renaissance houses, including verandas, balconies, and columns, are coated with PF resins (Mihailov 1970b).
- 1972 PF resins can be used for the consolidation of historic objects placed outdoors (Šujanova).
- 1978 Patent by Vichrov et al. for the conservation and consolidation of wood with a mixture of phenol alcohol (99.7–97.3 mass parts) and maleic acid anhydride (0.3–2.7 mass parts). The maleic acid anhydride, in the form of a 30% aqueous solution, is added to improve strength and the appearance of the wood.
- 1985 Schniewind mentions the use in Japan of phenolic resin microballoons as a filler for epoxy resin.
- 1987 Barclay and Grattan use Bakelite phenolic microballoons as filler for a silicon rubber gap filler.
- 1991 Ryu et al. investigate the biological resistance of wood treated with PF resins.
- 1993 Further contribution by Ryu et al. on the influence of relative molecular mass and other properties of PF resins on the biological resistance of wood impregnated with it.

Present Day

PF resin impregnation is of no importance to the consolidation of works of art and cultural property. The resins serve mainly as industrial adhesives for lumber and wood-based materials. Attempts are being made to improve the biological resistance of wood with the aid of water-soluble precondensates in order to lessen the use of traditional wood preservatives.

Uses with Waterlogged Wood**Historical**

- 1965 According to Noack, stabilization of waterlogged wood with PF resins is possible, but requires the use of a hardener or high temperatures.
- 1969 Mühlethaler (1969a,b) mentions PF resins for waterlogged wood conservation.
- 1972 USSR patent by Vichrov et al. for a conservation process for archaeological finds. The object is immersed in a 50% aqueous solution of

phenol alcohol at 93.3kPa for 1–2h, followed by an additional 3–4h in the solution at atmospheric pressure. The impregnation must be repeated for 7–10 days while refreshing the phenol alcohol solution. After the impregnation the wood is wiped and dried at 50–55°C until fine cracks appear. The wood is then immersed again in phenol alcohol solution until the cracks close. After drying, the cycle of immersion and drying is repeated five to six times, and the resin contained in the wood is finally hardened at 100°C. The treated objects reportedly have high resistance to moisture and high strength, while maintaining the appearance of the grain.

- 1973 Kazanskaya describes the preparation of a PF precondensate: phenol and formaldehyde are mixed in the proportion of 1:2.5, followed by the addition of 3% sodium hydroxide, based on the amount of phenol, and condensation for 12h at 50°C. Furfural and lactic acid may also be added. Shape and size should not change after impregnation of wood samples.

Kolčin treats waterlogged wood with sucrose solution and phenol alcohol (cf. sucrose).

- 1974 Nikitina et al. test the method of Minsk developed by Vichrov and collaborators (cf. 1972).

Wood artifacts from the eleventh to thirteenth centuries are impregnated with oligomeric phenolic resins in the presence of a 4% hexamethylenetetramine or a 7% paraformaldehyde solution as hardener (Vichrov et al.).

- 1976 Wood parts are glued with a PF adhesive (Hüllen). The surfaces to be glued are dried with infrared lamps, while adjacent areas of the wood are covered with aluminum foil.
- 1979 Impregnation of archaeological wood finds with phenol alcohols which are hardened thermocatalytically. The wood takes up 45–75% resin (Kazanskaya).
- 1980 Overview by Bulatov on the conservation of archaeological wood finds, including Vichrov's method of impregnating excavated wood remains with low relative molecular mass, water-soluble resins having phenol alcohol as the main component. The surfaces of objects such as beams are first brushed with phenol alcohol and the solution is then injected into the wood by means of a pressure tank, connecting hoses and hollow needles at a pressure of 0.98 MPa. The impregnated wood is then treated with hot air at 60–120°C to harden the phenol alcohol in the wood.
- 1984 Combined treatment of waterlogged wood with PF resin and aqueous sugar solution (Kazanskaya and Nikitina 1985; cf. sucrose).
- 1990 Modification of the method of Minsk by Kazanskaya and Nikitina (1991; cf. sucrose).
- 1991 Kazanskaya (1992) introduces new results on the method of Minsk (cf. sucrose).

Present Day

The treatment of archaeological finds with phenol alcohol (method of Minsk) is not of far-reaching importance in waterlogged wood conservation.

Advantages/Disadvantages

For dry wood, PF resins are not suitable for consolidation of valuable cultural property because of shallow penetration and because they can change the appearance of objects. The resins cross-link in the wood irreversibly. Using PF resin adhesives assures durable joints between wood parts in composite objects.

For waterlogged wood, the precondensates are water-soluble and can therefore be used to impregnate small and medium sized objects, and impregnation times are relatively short. When acid hardeners are used, residual acids may attack the wood. PF resins are not suitable for large objects because of the short hardening times. The cross-linked PF resins cannot be removed with solvents. Wood treated with phenol alcohol is not resistant to biological agents but can be tinted and glued normally.

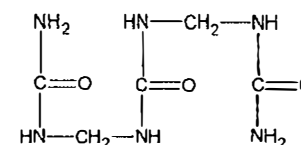
11.3.8.2

Urea-Formaldehyde Resins

Short designation: UF

Trade names: In USA: Beetleurea; in Great Britain: Mouldrite; in Germany: Celodal, Kaurit, Plastopal, Resopal; in Hungary: Arbocol

Formula:



linear precondensate of urea and formaldehyde

Properties: Aqueous liquid or powder products; the aqueous precondensates are hardened by addition of an acid catalyst. When hardened, the resins are virtually unaffected by ethanol, diethyl ether, ester, aromatic and chlorinated hydrocarbons, gasoline and oils. Not resistant to boiling water, and oxidizing and reducing agents

Toxicology: cf. PF resins

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

- 1884 Tollens describes the reaction of urea with formaldehyde (Koesling 1993a).
- 1918 John obtains a patent for a UF adhesive (Koesling 1993a).
- After 1945 Schniewind (1985) refers to gluing of door parts and consolidation of structural members of historic buildings with UF resin in Japan.
- 1956 UF resin as a finish for wood surfaces (Plenderleith).
- 1963 Straub lists UF resins among adhesives. They are reported to be durable and resistant to microorganisms. The addition of 20% PVA to the UF resin improves elasticity and pot life.
- 1968 According to Aberle and Koller, UF adhesives used as wood consolidants harden well, but penetration is shallow, the wood swells, and the adhesive becomes brittle.
- 1970 Wood elements of verandas and balconies are coated with UF resins (Mihailov 1970b).
- 1972 Objects placed outdoors can be consolidated with UF resins (Šujanova).
- 1973 Kazanskaya gives recipes for the preparation of UF condensates.
- 1987 Decsi consolidates a beech chest with Arbocol H.
- 1989 Aberle and Koller point out the shallow penetration and swelling, as well as the poor aging characteristics of UF adhesives used as consolidants.

Present Day

UF resins are of only minor importance for the consolidation of cultural property. They are occasionally used industrially to impregnate wood, but their principal use is as an adhesive (cf. Chap.12).

Uses with Waterlogged Wood

Historical

- ca. 1938 Impregnation experiments with water-soluble UF resin (Celodal), with hardening by addition of catalyst (von Stockar 1939).
- ca. 1960–1970 Use of UF resins in Hungary (Mórgos 1993).
- 1965 Cott describes impregnation with Celodal by mixing 1 l water and 1 l UF precondensate at 40°C. The wood is placed into the solution and left there until it sinks. A new solution of 2 parts precondensate and 1 part water is then prepared and the object is submerged in it. The treated wood is rinsed and dried at 20–25°C.
- 1968 Conservation of a wooden bucket with UF resin (Biek et al.).
- 1975 Waterlogged wood is saturated with a 10% solution of urea resin in a mixture of water, glycerol and methanol (1:2:3). The object is then treated with formaldehyde and ammonium chloride (Lehmann).

- 1977 Impregnation of the water-saturated or dewatered wood with a UF precondensate with the addition of 2% aluminum(III) chloride based on the solids content (De Jong 1977a).
- 1980 Bulatov uses UF resins to impregnate wood objects (cf. PF resins).
Combination of UF resins and alum to increase resistance to fracture of the objects (Szalay).
- 1982 Use of a mixture of 50–60% monomethylol urea and/or dimethylol urea, 30–35% water and 10–15% alcohol to conserve archaeological finds (Kazanskaya and Vichrov).
- 1984 Kazanskaya and Nikitina (1985) recommend UF resins to preserve light colors of wood objects.

Present Day

UF resins are only rarely used for the stabilization of waterlogged wood finds.

Advantages/Disadvantages

For dry wood, UFs are not well-suited for the consolidation of valuable objects, especially because of their irreversibility. The aqueous precondensates can cause significant swelling of the wood, and the penetration is poor. The resins darken over time, shrink somewhat, become brittle, and thick layers of resin tend to crack.

For waterlogged wood, UF resins have the same advantages and disadvantages as PF resins.

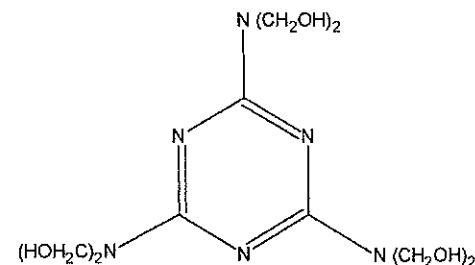
11.3.8.3

Melamine-Formaldehyde Resins

Short designation: MF

Trade names: In Germany: Kauramin; in former East Germany: Piazep ME/2; in Switzerland: Arigal C, Lyofix 4036, Lyofix DML.

Formula:



hexamethylol melamine
(from melamine and formaldehyde)

- Properties:** Aqueous liquid products or powders. The aqueous precondensates are hardened with acid catalysts and/or application of heat. Water-soluble before hardening, but afterwards resistant to alcohols, ketones, esters, diethyl ether, benzene, gasoline and oils
- Toxicology:** See under PF resins
- Analysis:** IR spectroscopy, Raman spectroscopy

Uses with Dry Wood

Historical

- 1834 Discovery of melamine by Justus von Liebig (Domininghaus 1998).
- 1935 First production of melamine resins in Germany and Switzerland (Domininghaus 1998).
- 1972 Conservation of objects placed outdoors with MF resins (Šujanova).
- 1973 Report by Kazanskaya with procedures for preparing MF precondensates.
- 1987 Nicholas and Williams use dimethylol compounds for the dimensional stabilization of wood.
- 1993 Inoue et al. treat wood with MF resins and determine its dimensional stability and its elasto-mechanical properties.
- 1995 Report by Rapp and Peek on the use of water-soluble resins for wood protection. MF and UF resins increase hardness and ASE of the treated wood significantly.
- 1996 Wood impregnated with MF resins has increased resistance to wood-destroying fungi (Rapp and Peek).
- 1998 Investigation of the time dependence of MF resin uptake (Lukowsky and Peek) and the effect of hardening conditions (Lukowsky et al.) on the resistance to fungi of impregnated wood. Comparison of the bioresistance of wood treated with MF resins and with drying oils by Sailer et al.
- 1999 Modification of wood damaged by fungi with MF resins improves the modulus of elasticity (Reinprecht and Varinska; cf. epoxy resins).

Present Day

MF resins are rarely used to consolidate cultural property. They are mainly used to produce high-pressure laminates and as adhesives, usually in combination with UF resins, for particleboards and plywood. Attempts are also being made to improve the resistance of solid wood to wood-destroying and staining fungi by impregnation with MF resins sufficiently to dispense with traditional wood preservatives. Because of their higher prices the use of impregnated wood would probably be limited to high end products such as doors and windows.

Uses with Waterlogged Wood

Historical

- Since 1957 Mueller-Beck and Haas (1959, 1960, 1961) use Arigal C for the conservation of waterlogged wood.
- 1962 Lehmann refers to the stabilization of archaeological wood with MF resins.
- 1964 Haas reports on his experiences with Arigal C conservation. Insufficient watering leads to premature precipitation of Arigal C. Solutions which already show some precipitation can be salvaged by addition of catalyst. The formation of white deposits on the surface of the object can be prevented with dampened pulp sheets.
- 1965 Description of the Arigal C process and his own method using Piazep ME/2 by Cott.
- 1968 Satisfactory results from conservation of a paddle with Piazep ME/2 (Cott).
- 1969 Combined bore hole and vacuum impregnation with Arigal C by Haas. Tomashevich lists ammonium chloride as a catalyst for MF resins.
- 1977 Ebert uses Lyofix 4036 as a substitute for Arigal C for conservation. The preparation represents a 75% solution of a partially etherified dimethylol melamine. For impregnation, a 25% solution is prepared by mixing 1 part Lyofix 4036 solution and 2 parts water at 60°C, stirring for 3–5 min. The catalyst is 1,3-glycerol diacetate (diacetin). Also added is 0.5% triethanolamine, based on the amount of Lyofix, to raise the pH from 7.3 to 9.0, which prevents premature precipitation.
- MF resins do not penetrate sufficiently into heartwood of oak (Blackshaw).
- De Jong (1977a) discusses the Arigal C method and considers the short impregnation and hardening times as a disadvantage.
- 1979 Comprehensive description of the Arigal C method by Hug (1979a). The wood is cleaned under running water and placed for 2 weeks into salt-free water at 60°C, replacing the water every 2 days. Immediately prior to treatment, the object is briefly submerged in hot water at 80°C. Its surface is then blotted, it is placed on pulp sheets, and placed in a plastic bag. The required amount of conservation material corresponds to three times the mass of the waterlogged wood. The 16% impregnation solution is prepared by heating 200 g Arigal C in 1 l distilled water to 75°C while stirring. After the solution has cooled to 50°C, the object is submerged, and will sink when sufficient resin has been absorbed. The object is then taken from the impregnation tank for 2 days, and the solution alone is heated to 50°C before the wood is submerged again. After adding 10% 1,3-glycerol diacetate (diacetin) based on the dissolved amount of Arigal C, the wood remains for 24 h in the solution with the catalyst. It is then rinsed with 80°C water which reduces the white deposits of Arigal C on the wood surface. The object is wrapped in

dampened pulp sheets, sealed in a plastic bag, and placed in an oven at 60°C for 2 days. When the bag is opened the object must be air-dried for 24h. This followed by a second treatment with somewhat different parameters and, if crack formation has occurred, a third impregnation may be required. Broken parts can be mended with cellulose nitrate adhesive and loss compensation can be done with mixtures of plaster of Paris and white glue. The wood surface can be treated with micro-crystalline wax.

- Haas proposes Lyofix DML (75% solution of an etherified MF resin) as a substitute for Arigal C. First, a 15% aqueous solution is prepared (5l to 1kg waterlogged wood) and its pH value raised from 8.5 to 9.5 with triethanolamine (3ml for 1l solution) before the wood is placed into it. As the water is exchanged for the precondensate, the wood will sink after 8–20h. The water rising to the surface must be suctioned off and the volume of liquid maintained constant by adding Lyofix solution. The object remains in the solution until the pH value reaches 8.1, and then 10% 1,3-glycerol diacetate (diacetin), based on the dry substance contained in the 15% solution, is added. After 12h the wood should be taken from the impregnation tank, wrapped in damp pulp sheets, inserted into a plastic bag, and placed into an oven at 65°C for 24h to complete the hardening. After drying the object for 2h, a second impregnation with a 25% solution of Lyofix is begun, lasting about 30 days. At the conclusion of the treatment the wood is brushed off and dried for 1–2 months.
- 1982 Grattan (1982a) compares different methods including the Arigal C method for the conservation of waterlogged wood.
- 1983 Xu discusses the Arigal C method in connection with the conservation of excavated Chinese lacquer objects.
- 1985 The penetration of Lyofix DML solutions into large-dimension wood can be increased by ultrasound treatments for 20min twice a day (Haas). Instructions are given for the preparation of Lyofix DML.
- 1987 Grattan and Clarke report on and evaluate the Arigal C and Lyofix methods.
- 1995 Schaudy mentions the Arigal C method.
- 1998 Use of the impregnation resin Kauramin CE 5549 for the stabilization of boat and ship timbers by Wittköpper, and Hoffmann and Wittköpper (1999). The impregnation and hardening procedures are analogous to the Arigal C and Lyofix methods. The most important step is the drying of the treated, still water-saturated wood using microwaves and water-permeable PE film.

Wet wood lacquerware shows very good dimensional stabilization with the Kauramin method (Hoffmann et al. 1999).

Present Day

Conservation of waterlogged wood with MF resins is only done occasionally. For large shipwrecks these methods are of no significance.

Advantages/Disadvantages

For dry wood, improvements in dimensional stability, elasto-mechanical properties, and resistance to fungi by impregnating wood with MF resins is possible, but because the resins harden irreversibly they should be rejected for the conservation of valuable cultural properties. The aqueous precondensates have a limited shelf life and can cause large swelling of the wood. Pot life in contact with woods with a low pH value is short. The temperatures required for complete hardening in the absence of hardener are not acceptable for sensitive cultural property. MF resin films are generally more resistant to water than UF resins, but are not resistant to weathering. Adhesive qualities and resistance to light exposure are considered good to very good.

For waterlogged wood, sufficient penetration and therefore good stabilization of the wood structure can be obtained regardless of wood species. The exchange of water for MF resin is faster in woods with large pores than in those with smaller pores. Charred wood, twigs, bark, as well as wood in combination with other materials such as stone, bone, leather, metal, and textile remains can be treated as well. Treatment with Lyofix DML results in a small but irreversible increase in volume. Impregnated parts can be glued and losses can be compensated. Treated objects are unchanged years later, and are protected from attack by microorganisms by the formaldehyde content. Determination of the wood species is still possible after treatment, but ¹⁴C analysis can no longer be done. The largest object treated by Haas (1979) had a mass of 15kg when wet and its size was approximately 500 × 400 × 150mm. Conservation of even larger objects is considered too expensive. Objects are sometimes bleached and changed in color by the treatment. Fast drying causes cross breaks and volume changes. Additional treatments of the wood are possible. Direct exposure to sunlight can lead to crack formation.

11.3.9

Polyvinyl Compounds

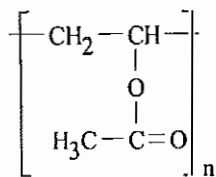
11.3.9.1

Poly(vinyl acetate)

Short designation: PVA or PVAC

Trade names: In Germany: Mowilith, Mowicoll, Vinnapas, Ponal (PVA emulsion), Acronal D 300 (Copolymer of *n*-butyl acrylate, vinyl acetate and vinyl chloride); in France: Rhodopas; in Italy: Vinavil; in Poland: Vinacet (or Winacet); in Switzerland: Vipolit; in USA: Bakelite AYAA, AYAC, AYAF, AYAT, Gelva V 7, Vinac B 800, Elvacet, Vinylite

Formula:



Properties: Clear as glass, brittle, light and heat resistant thermoplastic polymer; readily soluble in lower alcohols, esters, ketones, and chlorinated hydrocarbons; insoluble in water, higher alcohols and gasoline

Toxicology: No danger to health

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

- 1912 Klatte experiments with polymerization of vinyl acetate (Koesling 1993a).
- 1930/1931 Production of PVA begins in Germany (Koesling 1993a).
- 1935/1936 Discussion of using PVA in painting conservation (Schiessl 1984).
- After 1945 PVA dispersions and emulsions become increasingly important as adhesives and binders (Aberle and Koller 1968).
- 1956 Consolidation of wooden works of art with PVA, dissolved in 9 volume parts of toluene and 1 volume part acetone. Bark layers in basketry are sprayed with PVA (Plenderleith).
- 1958 According to Losos, the polymer is unsuitable for the stabilization of hardwoods and polychrome objects. A vinyl acetate/vinyl chloride (VAC/VC) copolymer also does not meet requirements.
- 1963 Straub states that PVA is well suited for gluing joints in paintings. PVA dissolved in toluene can be used for wood stabilization (Weihs).
- 1966 Consolidation of the backs of bark paintings by Australian aborigines with a PVA copolymer (Boustead).
- Manková soaks oak and linden samples in 5–20% solutions of PVA for 8 days, but the treatment was not very effective.
- 1968 PVA serves as a stabilizer for old wood in buildings (Czajnik).
- 1970 Mihailov (1970a) uses Vinavil K-45 in ethanol as consolidant. Five to 8% PVA solutions are used as a surface treatment for interior trim.
- Consolidation of a polychrome wood sculpture with AYAF (Vinylite). A mixture of Vinylite and sand is used for loss compensation and fills (Thielker).
- 1972 PVA with an added insecticide is used to consolidate polychrome wood (Šujanova).
- 1973 Broken wood articles are glued with PVA and open joints are sealed with PVA filled with cork and sawdust (Mühlethaler).

- 1974 Mihailov et al. use a 20% solution of Vinavil K-50 in ethanol for consolidation, and as a paste containing sawdust to fill cracks in structural timbers.
- 1976 Consolidation of a polychrome wood sculpture with PVA in Australia (Byrne).
- 1977 Loose paint pigments on wooden war shields are fixed with Vinac B 800 in acetone (Vandyke-Lee).
- 1978 Gabricevic consolidates a disintegrating dugout canoe with PVA. Oellermann consolidates original paint on sculptures with dilute PVA solution or with wax.
- 1979 Hüchel uses Ponal along with Calaton (cf. polyamides) for the conservation of a sarcophagus.
- 1981 Soldenhoff impregnates linden wood with Mowilith 40 and determines uptake, mechanical durability, and distribution of the resin.
- 1982 Schaible (1983) bores 3-mm holes into the edges of altar wings in a fish-bone pattern and inserts brass tubes of 2 mm diameter. PVA solution is introduced via the tubes; after the first impregnation the tubes are withdrawn 50 mm and another impregnation is carried out.
- 1984 Schiessl mentions the use of PVA as a consolidant.
- Schniewind and Kronkright spray a severely deteriorated dugout canoe of ponderosa pine with a 13% solution of AYAF in methanol. They also determine increases in bending strength of sound wood and wood deteriorated by bacterial attack after treatment with various PVA types, Butvar B98 [cf. poly(vinyl butyral)] and Acryloid B72 (cf. ethyl methacrylate), where PVA was the least effective. They also found that the relative improvement in strength properties is proportional to the degree of deterioration.
- 1986 According to Kadry, treatment with a PVA solution in acetone results only in consolidation of surface layers and causes undesirable deepening of the color.
- Consolidation of African Camwood (a special wood composite) with 5 or 10% solutions of PVA (AYAF) in toluene by Pouliot (1988).
- 1988 Schniewind tested the thermoplastics AYAT, Acryloid B72 and Butvar B98, and found that AYAT had the best reversibility. The use of polar solvents gave better results with respect to reversibility than nonpolar solvents.
- Comprehensive contribution by Schniewind (1990a) on the suitability of thermoplastic resins such as PVA (AYAT and others) for the consolidation of dry archaeological wood.
- 1989 The strengthening effect of PVA (Mowilith 35/73, white glues) depends on the particle size of the dispersion. Wood swelling takes place, and drying cracks appear. The aging characteristics are not particularly good (Aberle and Koller).
- Catalano Fenicia consolidates the back of an altar with a PVA solution in ethanol.

Detailed investigation by Cuany et al. of penetration, strengthening, and response to moisture of wood deteriorated by insects and fungi after treatment with 10–40% solutions of Mowilith 30 in toluene and ethyl acetate. Strength increases are minor, and the wood becomes greatly discolored.

- 1990 Buchenrieder mentions Mowilith 30 solutions in ethyl acetate as a consolidant for painted objects.

According to Hansen et al. the aging characteristics of PVA place it into Class A (stability >100 years).

The wood chassis of a carriage is consolidated, among others, with Mowilith 35/73 (Leconte and Oudry).

Sakuno and Schniewind determine the adhesive strength of Acryloid B72, Butvar B98 and AYAT as 15% solutions in polar and nonpolar solvents using samples of Douglas-fir foundation piles with bacterial attack. Polar solvents give better results than nonpolar solvents, but adhesive strength does not reach the values obtained with a commercial PVA emulsion adhesive.

Report by Schniewind (1990b) on solvent retention and the influence of polymers, including AYAT solutions, on the hygroscopicity of treated wood.

- 1993 Comprehensive report by Paciorek on the impregnation of linden wood with thermoplastic resins. Among others he uses a 50% solution of PVA in methanol and determines water absorption, dimensional stability, and resistance to wood-destroying fungi of the treated wood.

- 1994 Wächter discusses aging characteristics of PVA.

- 1995 Comprehensive review by Schniewind (1998) of various consolidants, including PVA, their application, effectiveness, and reversibility as related to their use for wood painting supports.

Unger and Unger (1995b) publish an overview of the resistance of wood-polymer composites to wood-damaging fungi and wood-destroying insects. Wood treated with PVA has only moderate biostability.

- 1996 Down et al. test 27 PVA adhesives with respect to their use in the preservation of cultural property (cf. Chap. 12).

According to tests by Heyn et al., Mowilith 20 and Mowilith DM5 are decomposed by microorganisms more severely than Paraloid B72 and Primal AC 33.

Unger et al. discover that insect-damaged wood treated with Mowilith 30 can be attacked again by larvae of house longhorn beetles.

- 1997 Detailed report by Hedlund on the use of Acronal D 300 as consolidant for polychrome wood sculptures in Sweden.

Present Day

PVA is of only secondary importance as a consolidant. It serves mainly as an adhesive (cf. Chap. 12), but is also used to fasten down paint and ground layers

and to consolidate paints in the form of pure PVA or in mixture with poly(vinyl alcohol).

Uses with Waterlogged Wood

Historical

- 1958 PVA suffices for preliminary conservation of archaeological finds (Losos).

- 1970 Experiments by Brorson Christensen (1970b) to consolidate waterlogged wood by stepwise exchange of water for methanol and vinyl acetate, followed by radiation-induced polymerization of the vinyl acetate inside the wood.

Advantages/Disadvantages

For dry and waterlogged wood, improvements of the elasto-mechanical properties of wood by treatments with PVA can be considered no more than moderately satisfactory when compared with other thermoplastic resins. PVA is flexible but, for the stabilization of wood, not hard enough. Usually only the surface layers are sufficiently impregnated, and this is accompanied by noticeable deepening of the color. Compared with other polymers the ASE is low. Aging characteristics and bioresistance are classified as satisfactory to good. PVA is reversible, but because of its relatively low glass transition temperature it is subject to creep (cold flow).

11.3.9.2

Poly(vinyl alcohol)

Short designation: PVAL

Trade names: In Germany: Mowiol, Polyviol; in USA: Elvanol, Gelvatol

Formula:
$$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \\ | \\ \text{OH} \end{array} \right]_n$$

Properties: Whitish-yellowish powder or granulate; soluble in water, dimethyl formamide and dimethyl sulfoxide; insoluble in chlorinated hydrocarbons, esters, and oils

Toxicology: The substance is classified as harmless and is sometimes biodegradable

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

- 1926 Development of PVAL begins in Germany.
- 1958 Domański protects paint layers with tissue paper impregnated with a PVAL solution prior to stabilizing the wooden painting support with a 20% solution of poly(vinyl chloride) (PVC) in chlorobenzene or 1,2-dichloroethane.
- 1974 Mitano and Kabaivanov test the suitability of a 6% aqueous solution of PVAL for fixing paint layers on wood.
- 1978 According to Schaffer, PVAL samples exposed for 450h to UV light maintain their water solubility (reversibility).
- 1990 Hansen et al. report that PVAL is resistant to aging for <20 years.
- 1992 Loose paint layers are laid down with a mixture of PEG 2000 and PVAL by Niedzielska.
- 1996 According to Heyn et al., Mowiol 4-98 is very susceptible to attack by microorganisms.

Uses with Waterlogged Wood

Historical

- 1958 According to Losos, PVAL emulsion can be used to consolidate waterlogged wood.
Rumáncsev uses a mixture of PVAL and glycerol to stabilize waterlogged wood finds. He adds 15–20g PVAL powder to 780cm³ water and after 6–8h heats the mixture in a water bath with continuous agitation to 65–70 °C until everything has been dissolved. He then adds 200g glycerol and impregnates the wood with the warm solution.
- 1966 Medieval wood finds are consolidated with PVAL by Müller and Thieme.
- 1969 Tomashevich discusses the PVAL/glycerol method.
- 1970 The surface of wood impregnated with PEG is treated with PVAL (Brorson Christensen 1970a).
- 1974 Nikitina et al. mention replacing water with glycerol and PVAL.

Present Day

PVAL is not used for wood consolidation, but does find application in laying down and fixing loose paint layers in mixtures with PVA and other suitable polymers.

Advantages/Disadvantages

For dry and waterlogged wood, PVAL is reversible. The dimensional stability and the elasto-mechanical properties of the wood are not improved very much. The aging characteristics of the polymer, and its bioresistance are not satisfactory.

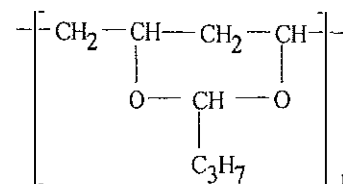
11.3.9.3

Poly(vinyl butyral)

Short designation: PVB

Trade names: In Germany: Mowital B 30 H, Mowital B 60 H; in USA: Butvar B79, Butvar B90, Butvar B98, Bakelite XYHL

Formula:



Properties: White to pale yellow powder; insoluble in water; soluble in lower alcohols, ethyl acetate, ketones, tetrahydrofuran and chloroform-methanol (9:1); insoluble in benzene and its homologues, mineral oils, gasoline, higher esters and fatty oils

Toxicology: No danger to health

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

- 1958 According to Losos, PVB is not suitable for impregnating wood.
- 1970 Pluska stabilizes a polychrome wood sculpture with a poly(vinyl acetal). He removes the greatly deteriorated wood from the interior of the sculpture and consolidates the remaining wood with a 5% solution of poly(vinyl acetal) in acetone. The use of acetone prevents dissolution of protective coatings of paraffin wax and stearin on the object's surface. After the acetone evaporates, the walls of the interior void spaces are covered with a layer of the polymer. Cracks and splits are filled with a mixture of poly(vinyl acetal) and sawdust.
- 1981 Barclay consolidates the wood parts (mostly oak) of a fire engine dating to 1783 with PVB. The water container and the superstructure are brushed with a 5% solution of PVB in ethanol, and the wheels and the running boards are impregnated with a 20% solution at reduced pressure. Excess PVB is removed and the objects are slowly dried under PE film with air circulation over a period of 2 months. Surface gloss is removed by wiping with ethanol.

Consolidation of ground and paint layers of ancient Egyptian sarcophagi and sculptures with PVB in alcohol by Natchinkina and Cheinina.

1984 Payton recommends PVB for furniture treated with paraffin after the paraffin has been removed.

Dendroglyphs are treated with a mixture of PVB, kaolin, paper pulp, acetone, amyl acetate, xylene and water (Peters; cf. beeswax).

Impregnation with a 15% solution of Butvar B98 increases the bending strength of bacterially deteriorated wood the most when compared with Acryloid B72 and the poly(vinyl acetate) AYAF (Schniewind and Kronkright).

1985 According to Wang and Schniewind, Butvar B98 strengthens wood somewhat better than Butvar B90. If the impregnated wood is dried slowly, the strength of wood consolidated with Butvar becomes less as compared with Acryloid B72.

1986 Kadry tests PVB in alcohol for consolidation of wood from the Solar Boat of Cheops.

Simpson and Payton publish a further report on the renewed conservation of furniture remains from Gordion (cf. Payton 1984).

1987 Consolidation of a double flask with a 10% solution of PVB in acetone by Nacsa.

Paterakis tests Butvar B79 and B98 with regard to hardness, flexibility, penetration, and darkening for a planned use on a totem pole.

Sakuno and Schniewind investigate the adhesive properties of synthetic resins, including Butvar B98, which are used for the consolidation of deteriorated wood.

Storch uses a 5% solution (w/v) of Butvar B98 in alcohol, with 5% *n*-butanol added, to consolidate parts of a wooden gate.

1988 Investigations by Schniewind of the reversibility of synthetic resins which had been used to treat deteriorated wood. Butvar B98 is least reversible when compared with AYAT and Acryloid B72, but the amount remaining in the wood is very small with all polymers tested and is of no practical significance. Continuous stirring and the use of polar solvents are advantageous for resin extraction.

Overview of the consolidation of dry archaeological wood with thermoplastic resins including PVB by Schniewind (1990a), discussing solvent selection, strength improvement, capacity for solvent retention by the resins, adhesive characteristics of the resins and their reversibility.

1990 Carlson and Schniewind investigate the effect of solvent retention on bending strength after consolidation of bacterially deteriorated Douglas-fir wood with Butvar B98 and Acryloid B72. Disadvantageous softening of the polymers by retained solvent can be reduced by using solvents with low boiling points.

Sakuno and Schniewind determine the shear strength of adhesive joints made with Butvar B98 and other thermoplastic resins formulated as consolidant solutions. Polar solvents produce stronger joints than nonpolar solvents.

According to Schniewind (1990b), wood treated with solutions of polymers in organic solvents will exhibit swelling proportional to the swelling capacity of the solvent used. In this respect, nonpolar solvents are therefore more suitable than polar ones. The polymers, including Butvar B98, do not appear to have a significant effect on the hygroscopicity of wood because of their large relative molecular mass.

According to Hansen et al., the resistance to aging of PVB is in the range of 20 to 100 years (Class B).

1991 Further report by Schniewind on the impregnation of deteriorated wood with thermoplastic resins such as Butvar B98.

1992 Experiments on the consolidation of an unpainted wood sculpture with severe deterioration by brown rot, using 5 and 10% solutions of Mowital B 30 H and Mowital B 60 H in methanol, ethanol, 1-propanol, and 1-butanol by Martens and Unger. After treatment of the sculpture with a 5% solution of Mowital B 60 H in methanol, the conserved portions were sufficiently consolidated and did not show any surface gloss.

Schniewind and Eastman determine resin distribution by scanning electron microscopy following vacuum impregnation of wood with thermoplastic resins including two Butvar types in various solvents. Resin deposits are readily visible in the earlywood, and their distribution is uneven, the surface layers showing higher resin concentration than the core.

1995 Discussion of problems in the consolidation of wooden painting supports with synthetic resins including PVB by Schniewind (1998).

1996 Stone investigates 15-year-old consolidations of wood objects with Butvar B90 and Mowital B 30 H, and finds neither noticeable yellowing nor marked strength losses.

Present Day

Compared with acrylates and epoxy resins, PVB is used only to a small extent for the consolidation of wood objects.

Uses with Waterlogged Wood

Historical

1978 Conservation of a pulley shave from the Dutch ship *Zeewijk* by Gilroy. He dissolves 10 g PVB powder (Bakelite Vinyl Butyral) with heat application in 100 ml 1-butanol, adds 100 ml acetone and submerges the object in the solution for 1 week. The surface is then brushed to saturation with a 10% solution of PVB in 1-butanol. Excess PVB can be removed with acetone.

1994 Caple and Murray dewater samples of charred oak with industrial methylated spirits (IMS) and consolidate them with a 5% solution

of Butvar B98 in IMS, but penetration is poor, the wood shrinks and develops cracks.

Present Day

PVB is not used in waterlogged wood conservation.

Advantages/Disadvantages

For dry and waterlogged wood, PVB is reversible and can be removed from treated wood almost entirely. Unlike other thermoplastic resins, PVB is soluble in lower alcohols, which facilitates its use from a toxicological point of view. Penetration into wood of PVB solutions of low concentration is moderate and the depth of penetration is shallow. Consolidated regions are satisfactorily strengthened; the wood surface is changed little and becomes hard. Treated objects have a natural appearance. Adhesive joints are generally not affected by the PVB solutions. The aging characteristics of PVB are considered good.

11.3.9.4

Poly(vinyl chloride)

Short designation: PVC

Trade names: In Germany: Vinoflex MP 400 (copolymer of PVC and vinylisobutyl ether), Acronal D 300 (copolymer of *n*-butyl acrylate, vinyl acetate and vinyl chloride)

Formula:
$$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \\ | \\ \text{Cl} \end{array} \right]_n$$

Properties: Small, white to pale yellow particles which may be smooth, compact, irregularly shaped, or porous; soluble in tetrahydrofuran, 1,2-dichloroethane, mixtures of carbon disulfide and acetone, dioxane, cyclohexanone and 1,2-dichlorobenzene. Benzene and gasoline mixtures cause swelling

Toxicology: Unconverted vinyl chloride, which is highly toxic and carcinogenic, is present in PVC only in small amounts of 0.01–0.1 ppm and will be emitted during use. PVC additives such as plasticizers, some of which are suspected carcinogens, will also be emitted. In case of fire, hydrogen chloride (highly irritating and corrosive), carbon monoxide (toxic), dioxins and furans (very toxic) are formed

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

1835 Regnault discovers vinyl chloride and vinylidene chloride (Domininghaus 1998).

1912/1913 Patents by Ostromislensky and by Klatte for PVC (Domininghaus 1998).

1958 Consolidation of a wood panel with PVC (Domasłowski; cf. PVAL). Losos tests a VAC and VC copolymer (cf. PVA).

1968 Czajnik mentions Vinoflex and post-chlorinated PVC among materials for wood conservation in old buildings.

1970 Oak carvings which were treated in 1962 first with a solution of pentachlorophenol (cf. Chap. 7) and then with a solution of Vinoflex MP 400 in 1,2-dichloroethane are still in perfect condition (Wazny).

1974 According to Mihailov et al., a 15% solution of PVC in 1,2-dichloroethane is suitable for the consolidation of wood structures.

After 1981 Stawicka stabilizes polychrome wood ceilings from the seventeenth century with Vinoflex MP 400 and PVC. Small cracks are filled with a mixture of Vinoflex MP 400 and sawdust, and chalk ground reinforced with PVC solution is then applied.

Present Day

PVC is not used in wood conservation.

Uses with Waterlogged Wood

Historical

1964 After storing a soft, spongy wood spoon in water with mercury(II) chloride added (cf. Chap. 7), Ypey impregnates it with PVC solution. The spoon is still solid and dimensionally stable 10 years later.

Present Day

PVC is not used in waterlogged wood conservation.

Advantages/Disadvantages

For dry wood, PVC is reversible but not very heat resistant. Strength and dimensional stability of wood can be improved with PVC solutions, but penetration is shallow. Aging processes can lead to emission of HCl and plasticizers. Hard PVC has good resistance to biological attack by fungi, bacteria and insects, but soft PVC is not as resistant.

11.3.9.5

Poly(vinylidene chloride) (PVDC) and Poly(vinyl pyrrolidone) (PVP)

In past years Saran (vinylidene chloride and acrylonitrile copolymer) has been used as a moisture barrier on the backs of wood panel paintings (Straub 1962; Buck 1978; Spurlock 1978; Brewer 1991; Rothe and Marussich 1998).

PVP has been used experimentally in waterlogged wood conservation by direct exchange with water and subsequent polymerization inside wood (Tran et al. 1990), or in the form of the commercial product Luviskol as a consolidant (Richards 1990).

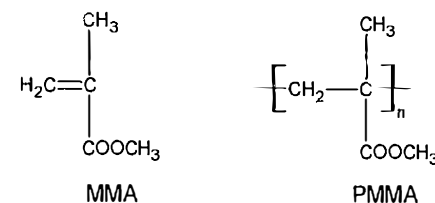
11.3.9.6

Poly(methyl methacrylate)

Short designation: Monomer – MMA, polymer – PMMA

Trade names:	Composition	Country
Plexigum MB 319	Copolymer of MMA and ethyl acrylate	Germany
Plextol B 500	Copolymer of MMA and ethyl acrylate (~50% solids content)	
Plextol D 360	Copolymer of MMA and butyl acrylate (~60% solids content)	
Paraloid B-44, Paraloid B-48-N	MMA copolymer	
Piaflex LT 30	Copolymer of MMA and BMA (~40% solids content)	Former East Germany
Bedacryl L.	PMMA solution (~18–20% solids content)	Great Britain
Acrylit X 20/5	PMMA solution (~26% solids content)	USA
Elvacite 2013	Methyl methacrylate and <i>n</i> -butyl methacrylate resin	
Acryloid B-44 and Acryloid B-48-N	MMA copolymer	
Primal AC and Rhoplex AC 33	Copolymer of MMA and ethyl acrylate	

Formula:



Properties:

MMA: colorless, clear as water, combustible liquid with a pungent odor; m.p. –48 °C, b.p. 100–101 °C; insoluble in water, soluble in ethanol, diethyl ether, and acetone; PMMA: clear as glass, hard and elastic products; soluble in aromatic and chlorinated hydrocarbons, esters, ketones, propanol, butanol, turpentine and in the monomer

Toxicology:

MMA vapors irritate eyes and the respiratory tract; lung edema is a possibility. At high concentrations of the vapor or extended ingestion, a paralyzing effect on the central nervous system is to be expected. Contact with the liquid leads to eye and skin irritation, and there is danger of sensitization. PMMA represents no danger to health

Analysis:

MMA by GC; PMMA by IR spectroscopy

In Situ Polymerization of MMA with Dry Wood**Historical**

- 1873 Caspary and Tollens describe acrylic acid polymers (Domininghaus 1998).
- 1928 R. Hill in England and W. Bauer in Germany polymerize the ester of methacrylic acid (Koesling 1993a).
- 1934 ICI establishes the first British PMMA factory, with the trade name Perspex (Plexiglas in Germany and USA; Koesling 1993a).
- 1958 Kenaga applies for a patent for the impregnation of wood with acrylic monomers and polymerization by irradiation.
- 1969 Munnikendam and Wolschrijn impregnate wood with MMA. To prevent premature evaporation of the monomer, the impregnated specimens are wetted with water or ethylene glycol, both of which have been made more viscous by the addition of thickeners. The pot life of MMA, with 2% dibenzoyl peroxide and 0.8% dimethyl-4-toluidine added, is 90 min at 20 °C.
- 1973/1974 Following consolidation with MMA it is possible to make microtome sections of fragile wood (Vynckier).
- 1974 According to Mihailov et al., a 20% solution of Paraloid B72 in MMA with 0.3% dibenzoyl peroxide as initiator is suitable for the stabilization of museum objects.

Mitanov and Kabaivanov (1974, 1975) use acrylic and methacrylic monomers to consolidate small test boards with paint layers.

Schaffer treats painted wood artifacts by in situ polymerization of MMA by irradiation and by thermo-catalytic action.

- 1975 Delbourgo reports on the vacuum impregnation of painted wood samples with monomers, their polymerization by irradiation, and changes in the polychromy.

De Tassigny reports on the results of the conservation of cultural property at the French Nuclear Research Center in Grenoble by in situ irradiation polymerization of acrylic and methacrylic compounds.

- 1979 Conservation of a double wood statue from Oceania with a MMA/BMA mixture by Mesterházy. Dibenzoyl peroxide and dimethyl aniline serve as initiator and accelerator, respectively.

- 1981 Šimůnková and Zelinger describe the effects of polymerization of MMA and BMA in wood with 2-butanone peroxide, dibenzoyl peroxide, redox systems or gamma irradiation. The chemically initiated polymerization of MMA achieves only 10% conversion to poly(methyl methacrylate) in the wood, whereas at a total dosage of ~40 kGy irradiation nearly 100% conversion can be obtained.

Impregnation of pistol grips with mixtures of MMA and styrene, and of MMA, styrene, and unsaturated polyester resin, with crotonaldehyde added followed by thermo-catalytic hardening (Unger et al. 1981a).

- 1982 Determination of the properties of MMA block polymers after irradiation polymerization at a total dosage of 60 kGy by Schaudy et al. (1982a,b). In contrast to other consolidants, MMA does not cross-link but becomes very hard and brittle.

Unger et al. conserve oak parts of a gun carriage with a mixture of MMA and crotonaldehyde which does not harden until the application of ~80 kGy in a pure nitrogen atmosphere. The appearance of the wood is almost unchanged by the MMA treatment.

- 1983 Impregnation of chemically and biologically deteriorated wood samples with MMA, styrene, and unsaturated polyester resins by Schaudy and Slais. The disadvantageous shrinkage of MMA is compensated for by its slight interaction with the wood matrix. Wood colors deepen but the aesthetic appearance is good.

Detailed report by Šimůnková et al. on the impregnation of wood with MMA and BMA followed by thermo-catalytic or irradiation polymerization. Polymerization by gamma irradiation is more effective. The properties of the consolidated wood, namely dimensional stability, water uptake, swelling and compression strength parallel to the grain depend on the polymer loading in the wood, the composition of the polymer, wood species and its structure. Copolymerization of MMA and BMA does not improve wood properties.

- 1984 Report by Unger et al. (1984) and Lachmann et al. (1986) on the consolidation of the oak carriage of an historic giant gun with MMA and



Fig. 11.5. Giant gun with an oak carriage consolidated with methyl methacrylate by in situ polymerization. (Photograph courtesy of Military Museum Dresden)

crotonaldehyde using 1% of 2,2'-azobisisobutyronitrile as initiator (Fig. 11.5). Polymerization is effected with heating blankets at 50°C over a period of 17–20h.

- 1985 Experiments on consolidation of insect damaged wood samples with MMA followed by regilding (Perleberg and Unger). At a polymer loading of about 50% very good stabilization is obtained. The procedure can also be applied to picture frames.

- 1987 Šimůnková and Josef discuss the possibilities for using in situ irradiation polymerization of MMA in structural timbers of buildings.

Characterization of the process of in situ polymerization of MMA in a picture frame and a putto by X-ray computer tomography (Unger and Perleberg; cf. Chap.6).

Review by Unger and Unger on the consolidation of cultural property, including the use of MMA and in situ polymerization.

- 1988 Šimůnková uses MMA, BMA, and their mixtures for irradiation polymerization at dosages of 0.03–1 kGy/h. Polymer loading and swelling during polymerization are determined for wood with and without polychromy.

The addition of BMA to MMA increases polymer loading in the wood and reduces its irreversible swelling (Šimůnková et al.).

- 1990 Because of the low viscosity of MMA, Šimůnková recommends the use of a solution of polymer in the monomer for polymerization by irradiation. The method is suitable for objects without polychromy.

1993 Šimůnková and Kozany investigate the effect of MMA impregnation followed by polymerization by gamma irradiation on polychrome wood samples. Paint layers with polysaccharide binders do not show any damage.

A further report by Šimůnková et al. deals with grafting of MMA on wood constituents during irradiation polymerization.

1995 Wood-polymer composites produced by in situ polymerization of MMA in various wood species are clearly more resistant to wood-damaging fungi and the larvae of wood-destroying insects than untreated wood (Unger and Unger 1995b).

Present Day

In situ polymerization of MMA in works of art and cultural property by both the thermo-catalytic and the irradiation methods are used only to a very limited extent because of the great expense.

In Situ Polymerization of MMA with Waterlogged Wood

Historical

1966 Conservation of waterlogged wood with MMA in acetone by Brendel.

Impregnation of small wood cubes of neolithic ash wood with MMA or methyl acrylate. Polymerization effected by a ^{60}Co source at a dosage rate of 6 kGy/h (De Guichen et al.).

1967 Munnikendam treats waterlogged wood samples of oak with MMA. The water in wood is exchanged with methanol, which in turn is exchanged for MMA over 3–5 days each. The samples are then wrapped in foil and exposed to a ^{60}Co source with a dosage rate of 1 kGy/h (total dosage 50 kGy).

1970 Method of Brorson Christensen (1970a) for embedding very soft, small waterlogged wood finds in PMMA. The wood is dewatered with ethanol which is then exchanged for MMA with dibenzoyl peroxide as initiator and polymerized at 45°C.

1974 Exchange of water in wood for mixtures of acetone and MMA or ethanol and MMA in continuously running equipment, followed by polymerization using gamma irradiation (Detanger et al.).

Use of acrylic monomers for the conservation of excavated wood by Masuzawa and Takada.

1977 De Jong (1977a) describes the tert-butanol/MMA exchange (cf. butyl methacrylate).

1978 Stabilization of charred wood pieces with MMA by Schaudy and Kies. The wood is placed into a desiccator and vacuum is drawn for 20 min to remove the water. The object is then covered with MMA and impregnated thoroughly by a pressure change. Polymerization is effected in double-walled PE bags filled with pure nitrogen using a ^{60}Co source with

a dosage rate of 11.8 kGy/h (total dosage 30 kGy). Residual monomer is removed by heating to 45°C.

1981/1982 Mavroyannakis (1981, 1982) reports on the aging characteristics of waterlogged wood finds which had been impregnated with MMA, vinyl acetate or styrene-polyester resin followed by gamma irradiation. The combined polymer and old wood do not show any cracks after 4 years, and biological deterioration is minor after 2 years.

Šimůnková et al. (1981) describe the continuous extraction of water from waterlogged wood with systems such as MMA/ethanol or MMA/methanol (cf. styrene).

1988/1989 Reports by Gäumann et al. (1988, 1989) on the polymerization of MMA in waterlogged wood by means of a ^{60}Co source. It is not necessary that the object being treated is completely saturated with monomer.

1994 Wang et al. dewater wooden drainage pipes first with aqueous ethanol solutions, and then with mixtures of ether and ethanol. The wood is then impregnated with MMA 100 (mass ratio), 2,2'-azobisisobutyronitrile 0.06, dioctyl-*p*-phthalate 5, stearic acid 0.7, and Meidi 0.02. The polymerization is done at 55–60°C; higher temperatures reportedly cause implosion.

Present Day

MMA and in situ polymerization are used only in a few cases for smaller waterlogged wood objects.

PMMA in Solution with Dry Wood

Historical

1958 According to Losos, Acrylit X 20/5 can be used for impregnation.

1966 PMMA solutions (Acrylit X 20/5) can be used for wood consolidation (Manková).

1968 Aberle and Koller express the opinion that clear judgment of the suitability of acrylic resins for consolidation is not yet possible.

Czajnik lists poly(methacrylate) solutions among materials for the conservation of old wood in buildings.

Wood panel paintings and wood sculptures can be consolidated with an 18–20% solution of PMMA (Bedacryl L; Lodewijks). The concentration of the consolidant is higher in the surface layers.

1972 Šujanová recommends polyacrylates for the consolidation of polychrome objects.

1978 Stabilization of a softwood panel painting with a 10% solution of PMMA/PBMA in xylene with 2% pentachlorophenol added (Hamsik).

Present Day

Pure PMMA solutions are rarely used to consolidate unpainted and painted objects; solutions of copolymers of MMA and other acrylic or methacrylic compounds are most common.

PMMA in Solution with Waterlogged Wood

Historical

1957 Objects from the *Oseberg* find (Norway) which had been stored in formalin are dewatered in baths of tert-butanol and consolidated with a dilute solution of PMMA in benzene (Rosenqvist).

Advantages/Disadvantages

MMA Impregnation of Wood and In Situ Polymerization

For dry wood, MMA has low relative molecular mass and low viscosity and can be applied undiluted. Complete saturation of the wood is possible. Since no solvents are used, all of the impregnated MMA serves for consolidation. Impregnation time is short for old wood deteriorated by insects or fungi. For thermo-catalytic polymerization a catalyst has to be added to the MMA, which limits the durability of the monomer; a catalyst is not required for polymerization by irradiation. MMA is fugitive and impregnated objects must therefore be wrapped with PE or polyamide film or aluminum foil. Polymerization time is short for both thermo-catalytic and irradiation processes. MMA swells sound wood, but insect damaged wood shows almost no swelling. Unlike epoxy resins, MMA shrinks about 18% during polymerization, but in wood this disadvantage is compensated for by the interaction between MMA and wood constituents. After polymerization the strength properties of wood and its resistance to agents of biodeterioration is significantly improved. Even frass left by insects is consolidated. During thermo-catalytic polymerization, cross-linking of MMA does not take place, but with irradiation some of the MMA is grafted irreversibly onto wood constituents. The PMMA produced thermo-catalytically inside wood is reversible in principle, but in conservation practice it probably cannot be removed again completely. Homopolymer on the surface of MMA treated objects can be removed with monomer or other organic solvents such as ethyl acetate. Surface gloss after MMA treatment does not occur because the monomer evaporates from the surface prior to polymerization. PMMA has good resistance to UV radiation, thermal deformation and aging. MMA treatments cause some deepening of color of wood and paint layers. The liquid MMA can swell and dissolve paint layers with oil and resin binders. Tempera is attacked to a lesser extent. Detailed studies of the solvent action of MMA on paints, old polishes, varnishes and lacquers are still lacking. Objects treated with MMA become

charged electrostatically and attract dust. MMA and PMMA are combustible, and treated objects therefore have increased combustibility. In situ polymerization of MMA requires knowledge of chemistry and suitable equipment. The process can only be recommended for unpainted objects.

For waterlogged wood, MMA is not miscible with water, so that the water must first be exchanged for organic solvents such as methanol, ethanol, tert-butanol, or acetone. The stepwise exchange takes considerable time, especially in the case of larger objects. Dewatering with acetone may cause some wood shrinkage. Polymerization is rapid so that corrections can no longer be made. Heat produced during polymerization can cause shrinkage and warping in wood.

Treating Objects with PMMA in Solution

For dry and waterlogged wood, penetration of PMMA solutions, which have higher viscosity, is less than with MMA. Only part of the impregnated material, namely the solids content, is available to consolidate wood mainly in the surface layers. Penetration into the wood is uneven. Since no catalyst is present, the PMMA solutions are durable. Impregnation with dissolved PMMA takes time, and the subsequent evaporation of the solvent may extend over weeks or months. Residual solvents in the polymer have a plasticizing effect. Depending on the solvent used, wood may swell to a lesser or greater extent. In most cases insect frass remains unconsolidated. Owing to differences in application, namely complete impregnation of the entire object for MMA, and localized injection or infusion of PMMA solutions, the latter can also be used for polychrome objects and localized consolidation.

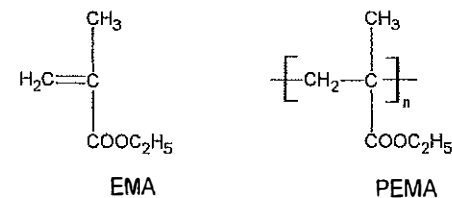
11.3.9.7

Poly(ethyl methacrylate)

Short designation: Monomer: EMA, polymer: PEMA

Trade names: In Germany: Paraloid B72 and Plexigum N 80; in USA: Acryloid B72. All are copolymers of EMA and methyl acrylate

Formula:



Properties: EMA is a colorless, clear-as-water, flammable liquid of unpleasant odor. Vapors form an explosive mixture with air. Strong oxidants can trigger a violent reaction or ignition. m.p. < -75°C; b.p. 117°C; not very soluble in water.

PEMA is clear as glass and hard. Paraloid B72 and Acryloid B72 (Rohm & Haas, Frankfurt/M. and Philadelphia) are granular, soluble in toluene, xylene, ethyl acetate, and acetone; insoluble in white spirit; can be dispersed in ethanol. Solutions in toluene can be diluted with ethanol or white spirit

Toxicology: EMA in liquid or vapor form irritates skin and mucous membranes. In severe cases nausea, vomiting, dizziness, feelings of oppression, and headaches can develop. Chronic poisoning is unknown. The odor is so disagreeable that concentrations high enough to cause irritation of mucous membranes and damaging absorption practically cannot be tolerated. PEMA is not dangerous to health

Analysis: EMA by GC; PEMA by IR spectroscopy

In Situ Polymerization of EMA with Dry and Waterlogged Wood

Not used for wood consolidation.

Uses of PEMA in Solution

Uses of the Copolymers Paraloid B72 or Acryloid B72 with

Dry Wood

Historical

Since 1950 Use of Paraloid B72 in conservation (Robson 1993).

1970 Caprara reports on the treatment of the Uffizi doors in Florence with Paraloid B72 in Shellsol.

Mihailov (1970a,b) uses Paraloid B72 in toluene to consolidate wood iconostases in several Bulgarian churches. Interior woodwork is coated with 8–15% solutions of Paraloid B72.

1974 Paraloid B72 as a 20% solution in toluene is recommended for the stabilization of wood objects of artistic value (Mihailov et al.).

Mitanov and Kabaivanov use 4, 8 and 10% solutions of Paraloid B72 for the consolidation of small boards with ground and paint layers.

1977 Treatment of a painted pine sculpture with Acryloid B72 by Wrubel.

1981 Report by Soldenhoff on the impregnation of linden wood with Paraloid B72, determination of consolidant distribution, and properties of the treated wood.

1982 Emmenegger (1983) mentions Paraloid in toluene or xylene as a material for partial consolidation of wood.

1984 Linden wood swells when impregnated with 20–27% (v/v) solutions of Paraloid B72 in toluene (Mateyak and Sheika).

A 15% solution of Butvar B98 produces greater improvement in bending strength of deteriorated Douglas-fir than an Acryloid B72 solution in acetone of equal concentration (Schniewind and Kronkright).

1985 According to Wang and Schniewind, Butvar B98 and B90 improve the strength of deteriorated Douglas-fir more than Acryloid B72. Solvent retention by the latter is observed.

1986 Hatchfield prepares a pourable filler for an ancient Egyptian mummy mask by mixing equal volume parts of 15% Acryloid B72 in an acetone and ethanol mixture (1:1) and glass microballoons with a diameter of 177 μm .

Kadry tests Paraloid B72 in trichloroethylene for consolidation of the Solar Boat of Cheops.

Camwood, a paste made from fibers of *Pterocarpus tinctorius* which is baked, can be stabilized with 5–10% solutions of Acryloid B72 in toluene (Pouliot 1988).

1987 Use of Paraloid B72 in various solvents for the consolidation of a chest of drawers (Czakó) and various chests (Petrovski, also Ujszaszy).

Paterakis investigates the properties of Paraloid B72 in regard to its use on a totem pole.

1988 Consolidation of intarsia doors of a church with Paraloid B72 (Canuti).

Acryloid B72 can be largely extracted by soaking with agitation at room temperature; the polar acetone is more effective than the nonpolar toluene (Schniewind).

Comparison of consolidation characteristics of Acryloid B72 with those of other thermoplastic resins (Schniewind 1990a).

1989 According to Aberle and Koller, a 10% solution of Paraloid B72 in a mixture of acetone, xylene, and Cellosolve (1:1:1) achieves excellent depth of penetration, but the solvents may be detrimental to oil paints and color luster.

Ten to 40% solutions of Paraloid B72 in toluene produce moderate to good strengthening of wood degraded by fungi or insects, but the wood is not fully impregnated (Cuany et al.).

The conference proceedings edited by Tampone (1989a,b) contain several contributions dealing with the application of dilute solutions of Paraloid B72 for the consolidation of wood in historic buildings.

1990 According to Carlson and Schniewind, the tendency toward solvent retention by Acryloid B72 and Butvar B98 makes solvents with low boiling points more suitable in order to minimize lowering of the glass transition temperature and the mechanical properties of the polymers.

The adhesive qualities of Acryloid B72 depend on the solvent used, where polar solvents lead to better results than nonpolar ones (Sakuno and Schniewind).

During consolidation with Acryloid B72 wood undergoes swelling depending on the solvent used (Schniewind 1990b).

According to Hansen et al., Paraloid B72 resists aging for >100 years. Verdu et al. discuss the aging characteristics of Paraloid B72 under exposure to gamma radiation, and Serck-Dewaide consolidates polychrome statues with the same material.

- 1992 Niedzielska stabilizes portions of a polychrome linden wood sculpture with a 20% solution of Acryloid B72 in xylene.

Schniewind and Eastman study the distribution and migration of Acryloid B72 in wood by SEM.

- 1993 Detailed investigation by Paciorek of consolidation with Paraloid B72 and other acrylates with regard to the influence of solvents, and the physical-mechanical properties, dimensional stability and resistance to biological agents of the treated wood. Vacuum impregnation of a polychrome sculpture with a 20% solution of Paraloid B72 in xylene results in complete saturation of the object without formation of surface barriers, as shown by CT analysis.

- 1994 Consolidation of wood panels painted black with a 5 or 10% solution of Paraloid in toluene, and gluing of wood parts with a thixotropic emulsion of acrylic resin by Nakasato.

- 1996 Paraloid B72 is one of the polymers used in conservation which are degraded only slowly by microorganisms (Heyn et al.).

Wood damaged by insects and sound wood treated with Paraloid B72 is attacked by egg larvae of house longhorn beetle (Unger, A et al. 1996; Unger, W et al. 1996).

Present Day

Paraloid B72 is one of the materials most often used for partial consolidation of wood objects. By combining solvents which are not very volatile with liquids which do not act as solvents, migration inside the wood is minimized and the time to solidification is extended. Solutions of 15–20% concentration in mixtures of toluene and various types of white spirit in ratios ranging from 2 : 1 to 9 : 1 have been recommended.

Uses of the Copolymers Paraloid B72 or Acryloid B72 with Waterlogged Wood

Historical

- 1981 Consolidation of a vermilion Japanese lacquer vessel by Sawada (1981b). The wood is first dewatered with increasing concentrations of ethanol, the ethanol is then replaced with xylene, and the xylene is exchanged stepwise for 3–7% solutions of Paraloid B72 in xylene. The lacquer coating completely maintains its adhesion to the wood base.

Present Day

Waterlogged wood objects are consolidated with Paraloid B72 only in exceptional cases.

Advantages/Disadvantages

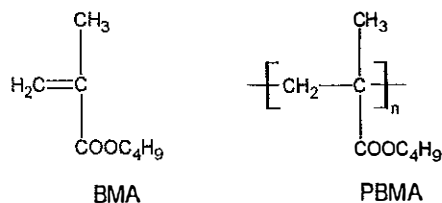
See PMMA solutions.

11.3.9.8

Poly(butyl methacrylate)

Short designation:	Monomer: BMA; polymer: PBMA	
Trade names:	Composition	Country
Plexigum P 26, P 28, P 675, PQ 610	<i>i</i> -PBMA	Germany
Plexisol P 550	<i>n</i> -PBMA, ca. 40% solids	
Xylamon or Basileum LX Härtend	<i>i</i> -PBMA (Plexigum P 28) since 1986, first with permethrin as a biocide, then without, then with fluoro. Ca. 30% solids	
Piaflex LT 30	Copolymer of MMA and BMA, 40% solution in toluene	Former East Germany
Solakryl BMX	Copolymer of BMA and MMA in xylene	Former Czechoslovakia
Osolan K	Copolymer of MMA and BMA (1:3); 50% solution in toluene	Poland
Osolan KL	50% solution of PBMA in ethyl acetate	
Bedacryl 122X	40% solution of PBMA in xylene	Great Britain
Elvacite 2013	Methyl methacrylate/ <i>n</i> -butyl methacrylate resin	USA
Paraloid B67	<i>i</i> -PBMA	

Formula:



Properties:

n-BMA is a colorless, clear-as-water, flammable liquid with an unpleasant odor; vapor forms an explosive mixture with air; b.p. 163 °C; not very soluble in water; miscible with acetone.

n-PBMA and *i*-PBMA are white powders; Plexigum P 26, P 28, P 675, PQ 610 are soluble in white spirit with ca. 20% aromatics, in esters and ketones; Plexigum P 28 is soluble in alcohol; Plexigum PQ 610 is soluble in white spirit free of aromatics; Plexisol P 550 contains white spirit as a solvent; Xylamon or Basileum LX Härtend early on contained trichloroethylene, later tetrachloroethylene, and finally Propylcellosolve acetate; Paraloid B67 is soluble in white spirit, *i*-propanol, *n*-butanol; insoluble in alcohol. Solutions in white spirit can be diluted with toluene or alcohol.

Toxicology:

n-BMA in high concentration can cause irritation of affected mucous membranes; in severe cases nausea, vomiting, dizziness, feelings of oppression, and headaches. Chronic poisoning is unknown. Odors are so disagreeable that damaging concentrations can hardly be tolerated. *n*-PBMA and *i*-PBMA represent no danger to health

Analysis:

GC for BMA; IR spectroscopy for PBMA

In Situ Polymerization of BMA with Dry Wood

Historical

- 1974 Consolidation of small boards, 15 × 50 × 130 mm, with paint layers using BMA (Mitanov and Kabaivanov 1974, 1975; cf. MMA).
- 1979 Stabilization of a wood statue with a mixture of MMA and BMA (cf. MMA).
- 1981 Šimůnková and Zelinger use BMA to produce improved wood (cf. MMA).
- 1988 Šimůnková, also Šimůnková et al. use polymerization by irradiation of BMA alone and in mixture with MMA on test samples with and without polychromy.

Present Day

In situ polymerization of BMA in wood objects is rarely used.

In Situ Polymerization of BMA with Waterlogged Wood

Historical

- 1964/1965 Nogid and Podzdnák treat bowls, spoons, arrows, spheres, and wedges of wood with BMA. The moisture in the objects is exchanged for acetone, and the acetone in turn is exchanged for BMA with 0.3–1% dibenzoyl peroxide. Polymerization of BMA in the wood is done at 65–95 °C over 8–9 h in a closed container. The surface of the wood is additionally consolidated with PBMA in xylene.
- 1977 Modification of the BMA treatment of waterlogged wood by De Jong (1977a). The objects are dewatered with tert-butanol until its azeotrope with water is reached. The azeotrope is then exchanged under vacuum for BMA with 1–3% dibenzoyl peroxide. The BMA is polymerized at 75 °C in 6 h, when tert-butanol and water are no longer liberated from the wood.
- 1988 Tran et al. (1990) describe the two-step exchange water-solvent and solvent-monomer, including *n*-BMA among others, and the following polymerization by irradiation in the wood.

Present Day

In situ polymerization of BMA is only rarely used for the stabilization of waterlogged wood.

PBMA in Solution with Dry Wood

Historical

- 1956 Plenderleith recommends Bedacryl 122 X in toluene for the consolidation of wooden works of art.
- 1970 Report by Gowers on the conservation of ethnographic objects with a solution of about 5% Bedacryl 122 X in acetone.
- 1972 Stabilization of charred carvings with PBMA in acetone (Gagen et al.).
- 1977 Vandyke-Lee uses Bedacryl 122 X for the consolidation of the wood of war shields. The paint layer is safeguarded with a 2% solution of Bedacryl 122 X in xylene.
- 1981 Treatment of polychrome wood sarcophagi with PBMA solutions by Natchinkina and Cheinina. Damaged areas on the surface of the objects are strengthened with a 8–12% solution of PBMA in acetone, and are then consolidated with a 10–15% solution of PBMA in xylene. The solution must be applied six to ten times while the objects are in a space saturated with xylene vapors to promote absorption of the solution. The impregnated sarcophagi are then dried.

- 1983 Vacuum impregnation of a polychrome wood sculpture damaged by insects with Solakryl BMX (Šimůnková). The object is wrapped with PE netting and placed inside a bag of 0.2mm-thick PE film. PE tubes are attached and sealed to both ends of the bag. The tube at the upper end is connected to a vacuum pump and the one at the lower end to the consolidant container. The air is evacuated from the bag and the consolidant, at a concentration of 18%, is drawn into the bag over a period of 20 min. The impregnation process is repeated five times and at the end any excess is washed off with toluene. Drying of the sculpture takes 80 days. At a depth of penetration of 25 mm a clear improvement of the physical and mechanical properties is obtained; appearance and coloration are not affected.
- 1984 Consolidation of crumbly parts of the Dürer Cabinet at the Wartburg, Germany, using Piaflex LT 30 with tributyltin oxide added (Michaelsen).
- 1985 Šimůnková and Škvaril impregnate deteriorated art objects in a PE bag with a 25% solution of PBMA in toluene using atmospheric or reduced pressure. PBMA loading after evaporation of the toluene is 33% for vacuum impregnation as compared to 17% when atmospheric pressure is employed. Vacuum impregnation is considered the superior process.
- 1986 Solutions of epoxy resin of low relative molecular mass are better suited for deep consolidation of wood than Solakryl BMX (Šimůnková).
- 1987 Xylamon LX Härtend is tested by Paterakis for its suitability as a consolidant for a totem pole.
Šimůnková and Josef use Solakryl BMX as a consolidant in historic buildings.
- 1988 Canuti uses Xylamon LX Härtend for the consolidation of church doors.
Belis et al. impregnate the wind-chests of two organs with an 18% solution of Solakryl BMX in toluene under vacuum.
According to Šimůnková and Josef, consolidant loading in wood increases with increases in solvent polarity when Solakryl BMX is used, but with polychrome objects caution in regard to swelling is indicated.
- 1989 Cuany et al. determine the properties of wood damaged by fungi and insects after consolidation with 10–40% solutions of Plexigum P 28 in white spirit. The solutions are applied dropwise to the samples. Penetration and distribution are only moderate.
Šimůnková and Josef compare the effect of solvents used with Solakryl BMX and a mixture of colophony and beeswax on water absorption and compressive strength of the treated wood. Polar solvents like alcohol improve the uptake of consolidants because they swell the wood. The mixture of colophony and beeswax, owing to its small molecular size and the resultant better penetration, achieves better values for water absorption and compressive strength than Solakryl BMX.

- 1990 Buchenrieder mentions the use of Xylamon LX Härtend in trichloroethylene and tetrachloroethylene for the consolidation of polychrome carvings.
- 1996 According to Unger A et al., insect-damaged samples consolidated with Plexigum P 28 have poor resistance to renewed attack by wood-destroying insects.

Present Day

PBMA, owing to its solubility in white spirit containing aromatics, is used in the form of various commercial products for the stabilization of wood objects deteriorated by fungi and insects, particularly in Europe.

PBMA in Solution with Waterlogged Wood

Present Day

PBMA in solution is used only in exceptional cases, such as consolidation of bamboo after dewatering.

Advantages/Disadvantages

BMA Impregnation of Wood and In Situ Polymerization

For dry wood, improvements in strength are considerable. Color and grain of unpainted wood remains largely unchanged. Stabilization of wood with ground and paint layers is possible. Since BMA has a higher boiling point, losses from evaporation during polymerization are less than with MMA. For additional information see under MMA.

For waterlogged wood, see under MMA.

Treatment of Objects with PBMA in Solution

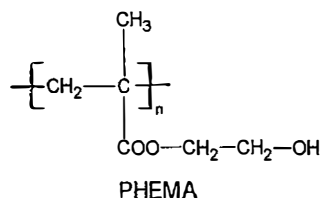
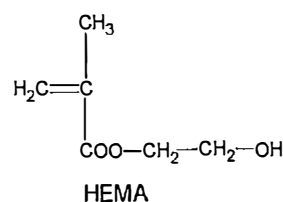
During treatment at normal pressure the dissolved PBMA will, depending on concentration, penetrate more or less deeply into the areas near the surface of insect and fungus damaged wood, but the depth of penetration can be increased significantly by using vacuum impregnation. Increased loading of polymer will also improve the strength properties of the wood. Treated objects react more slowly to changes in temperature and humidity, and texture and coloration of the wood are barely changed. The resistance to biological agents of wood treated with PBMA solutions, because of uneven penetration, is not as good as with in situ polymerization of BMA. See also under PMMA.

11.3.9.9

Poly(2-hydroxyethyl methacrylate) [Poly(glycol methacrylate)]

Short designation: Monomer: HEMA, polymer: PHEMA

Formula:



Properties: HEMA is a colorless liquid; b.p. 85–86°C at 0.67 kPa, 99°C at 1.60 kPa; readily soluble in water. PHEMA is a white powder soluble in organic solvents

Toxicology: For HEMA see under MMA; PHEMA does not present any danger to health

Analysis: GC for HEMA; IR spectroscopy for PHEMA

In Situ Polymerization of HEMA with Dry Wood

Historical

1974 Mitano and Kabaivanov consolidate small boards with ground and paint layers with HEMA using irradiation polymerization (cf. MMA).

In Situ Polymerization of HEMA with Waterlogged Wood

Historical

1967 Munnikendam impregnates oak samples with HEMA, encloses them in film, and exposes them to a ^{60}Co source with a dosage rate of 1 kGy/h (total dosage 50 kGy), but after treatment cracks form in the samples.

1972/1973 Further reports by Munnikendam (1972b, 1973) on the consolidation of waterlogged wood with HEMA. Oak samples are impregnated with the monomer which circulates under thermostatic control at 15°C for 2 months. Polymerization takes place at 70°C within 2 days, without addition of a catalyst and without using precautions to reduce monomer evaporation.

1975 De Jong (1975b) mentions the HEMA method.

1977 De Jong (1977a,b) exchanges water in wood for HEMA and effects polymerization with 2,2'-azobisisobutyronitrile or dibenzoyl peroxide and heat application.

1981 Šimůnková et al. impregnate oak samples 40 × 210 × 360 mm with a mixture of HEMA and MMA (80:20) at 12°C over 2 months. Polymerization takes place at 70°C in 2 days.

1982 According to Grattan (1982a), HEMA treatment of waterlogged wood gives poorer results than other methods.

1987 Evaluation of in situ polymerization of MMA, HEMA and other vinyl monomers in waterlogged wood by Grattan and Clarke. Disadvantages outweigh advantages.

1988 Tran et al. (1990) mention water-soluble, hydroxylated methacrylates as consolidants.

Present Day

HEMA has no importance for waterlogged wood conservation since it has only limited suitability for smaller objects.

Advantages/Disadvantages

For dry wood, according to Mitano and Kabaivanov (1974) the strengthening effect is good.

For waterlogged wood, water in wood can be exchanged for the monomer directly. Catalyst is not required for thermally activated polymerization. Strength improvements are sufficient. Thermally activated polymerization causes more wood shrinkage than the use of irradiation, but the latter leads to crack formation. HEMA swells wood, and Šimůnková et al. (1981) consider a mixture of HEMA and MMA (80:20) as more advantageous.

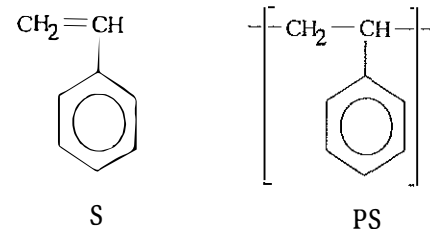
11.3.9.10

Styrene

Short designation: Monomer: S; polymer: PS

Trade names: For the polymer Styrodur and Styropor in Germany; Styron in USA

Formula:



Properties: S is a colorless, combustible liquid, not very fugitive, with a sweetly penetrating odor; b.p. 146°C; soluble in ethanol and diethyl ether, insoluble in water.

PS is a colorless, brittle product with a hard surface; soluble in chlorinated hydrocarbons, ketones, esters, benzene, dioxane, tetrahydrofuran and oil of turpentine; insoluble in water and ethanol

Toxicology: The liquid and concentrated vapors of the styrene monomer irritate skin, eyes, and the respiratory tract, and

cause disturbances of the central nervous system. Effects on well-being, dizziness, and nausea also occur. The styrene polymer presents no danger to health, but there are special rules for its use in food packaging

Analysis: GC for S; IR spectroscopy for PS

In Situ Polymerization of Styrene with Dry Wood

Historical

- 1975 Vacuum impregnation of museum objects with S followed by irradiation polymerization using a ^{60}Co source by De Tassigny.
- 1981 Treatment of pistol grips with mixtures containing S, MMA, polyester and crotonaldehyde, followed by thermo-catalytic polymerization (Unger et al. 1981a).
- 1982 Experiments by Schaudy et al. (1982a,b) on irradiation polymerization of consolidants, including determination of density, gel content, hardness and shrinkage.
- 1983 Impregnation of wood samples degraded by chemicals and fungi with monomers, including S, that can be polymerized by irradiation, by Schaudy and Slais. Total dosage for S, either alone or in mixture with other compounds, is 30 kGy. Uptake of consolidant and dimensional changes are determined.
- 1990 Gambetta and Orlandi impregnate test samples with S to saturation followed by thermo-catalytic polymerization. Test samples with a PS content of ca. 85% are exposed to attack by fungi, house longhorn beetle larvae, and marine borers. Mass loss is greatest by soft rot and by house longhorn beetle larvae of medium size. The modified wood is also attacked by marine borers.

Present Day

Styrene is rarely used in pure form, but most commonly in mixture with other polymerizable substances such as unsaturated polyester resins for the consolidation of individual objects.

In Situ Polymerization of Styrene with Waterlogged Wood

Historical

- 1966 De Guichen et al. impregnate samples of neolithic ash with pure S or in aqueous emulsion and effect polymerization with a ^{60}Co source (dosage rate 6 kGy/h). Results with styrene emulsions are not satisfactory.
- 1970 After exchange of the water in the wood, impregnation with a mixture of S and acrylonitrile (AN) and irradiation polymerization are possible (Brorson Christensen 1970a).

- 1981 Šimůnková et al. dewater wood either with methanol, ethanol or acetone and replace the solvent by S, or they extract the water directly with mixtures of S and either alcohol or acetone.

Present Day

In situ polymerization of S in waterlogged wood has only secondary importance for smaller wood finds.

Polystyrene in Solution with Dry Wood

Historical

- 1968 Czajnik cites PS solutions for the conservation of old wood in buildings.
- 1972 PS solutions can be used to consolidate polychrome wood (Šujanova).

Present Day

PS solutions are of no importance as consolidants.

Advantages/Disadvantages

Styrene Impregnation and In Situ Polymerization

For dry and waterlogged wood, objects damaged by insects and fungi can be impregnated almost completely. After polymerization, the strength of the wood is significantly increased, but the objects become rather hard and brittle. Styrene shrinks during polymerization; surface gloss does not develop. Chemically activated polymerization without application of heat is not possible. Thermo-catalytically polymerized S does not cross-link, but irradiation produces cross-linking. Wood modified with styrene burns with much soot formation.

Treatment of Objects with Polystyrene in Solution

For dry wood, regions near the surface of the wood are strengthened, but objects become hard and inflexible.

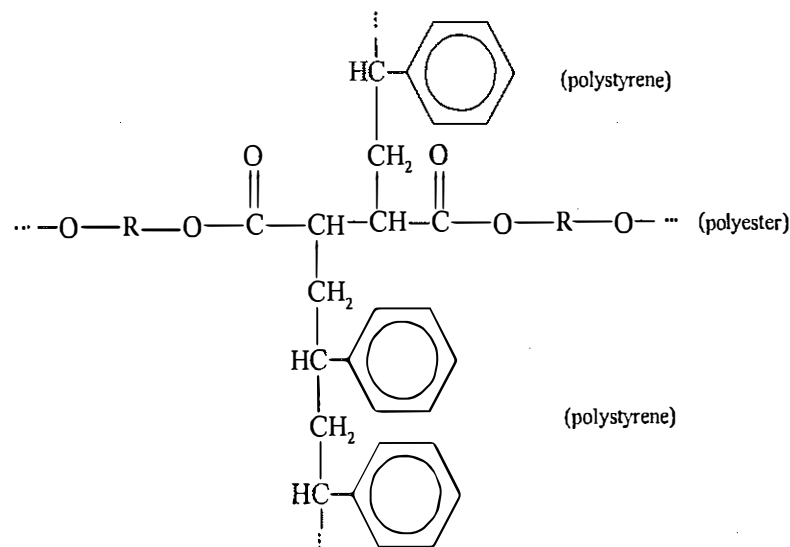
11.3.10

Unsaturated Polyester Resins

Short designation: UP

Trade names: In Germany: Leguval, Ludopal, Palatal, Vestopal; in the Netherlands: Synolite; in France: Stratyli; in Great Britain: Bondaglas, Crystik; in USA: Marco, Vibrin

Formula:



cross-linked polyester

- Properties:** UP resins are colorless to pale yellowish, viscous liquids; cross-linked UP resins are transparent, hard and brittle products. UP resins can be diluted with styrene and acetone; cross-linked UP resins can be dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol; lack resistance to acetone, benzene, chloroform, and ethyl acetate; resistant to hydrochloric acid, weak bases, and certain organic solvents
- Toxicology:** UP resins irritate eyes, conjunctiva, and mucous membranes of the throat because of their styrene component; skin and eyes can be etched by sprays of hardener (organic peroxides). Contact with accelerators such as metal soaps or tertiary amines can result in allergic skin diseases. Cross-linked UP resins do not represent any danger to health
- Analysis:** GC for UP resins; IR spectroscopy for cross-linked UP resins

Uses with Dry Wood

Historical

- 1934 Staudinger is the first to investigate cross-linking reactions of polyesters (Domininghaus 1998).

- 1936 Ellis and Forster obtain the first patent on the curing of unsaturated polyesters for molding tools (Domininghaus 1998).
- 1938 Production of UP glass fiber begins in USA (Koesling 1993a).
- 1956 Plenderleith lists Marco SB. 26C among consolidants for wood.
- 1963 According to Straub, UP resins of low viscosity have potential for wood consolidation.
- 1968 UP resins cure quickly without noticeable shrinkage (Aberle and Koller).
- 1970 Gowers reports on the treatment of ethnographic objects, including a canoe, with UP resin (Bondaglas). The objects are brushed with the resin, and voids are filled with a paste of resin and wood flour.
- 1972/1973 First research on the impregnation of cultural property of wood with styrene/polyester resins and curing by irradiation at the French Nuclear Research Center in Grenoble (Détanger et al. 1976).
- 1974 Schaffer impregnates test samples with the UP resin Vibrin 117. Depth of penetration is insufficient because of the viscosity of the resin.
- 1975 Vacuum impregnation of cultural property with UP resin diluted with styrene and irradiation with a ^{60}Co source by De Tassigny.
- 1980 Duval and Keisser use UP resins for the conservation of wooden beam-ends and girders by the Beta process.
- 1981 Characterization of the properties of old wood impregnated with styrene/polyester mixtures after irradiation curing by Mavroyannakis. Šimůnková and Zelinger also describe changes in wood properties after consolidation with UP resins.
For the treatment of pistol grips with mixtures of styrene, MMA and UP resin see under styrene.
- 1982 Schaudy et al. (1982a,b) investigate the properties of acryl-modified and unsaturated polyester resins after irradiation with a ^{60}Co source (cf. styrene).
- 1983 Impregnation of chemically or biologically degraded wood with Crystik UP R 176, Ludopal U 150, Stratyl 703 and Stratyl 750 followed by irradiation curing with a ^{60}Co source (dosage rate 7–8 kGy/h) by Schaudy and Slais. They also test a mixture of Ludopal U 150 and butyl acrylate (70:30).
- 1986 In 1982 Wagner and Chavannis had parts of a walnut chest treated by the "nucléart-method" of the Centre d'Etudes Nucléaires de Grenoble. First the insect infestation is killed off by irradiation and the wood is then consolidated with 50:50 mixture of styrene and polyester. Four years after the consolidation there is no evidence of aging.
- 1987 Use of UP resins with inorganic fillers for loss compensation in structural wood members using the Beta process by Erler.
Rumi uses the UP resin Titeron B 1 for the consolidation of the staves of a tub bottom, and fills missing areas with a mixture of the same resin and asbestos flakes (!).
- 1989 According to Aberle and Koller, UP resins are too hard and shrink too much during gluing and filling. Curing by irradiation of unpainted works of art appears to be problematic and too expensive.

- 1990 Further report by Erler on the use of UP resins extended with sand for the conservation of load-bearing wood members.
- 1995 Unger and Unger (1995b) review results to date on the resistance to biological agents of UP resin, alone or in the form of wood-polymer combinations.
- 1999 Review by Barthez et al. (1999a) of UP resin radiation-polymerization (Nucléart-method).

Present Day

When UP resins are used for the consolidation of cultural property it is usually with irradiation curing in certain countries such as France and Austria.

Uses with Waterlogged Wood

Historical

- 1959 Ketelsen exchanges the water in wood successively for ethanol, 2-propanol and acetone. The acetone is replaced by UP resin which is then cured. The wood shrinks 7%.
- 1969 Mühlethaler (1969a,b) mentions UP resins for the conservation of waterlogged wood finds.
- 1974 The water in wood is exchanged for a mixture of acetone and styrene/polyester in continuously running equipment (Détanger et al.). This is followed by curing with gamma radiation. Dimensional changes of the wood are kept to less than 2%.
- 1979 Detailed description by De Tassigny and Ginier-Gillet of irradiation curing of styrene/polyester mixtures. The object is dewatered in four successive acetone baths until the moisture content in the last bath is 1%. The acetone is then replaced by UP resin diluted with styrene (styrene content $\leq 50\%$) until an acetone content of 1% is reached. Impregnation time is 2 months for small objects, and 6 months for objects of up to 200 mm thickness. Irradiation is effected with a ^{60}Co source (dosage rate 625 Gy/h) at a total dosage of 30 kGy. Even warped wood can be brought back to its original shape during the treatment.
- 1981 Continuous extraction of water from waterlogged wood by the acetone-styrene/polyester system (Šimůnková et al.; cf. styrene).
- 1984 Ginier-Gillet et al. (1985) publish a further report on waterlogged wood conservation with UP resin and curing by irradiation. In addition to the improvements in physical and mechanical properties obtained by the treatment, the radiation also kills any microorganisms present in the wood.
- 1985 Consolidation of a freeze-dried object with Ludopal U 150 and irradiation curing (dosage rate 1 kGy/h) by Schaudy et al.

- 1988 Tran et al. (1990) describe the two-step exchange process for water insoluble consolidants such as UP resins followed by irradiation curing, and its effects on oak and beech wood.
- 1995 Schaudy mentions consolidation with styrene/polyester mixtures.

Present Day

UP resins are used for the consolidation of waterlogged wood finds only occasionally, for small objects.

Advantages/Disadvantages

For dry wood, the viscosity of curable UP resins is higher when compared with styrene and MMA, which results in less depth of penetration. In spite of this, considerable improvements in strength and resistance to wood-destroying organisms can be obtained. Shrinkage of the resin during curing is relatively low. UP resins cure irreversibly. When curing is done at room temperature, the surface of the objects can become sticky.

For waterlogged wood, users of the method give the following advantages: strengthening is permanent and homogeneous; cracks will close during curing; relative humidity changes and light do not cause any changes; the natural appearance of the wood is largely preserved; dating is still possible after conservation; and wood treated with Arigal C (cf. melamine-formaldehyde resins) can be retreated with UP resins. If the exchange of acetone for UP resin in the two-step process is insufficient, cracks will form after several months. It is therefore mandatory that the acetone content in the wood is reduced to $<1\%$.

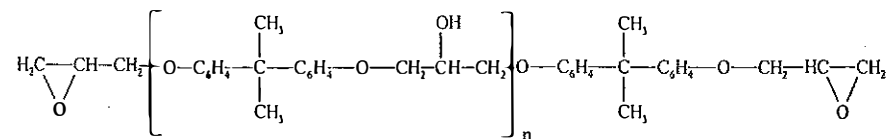
Other polyester resins: Gerasimova et al. (1981) tested poly(caprolactone) oligomers for the conservation of waterlogged wood.

11.3.11 Epoxy Resins

Short designation: EP

Trade names: In Austria: EP-BM 09; in Germany: Epikote, Rütapox; in Poland: Epidian; in the former Czechoslovakia: ChS Epoxy; in Hungary: Tipox; in Switzerland: Araldite, Master-Model-Paste (Araldite SV 426/HY 426 and microballoons); in the Netherlands: Setalux; in Norway: Epoxy Em; in USA: DOW DER, Shell Epon, ERL

Formula:



linear polyether



amine-cured epoxy resin

Properties: EP resins: viscous liquids, colorless, yellow, or brown. Cross-linked EP resins are hard, transparent products often of pale yellow color; EP resins are soluble in ketones, esters, aromatic and chlorinated hydrocarbons; cross-linked EP resins are largely resistant to organic solvents, but will swell greatly in 1,2-dichloromethane, 1,3-dioxolane, and in certain solvent mixtures (von Derschau and Unger 1998)

Toxicology: During processing of EP resins, hardeners such as acid anhydrides, multivalent amines and polyamino amides, as well as thinners can cause severe irritation of skin and mucous membranes. Cross-linked EP resins represent no danger to health, provided that excess hardener is not present

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

- 1934 Schlack produces phenolic poly(glycidyl ether)s (Domininghaus 1998).
- 1938 Castan obtains EP during laboratory experiments and applies for a patent (Domininghaus 1998).
- 1946 Ciba-Geigy begins production of EP (Koesling 1993a).
- 1956 Surface treatments of art objects with EP (Plenderleith). The resin does not shrink.
- 1958 The EP resin Upon 300 AC is suitable for the impregnation of severely deteriorated wood (Losos). A mixture of EP and polyamide can be used to treat wood panel paintings. However, the mixture forms a yellowed film which must be washed off with acetone.

1959 EP can be used to consolidate wood damaged by insects (Werner).

1963 Straub describes a very successful consolidation of a wood panel with dilute EP, without any ill effects on the oil paint layer.

Successful conservation of wooden head masks with EP by Werner.

1965 Attempts to impregnate the hull of the *Fram*, Norway, with an EP and coal tar compound in the presence of an amine hardener (Gaudel 1969).

1966 Manková impregnates samples of linden and oak with ChS Epoxy 2200 and 300 AC in the presence of triethylene tetramine as hardener. EP resins are well suited for stabilizing wood.

Mühlethaler describes the treatment of the surface of the dugout canoe of Kentmere, Great Britain, with a mixture of 50 mass parts Araldite CY 219, 25 mass parts hardener HY 977, 1 mass part accelerator CY 830 and 10 mass parts dibutyl phthalate. The outer, scale-like, flaking layers of the oak are satisfactorily consolidated.

1966/1967 Mühlethaler reports on the consolidation of a wood Buddha statue with Araldite GY 252 and hardener CY 208.

1968 EP hardens without noticeable shrinkage (Aberle and Koller).

According to Czajnik, wood is better protected against fungal attack with EP than with PVA or PMMA.

Domasłowski publishes results of the conservation of wood specimens with the resin Epidian 5.

Consolidation of insect-damaged wood panel paintings and sculptures with Araldite CY 219 (Lodewijks).

Consolidation of a polychrome wood statue from the fourteenth century with EP (Stehlik).

1970 Araldite SV 426 is well suited to fill cracks in cultural property made of wood (Iwasaki and Higuchi). It can be worked easily and permits the use of wooden nails.

1971 According to Munnikendam, impregnation of sculptures with thinned EP (Epon 812) results in a clear surface and great flexibility.

Schaffer treats moderately and severely attacked wood with the EP prepolymer ERL-2795 to which 10% butylglycidyl ether (ERL-0810) and 5% toluene have been added. As hardener, a polyamine (ZZL-0872) was added with the ratio of resin solution to hardener being 100:7. Moderately deteriorated wood is brushed with the prepolymer solution until uptake ceases, and is post-treated with pure solvent, achieving a maximum depth of penetration of 25 mm. Severely deteriorated wood is saturated with toluene over 4 h, then submerged in the prepolymer solution for 24 h and then allowed to dry for 30 days. If the solution has a high toluene content the EP is not transparent after curing. Impregnation results in very minor dimensional changes.

1972 Munnikendam (1972a) presents possibilities of reducing the viscosity of EP by adding reactive thinners. He uses a mixture of bisphenol A-diglycidyl ether and 11-13% butylglycidyl ether (viscosity 500-700 mPa·s) as the starting product (trade names Ciba Araldite 506,

Araldite E and H, DOW DER 334, Shell Epon 815, Union Carbide ERL-2795). This product is thinned either with 20% butylglycidyl ether or with 10% butylglycidyl ether and 5–25% toluene. However, most suitable is an EP mixture of 49.6% butanedioldiglycidyl ether (DY 022), 21.2% poly(propyleneglycol)-diglycidyl ether (DOW DER 736), 24.6% menthandiamine (Rütapox SG) and 4.8% 2-butanone. The strengthening effect is good, and tempera and oil paints are not affected.

Šujanova considers EP unsuitable for wood consolidation because of lack of reversibility.

- 1973 Balm applies for a patent for a special mixing head for injecting EP into wood.

Mühlethaler describes methods for protecting wood objects placed outdoors. Among others he prepares a mixture of 150 g Araldite laminating resin 556, 22.5 g Araldite R-D-1 and 44 g hardener 956. To this mixture he adds 120 g nitro lacquer or epoxy resin thinner and brushes it onto the wood. The object dries for a few days before the mixture, with another 60 g thinner added, is brushed onto the wood again. Following a period of drying the wood is treated with the undiluted mixture. Broken parts are joined with Araldite adhesive.

In Japan, wood members of historic buildings – Fukiji temple and tea house Jo-an – are consolidated with EP (Sekino 1973a). Fills for cracks and missing areas are made with Araldite SV 426 (phenolic resin mixed with EP). Surface treatment of damaged wood members is done with EP modified with Thiokols (trade name for thioplastics) to which fillers and pigments have been added. Important parts are stiffened with glass fiber fabric and EP.

- 1975 Nakasato consolidates a lacquered wooden saddle with Araldite SV 426 in order to prevent warping and flaking of the lacquer layers.

- 1977 Avent repairs timber trusses with EP. The resins are injected into cracks and splits under pressure. The method is not suitable for wood with fungal decay.

Consolidation of a cedar panel with EP by Higuchi (1978). After 2000 h of weather exposure neither cracks nor areas of flaking are noticeable.

Detailed discussion by Mühlethaler on the consolidation of porous organic materials with Araldite.

Stumes (1978) introduces the WER-system (wood-epoxy-reinforcement) for the stabilization and compensation of deteriorated structural wood members with EP and reinforcing bars. He also presents methods for nondestructive testing of the strength properties of the wood before and after the treatment (cf. Chap. 6).

Vandyke-Lee fills cracks in wooden war shields with EP.

- 1978 Hellwig consolidates insect-damaged parts of old musical instruments with Araldite 103/HY 991. For parts which contribute to the sound the resin is diluted with 20% toluene.

Introduction of the Dutch Beta process (cf. the WER system of Stumes 1978) for the conservation of beam-ends with EP by Klapwijk.

Bars of glass fiber-reinforced polyester are inserted into the decayed beam-ends before form work is applied. The forms are then filled with a gravel, sand and quartz mortar using a low viscosity EP as binder.

Oellermann describes the consolidation of a wood cross with diluted EP.

Comprehensive report by Phillips and Selwyn on the use of EP on building timbers in historic buildings.

Tintori and Rothe report on a process for the prevention of shrinkage of wood panel paintings using PVA and EP as well as a laminated stripboard.

Reinforcement of a 5 mm-thick panel painting using Master-Model-Paste to attach balsa blocks to the reverse (von Imhoff).

- 1979 Bosshard publishes his results on the consolidation of timber walls deteriorated by insects and fungi with EP in the form of a mixture of 100 mass parts Araldite DY 026, 40 mass parts hardener HY 2996 (polyamine) and 10% xylene. At the front of the walls the resin is injected into voids with a syringe and it is also brushed over the entire unpainted surface. Prewetting with acetone leads to more uniform distribution of the resin. Holes 150 mm apart are bored from the back diagonally into the edges of the walls, and thin glass tubes are inserted into the holes which are filled first with acetone, then several times with EP. To counteract the deepening of color by the EP mixture, the surface can be worked over with a wire brush.

Paul and Stumes conserve wood building members according to the Beta and WER processes, respectively.

- 1980 Use of the Beta process by Duval and Keisser (cf. UP resins).

Reinforcement of wood columns with glass fibers and EP (Higuchi et al.). A filler of EP and glass microballoons is used for loss compensation.

- 1981 Bratlie consolidates a ship model deteriorated by insects with the EP Epsilon E 1210-A/B.

Paul describes the stabilization of wood members of a half-timbered gable with EP by the Beta process.

Peters treats structural timbers and carvings of a Maori meeting house with low viscosity EP.

Šimůnková and Zelinger discuss changes in wood properties after impregnation with EP. The resin reduces wood hygroscopicity less and increases compression strength less than PMMA.

Contribution by Waterhouse on the use of the Beta process as an alternative to the complete removal of severely deteriorated wood.

- 1982 Consolidation of a timber wall with EP (Bosshard and English 1983, cf. Bosshard 1979).

Reinforcement of timber beams with bars and EP (Crisp).

Emmenegger (1983) uses different EP mixtures for wood members of moderate and severe degradation. Mixture 1 consists of Araldite BY 155 (100g) and hardener HY 2996 (26g); Mixture 2 of Araldite BY 158

(100g) and hardener HY 2996 (28 g). Both mixtures can be thinned with acetone or xylene at ratios of 1:5 to 1:7, where the use of xylene can lead to darkening of the wood surface.

Horioka and Higuchi (1983) reinforce portions of cultural property degraded by fungi and insects with EP modified with fillers.

Irradiation curing of acryl-modified EP and determination of properties by Schaudy et al. (1982a,b; cf. UP resin).

- 1983 Bratlie consolidates decayed wood in Norwegian stave churches with Araldite DY 026/HY 2996 or Epoxy Em 7530 A/B.

Heller uses carvable Araldite paste (AV 1253/HV1253) on wood panels.

Schaudy and Slais impregnate chemically and biologically degraded wood samples with a mixture of 60 parts Setalux UV-2276 and 40 parts butyl acetate and cure it with a total irradiation dosage of 30 kGy. The resulting dimensional changes are determined.

Vacuum impregnation of cultural property with EP of low relative molecular mass (ChS Epoxy 15) and determination of depth of penetration and dimensional stability of the wood by Šimůnková. Excess EP on the wood surface can only be removed with difficulty after curing. Wood swelling is not influenced significantly (Šimůnková and Zelinger).

- 1984 Determination of temperature effects on the epoxy to wood bond strength in the range of 21–260°C by Avent and Issa. Changes in epoxy-repaired joints in response to sudden exposure to high temperatures ranging from 95–165°C are measured.

Cebecauer and Straková use ChS Epoxy 300 AC and ChS Epoxy 1200 for the consolidation of deteriorated wood ceilings by the Beta process.

According to Rowell and Ellis, EP of low relative molecular mass will react with the hydroxyl groups in the cell wall if a weakly alkaline catalyst is added.

Schiessl lists advantages and disadvantages of the use of EP in wood consolidation.

- 1985 Schniewind reports on the use of EP modified with Thiokol and with sawdust filler, as well as use of Araldite SV 426 with microballoons for loss compensation in wood parts in Japan.
- 1985/1986 Consolidation of window frames with EP Sinmast Typ S 4 (Anonymous). Two parts resin and 1 part hardener are mixed and thinned to double the volume with butyl acetate. The mixture has a pot life of several hours and penetrates well into wood. The window frames are given a liberal brushing on the outside, and this is repeated while the first coat is still wet. Curing takes 1–2 days. A mixture of Sinmast S 4, pigments and filler, as well as Aerosil to impart thixotropy, is used as a gap filler.
- 1986 Avent (1986a,b) tests EP lap joints in wood for the influence of length of overlap, member thickness, grain orientation, wood age, and glue line thickness on joint shear strength.

According to Šimůnková, only an EP solution of low relative molecular mass is comparable to the acrylic copolymers Solakryl BMX and Petrifo for deep impregnation of wood.

- 1987 Hungarian conservators re-build missing parts of various wood objects such as chests, office furniture, and pails with Araldite SV 426 (Kiss) and Araldite SV 427 (Csere, Scheinring, also Vámosi). For chests, Araldite AW 106 (Lukács) and Tipox IHS (Morgós) are also used.

Paterakis tests the suitability of Araldite DY 026/HY 2996 and Ritapox R 1210 for the consolidation of a totem pole.

- 1988 Grattan and Barclay investigate the properties of 33 gap fillers, including EP with microballoons (cf. Chap. 12).

Wermuth (1990) uses dilute EP solutions for the stabilization of deteriorated wood.

- 1989 Aberle and Koller discuss advantages and disadvantages of EP such as Araldite and Sinmast in regard to structural strengthening, filling of voids, darkening under exposure to light, irreversible curing, and impairment of wettability and gluability. Master-Model-Paste is mentioned as a proven gap filler.

Tests of EP Araldite AZ 3456 with furfuryl alcohol as solvent, hardener 3456 and phenolic microballoons as gap filler for a totem pole (Barclay and Mathias).

Cuany et al. use Araldite BY 158 (200 g) and hardener HY 2996 (56 g) in a solvent mixture of xylene, ethyl acetate and isopropanol (75:15:10, 256 g) as well as Araldite DY 026, hardener 2996 and 10% xylene in the mass ratio of 100:40:14 for the consolidation of test samples deteriorated by fungi and insects. Besides the advantage of good strengthening, heat generation during curing and very serious discoloration are given as disadvantages.

Petersohn stabilizes the edges of a panel painting by cutting V-grooves and filling these with a mixture of Araldite AW 134, HY 994 and balsa wood flour. This step is also expected to act as a preventive against insect attack.

Prandtstetten explains the use of the Beta process.

The conference proceedings edited by Tampone (1989a,b) contain various applications of EP, such as Araldite and Eposet, in conservation of historic structures (Beta process, bore hole impregnation with EP) and of museum objects.

- 1990 Consolidation and loss compensation of a carriage with Araldite SV 427 and hardener HV 427 by Leconte and Oudry.

Prange stabilizes a dugout canoe, oar blades, and deck boards with Araldite D and hardener HY 956.

Use of EP by Rama Rao and Pandit Rao for the consolidation of an ox cart.

Tomaszewski et al. test 29 gap fillers of polyurethane and EP with wood fibers or wood flour added.

- 1992 Basic contribution by Selwitz on stone conservation with EP. The sections on chemistry, resin properties such as penetration capacity, discoloration, and bioresistance, as well as on the influence of solvents are also of great importance to the use of EP for wood objects.
- 1993 Paciorek impregnates linden wood samples with a mixture of 20% Araldite LY 554 in toluene and methanol (1 : 4). Damage to the wood structure after evaporation of solvent was observed by means of CT (cf. Chap. 6).
- 1995 Schniewind (1998) summarizes results to date with the use of EP for wood consolidation.
According to Unger and Unger (1995b), EP resins have good to very good bioresistance.
- 1996 Splitting open the test specimens of insect-damaged wood which were impregnated by Cuany et al. (1989) with Araldite BY 158 and Araldite DY 026, Unger et al. discover that the interior of the wood is sticky, which is attributed to residual solvent. The higher the EP content of treated wood, the greater its resistance to the larvae of wood-destroying beetles.
- 1997 Consolidation of polychrome wood sculptures with a 20% solution of the epoxy resin EP-BM 09 in alcohol/acetone (80/20; Höring and Richard).
- 1999 Modification with EP of wood attacked by the brown-rot fungus *Coniophora puteana* improves the modulus of elasticity and the modulus of rupture (Reinprecht and Varinska).

Present Day

EP resins are used above all in architectural and structural conservation for the consolidation and compensation of damaged building timbers, including important load-bearing members, by methods such as the Beta process and the WER system. Polyester rods reinforced with glass fibers and lamellae of carbon fibers are used for armatures. The resins are also often used for the conservation of museum objects placed outdoors. Wood sculptures, panel paintings and other valuable art objects are usually treated with EP only when they are degraded severely to very severely. Polyacrylates in solution can no longer provide sufficient strengthening in such cases.

Uses with Waterlogged Wood

The exchange of water in the wood, which is customary with other polymers, for solvents which can dissolve the polymer and transport it into the wood is not used with EP. Application of EP is therefore limited to objects which have been dewatered by other means or which have already been dried.

Historical

- 1954/1956 The surface of the parts of the *Oseberg* Ship, Norway, which had been impregnated with alum is sealed with Epolack, an epoxide ester of fatty acids in linseed oil. The resulting light surface is made matt with Mattolakk 565A (Rosenqvist 1969a,b).
- 1959 According to Werner, waterlogged wood with little degradation is dried slowly and its surface is then brushed with EP.
- 1961 Description of the conservation of a dugout canoe by Werner. The canoe is packed in sand at a cool place. After drying, EP can be brushed on in three coats. The EP mixture is composed of 50 parts Araldite CY 219, 25 parts hardener HY 219, 1 part accelerator DY 219 and 10 parts dibutyl phthalate.
- 1964 Consolidation of archaeological wood building members with a mixture of ChS Epoxy 300 AC and ethanol (1:1; Kordač). Before treatment 3.5 parts diethylene triamine or 4.5 parts dipropylene triamine are added to 100 parts resin.
- 1979 Bill reports on the consolidation of a woven helmet. The object is pretreated with EP, freeze-dried, and finally impregnated with low viscosity EP.
- 1996 Morgós (1999a) uses Araldite BY 158 with the hardener HY 2996 dissolved in xylene (resin concentration 10–30%) for the consolidation of extremely degraded, dried out oak timbers of a burial chamber. Holes and gaps are filled with a 10 or 20% solution of Paraloid B72 in xylene.
- 1999 Further report on low relative molecular mass EP treatment by Morgós (1999b).

Present Day

EP resins have only limited importance for waterlogged wood stabilization after the wood has been dried.

Advantages/Disadvantages

For dry and waterlogged wood, EP resins shrink minimally during curing. Cold curing is possible. The resins have good adhesion, high strength and flexibility, maintain their shape well at elevated temperatures and have favorable aging characteristics. Resistance to attack by fungi, insects and bacteria is good, and standard-reaction resins are not very combustible. Low relative molecular mass reaction products are not formed. Standard EP resins have a relatively high viscosity, resulting on average in less penetration compared with other polymers. Thinning with customary solvents or with so-called reactive thinners, the depth of penetration can be increased significantly. The heat liberated during curing of some EP resins can be detrimental to the wood structure. The dimensional stability of the wood is

not much improved by EP impregnation. In many cases impregnation of EP results in a deepening of the object's color. Gloss formation must also be expected. Cured EP resins are fixed irreversibly in the wood. Residuals of cured resin on the surface can be removed only mechanically, possibly after swelling with solvents, and with difficulty. Some EP resins tend to yellow. Recipes for mixing and curing of EP must be followed exactly, since pot life and compatibility with the wood substance depend on them. Excess of highly alkaline amine hardener can cause damage to the wood as well as any paint layers.

11.3.12

Linear Polyamides

Short designation: PA

Trade names: Soluble nylon is the name generally used for *N*-alkoxymethyl-polyamides; in Germany: Ultramid, Zytel; in Great Britain: Calaton (*N*-methoxymethyl-nylon), Calaton CB (original name: Maranyl Soluble Nylon C 109/P); in USA: Elvamide 8063.

Formula: $\cdots - \text{CH}_2 - \underset{\substack{\text{O} \\ \parallel}}{\text{C}} - \underset{\substack{| \\ \text{CH}_2\text{OR}}}{\text{N}} - \text{CH}_2 - \cdots$ R = alkyl group such as CH_3 -
soluble nylon
(from nylon 66, formaldehyde and an alcohol)

Properties: Soluble nylon is a white powder or an aqueous emulsion; m.p. 100–160 °C depending on the degree of substitution of nylon 6,6; soluble in methanol, ethanol and their mixtures with water and chloroform; also soluble in thymol and phenols; insoluble in aliphatic and chlorinated hydrocarbons, esters and ketones

Toxicology: No danger to health

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

1927/1928 Research on the production of polyamides begins under Carothers (Domininghaus 1998).

1938 Du Pont starts experimental production of nylon (Koesling 1993a).

1958/1959 Werner (1958, 1959) introduces soluble nylon as a new material for the conservation of porous objects. Soluble salts can be washed out with water after treatment.

1961 Marijnissen mentions soluble nylon for wood consolidation.

1966 For the conservation of wood sculptures 50 g Calaton CA should be dissolved in 50 ml water and 400 ml methanol, and 400 ml dichloromethane should then be added (Mager-Maag).

According to Schiessl (1984), paper conservators raised concerns regarding soluble nylon beginning no later than 1966 because of serious yellowing within a few months.

1969 Werner again lists soluble nylon as a new product for conservation. Using a 5% solution in alcohol reportedly produces a film on objects which is flexible, permeable to water vapor, free of shrinkage cracks and which forms a matte surface.

1970 Use of 5–8% solutions of Calaton CA in ethanol for the consolidation and protection of carvings and interior woodwork (Mihailov 1970a,b).

1977 According to Vandyke-Lee, Calaton CB is suitable for the consolidation of paint layers.

1979 Hüchel treats a sarcophagus with Calaton and Ponal (PVA).

1981 Detailed contribution by Sease, in which she recommends against the use of soluble nylon for the conservation of objects mainly because of its poor aging characteristics.

1984 Bockhoff et al. investigate soluble nylon by IR spectroscopy and find that within a relatively short time it will cross-link and thus become insoluble.

Critical evaluation of soluble nylon by Schiessl.

1988 Schniewind (1990) mentions the disadvantages of soluble nylon.

1995 As part of a discussion of consolidants for wood painting supports Schniewind (1998) also mentions the disadvantages of soluble nylon.

1998 Augerson uses Hydral ZF, a nylon and Kevlar product, instead of wooden dowels, because of its great flexibility.

Present Day

Soluble polyamides are not used in wood conservation because of their disadvantageous properties.

Advantages/Disadvantages

For dry wood, the depth of penetration of soluble nylon is shallow, so that only surface layers are consolidated. Films formed on the surface become dirty and dusty. They discolor objects, and darken paint layers. The nylon film is shiny and does not turn matte. It shrinks greatly, and parts of the object surface tend to flake off with the film. The film loses its flexibility over time, and becomes insoluble. Permeability to water, however, remains unchanged for extended periods.

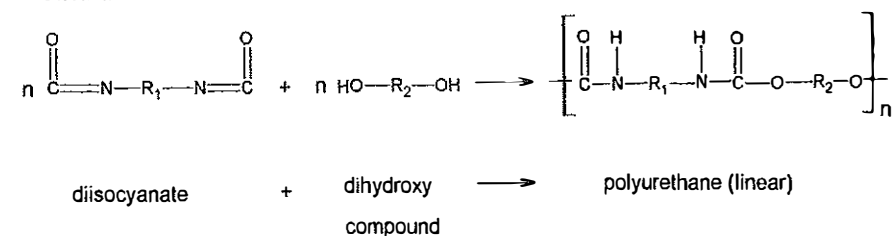
Other amid polymers: Poly(2-ethyl-2-oxazoline) (PEOX) has been used to secure paint layers to the porous wood substance of an armchair and other objects (Wolbers et al. 1998).

11.3.13 Polyurethanes

Short designation: PUR

Trade names: For multifunctional isocyanates Desmodur in Germany and Adiprene in USA; for polyhydroxy compounds Desmophen in Germany and Vibrathane in USA

Formula:



R_1 : e.g. $-(\text{CH}_2)_6-$; R_2 : e.g. $-(\text{CH}_2)_4-$

Properties: Cross-linked polyurethanes are not soluble without decomposition. Rigid foams of PUR which can serve a support function in severely degraded wood objects are resistant to aliphatic hydrocarbons and oils. They have limited resistance to hot water, alcohols, and ethers, and are not resistant to ketones and esters. They are partially soluble in dimethyl formamide and tetrahydrofuran

Toxicology: During application, cross-linking agents (isocyanates) can cause irritation of mucous membranes and the respiratory tract; extended exposure leads to bronchial and asthmatic complaints. Even small splashes to the eye can result in severe irritation. Repeated exposure can lead to damaged skin. Some isocyanates are carcinogenic and tumorigenic. Fully hardened PUR is not toxic

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

1937 O. Bayer begins development of PUR products (Domininghaus 1998).

1938 Du Pont takes up PUR research in USA (Domininghaus 1998).

After 1945 PUR becomes a material used in technology.

1973 Reinforcement of damaged wood building members with isocyanate prepolymers by Nakasato and Higuchi (see also Sekino 1973b). Weathering tests under natural conditions show no cracks after 3 years.

1974 According to a patent of Avella-Shaw for the dimensional stabilization of wood with PEG and isocyanates, the material is impregnated for 2 days with a 50% solution of PEG 100, 400 or 1000, and is then heated under a vacuum of 266.6Pa to 40–120°C. Liquid diisocyanates such as diisocyanato-toluene are then drawn by the existing vacuum into the impregnation tank containing the wood. The diisocyanates evaporate quickly and diffuse into the wood already impregnated with PEG, where they form polyurethanes.

1975 Strengthening of a wood saddle with isocyanate resin (Washcoat B) by Nakasato.

1977 Higuchi (1978) uses mixtures of isocyanate and PEG to consolidate damaged wood objects.

1981 Consolidation treatments of structural members in historic buildings in Japan (Higuchi).

1988 Rowell (1990) describes chemical modification of cell wall constituents with difunctional isocyanates as a possible approach for wood conservation.

Wermuth (1990) presents case studies in wood conservation where PUR foam is used to construct an inner and an outer matrix for objects.

1991 Brewer investigates, among other materials, a commercial PUR coating with regard to moisture sorption using test panels of four wood species.

1995 Rapp and Peek test polyisocyanate emulsions and PUR dispersions for the improvement of wood properties, namely water uptake, dimensional stability, bioresistance and mechanical properties.

1996 Paterakis fills losses in an iconostasis with the PUR resin A 2244.

Present Day

PUR foams are used especially in Japan and the USA to fill void spaces and to build up a supporting skeleton in damaged structural members of historic buildings, and for individual objects. Polyurethane varnishes are also used as surface treatments of wood objects exposed to the weather.

Uses with Waterlogged Wood

Historical

1965 Noack presents a method for gluing waterlogged wood treated with PEG. The PEG is first removed from the treated wood surface with toluene. The parts are then heated to the melting point of the particular PEG used, and then soaked for 1 h in a 25% solution of Desmodur L in ethyl acetate of the same temperature. When the parts are taken from the solution, the solvent evaporates so that the parts must be joined immediately.

1989 PUR foam is used to encase a boat for transport (Anonymous).

Present Day

PUR is not used for the internal consolidation of the wood structure, but does find application in the form of protective foam for the transport of waterlogged wood finds.

Advantages/Disadvantages

For dry and waterlogged wood, internal and external supports of PUR foam can improve the mechanical stability of severely degraded wood objects significantly, but PUR foams and varnishes adhere practically irreversibly to the wood surface. PUR foams without biocides do not resist termite attack (Unger and Unger 1984). Brown-rot and soft-rot fungi will colonize the foams but will not attack them (Unger and Doblinski 1976). Chemical modification of cultural property of wood with isocyanates (cf. Rowell 1990) should be rejected for conservation because of the irreversibility of the treatment and the extensive changes to the original wood structure.

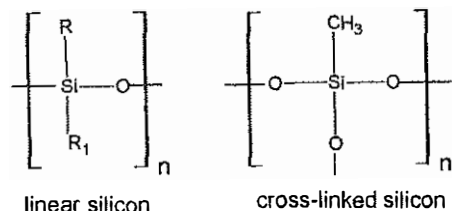
11.3.14

Organosilicon Compounds (Silicons, Polysiloxanes)

Short designation: SI, TEOS [tetraethyl (ortho)silicate, tetraethoxysilane]

Trade names: In Germany: Wacker Silicone, Baysilon; in USA: Silastic, Silastomer

Formulas:



tetraethyl(ortho)silicate: $\text{Si}(\text{OC}_2\text{H}_5)_4$

Properties:

Depending on the choice of initial components and intermediate products, and the processing method, liquid, oil-like silicons; solid, resin-like silicons; or elastic, rubbery silicons can be prepared. Silicon oils are clear-as-water liquids of low vapor pressure which can be heated to their boiling point without decomposition; soluble in benzene, gasoline, and tetrachloromethane. Silicon greases: highly viscous products which become neither solid nor liquid. Silicon dispersions: water-soluble products. Silicon resins: three-dimensionally cross-linked products with high surface hardness but low flexibility; resistant to temperature and weathering. Silicon varnishes: solutions of silicon resins in toluene, xylene, and other organic solvents.

Rigid silicon foam: insulation material incombustible in the temperature range from -180 to $+180^\circ\text{C}$. Silicon rubber: rubbery, deformable, strong swelling in polar and aromatic solvents. Silicic acid ester (alkyl silicate, alkoxysilane): liquids susceptible to hydrolysis. Tetraethyl (ortho)silicate: colorless, combustible liquid; b.p. 165 – 166°C ; hydrolyses in water, miscible with ethanol

Toxicology: Silicons do not give rise to any physiological concerns. Tetraethyl(ortho)silicate is poisonous, and irritates eyes, the respiratory tract and the skin

Analysis: IR spectroscopy

Uses with Dry Wood

Historical

- 1901 F.S. Kipping discovers the condensation of silanols to silicons (Koesling 1993a).
- 1931 The work of J.F. Hyde begins at Corning Glass Works (Domininghaus 1998).
- 1943 Silicons appear on the market in the USA (Koesling 1993a).
- 1974/1976 Reports by Kim and Won (1974a,b) and Kim et al. (1975a,b,c, 1976a,b) on experiments for the stabilization of historic wood remains with silicon resins. The wood is impregnated with poly(dimethylsiloxane-co-phenylsiloxane) or poly(phenylsiloxane) at 20°C over 50 h. The first compound is reacted by the addition of 5% tetraethoxysilane-dibutyltin-bis-2-ethylhexanoate at 20°C . The uptake of silicon by the wood is about 10–30%. Pretreatment of the wood with organic solvents has no effect on the penetration of the resin. The aging characteristics of poly(dimethylsiloxane-co-diphenylsiloxane) reportedly are better than those of poly(methyl methacrylate).
- 1976 Golubtsova et al. (1977) use organosilicon compounds to strengthen deteriorated wood parts. They prepare a mixture of the organosilicate E-2 and poly(butyl methacrylate) in toluene (1:1) and brush this on the wood surface. The wood regains 60–70% of its original strength and after treatment has high resistance to decay fungi.
- 1987 Barclay and Grattan use mixtures of silicon rubber [poly(dimethylsiloxane)] and microballoons as gap fillers. Dow Corning 734 RTV releases acetic acid during curing, Dow Corning 738 RTV releases methanol (RTV = room temperature vulcanizing). Phenolic resin or glass microballoons range in particle size from 0.005–0.125 mm, the ratio of silicon rubber to microballoons being 2.5 to 3:1. Flexibility in the joined crack is assured.

Treatment of wood with silicon acrylates and description of the properties of the composite materials by Morgós and Czikovsky.

Makes and Pühringer recommend as a preventive treatment against mold fungi impregnation with alkoxysilanes and making the surface hydrophobic with alkylsilanes. Alkoxysilanes consolidate the wood at the same time.

Storch uses the silicon rubbers 734 RTV and 738 RTV to fill cracks in a gate.

1988/1989 Reports by Fries et al. (1988) and Fries (1989) on the treatment of resonance wood with Ethylsilicate 40 (partially condensed tetraethoxysilicate with 40% SiO₂).

1993 Morgós (1993b) uses reactive silicon oils to prevent water adsorption by wood.

1994 Pokrovskaya et al. propose a two-step treatment to consolidate degraded wood with oligo(furfuryloxysiloxane) (08 HS 1.50) and benzenesulfonic acids as hardener.

Report by Storch on the use of RTV silicones as gap filler for architectural wood members. Their flexibility is considered a particular advantage in view of movement of wood with climatic variations.

Present Day

Silicones are used mainly as flexible materials to rejoin and seal cracks and splits in wood. They are also used on wood surfaces to make them hydrophobic. Additional uses are as adhesives, for casting forms, and for isolating wood from metals such as aluminum which are susceptible to corrosion. Modern furniture polishes often contain silicones.

Uses with Waterlogged Wood

Historical

1965 The hull of the *Wasa*, Sweden, is sprayed with a mixture of PEG, boric acid, borax, and methylpolysiloxane (Modolog antiqua; Barkman, cf. PEG).

1975 Testing of TEOS for the protection of waterlogged wood by Semczak.

Yashvili reports on the conservation of various archaeological wood finds with α,ω -di-(methyl methacrylate)-dimethylsiloxane oligomers. Oak remains are soaked in an oligomer in the presence of 0.1–0.5% of an organic peroxide such as dibenzoyl peroxide for 2–18 days. The tank with the samples is then heated to 55–60 °C. The polymerization of the oligomer takes place within 1–48 h. Silicon films on the surface are removed mechanically. A wooden funeral bed barrow is first bleached with 5% hydrogen peroxide and the water in the wood is then exchanged for ethanol and ether. After the siloxane oligomer is added, the ether is evaporated by increased air circulation and polymerization

of the oligomer is effected at 55 °C. Wooden charters are brushed with a solution of the polymer in benzene.

1976 Waterlogged wood is dewatered with acetone and submerged in a solution of TEOS in acetone (Irwin and Wessen 1976; Irwin 1977). After the acetone evaporates, the TEOS hydrolyzes under formation of silicon dioxide.

Leo and Barghoorn dip heated wood first into water and then impregnate it with an aqueous solution of TEOS. For curing, the object is kept for several months in a heat chamber and finally treated with a mixture of nitric acid and potassium chlorate.

1977 Further report by Semczak on treating waterlogged wood with TEOS.

1978 Yashvili recommends the following siloxanes for the stabilization of larger objects such as beams: poly(siloxane), poly(methylsiloxane), poly(phenylsiloxane), poly(methylphenylsiloxane), poly(aminohydrosiloxane) and poly(cyclosiloxane). The siloxanes in the form of aqueous emulsions are brushed on the object three times a day, the object is then pressure impregnated, followed by slow heating from 40 to 100 °C in a heating chamber or with infrared lamps.

1979 Bright conserves a canoe with TEOS.

1981 According to Jespersen (1982), stabilization of waterlogged wood with TEOS should be avoided.

1982 Grattan (1982a,b) evaluates the TEOS method using wood samples of various degrees of degradation.

1983 Xu mentions in situ polymerization of organosilicon compounds.

1987 Description and evaluation of the use of TEOS on waterlogged wood by Grattan and Clarke.

1988 Patent of Jones for the rapid silicification of wood artifacts with silicon chelates, such as catechol chelate in the form of the ammonium salt, by soaking for 8 days at 20–25 °C under exclusion of air.

1992 Sawada comments on the conservation of waterlogged wood with silicon resins.

Present Day

Generally, waterlogged wood finds are conserved only rarely with organosilicon compounds, but silicones are often used in the recovery of finds and for taking casts.

Advantages/Disadvantages

For dry wood, dimensional stability and strength of the objects are increased by the treatment. They show high resistance to fungal attack and have satisfactory aging characteristics. Color and grain of the wood are changed little. Organosilicon compounds become irreversibly fixed in the wood. Waxes and polishes containing silicon should therefore not be used for furniture.

For waterlogged wood, objects silicified with TEOS have increased stability and AES, but the grain pattern becomes reversed. Deposits of white silicates on the surface impair the aesthetic appearance of the objects. Often cracks develop, and the wood becomes brittle.

After treatment with acrylate-siloxane oligomers the wood surface reportedly appears natural and shows neither sheen nor color changes. Treated objects reportedly shrink little and remain free of cracks. After 6 months of artificial weathering, the aging characteristics were found to be satisfactory.

Silicon emulsions can consolidate the wood surface layers and make them hydrophobic to a depth of 4–5 mm.

11.4 Consolidation Processes

11.4.1 Nature of Consolidation Processes

Consolidation of dry wood involves two phases, the first being the partial or total impregnation of the wood with consolidant, and the second its curing. In principle, the same processes used for treating objects with wood preservatives (cf. Chap. 7) are also applicable for the impregnation of wood with consolidants, and will therefore not be discussed here further. Criteria for the selection of impregnation methods have already been dealt with in Section 11.1. Procedures for curing depend on whether polymers or other materials in solution are used, or whether consolidation involves the polymerization of monomers, oligomers, or prepolymers. In the first case it is merely a matter of removing the solvent at atmospheric or reduced pressure, whereas in the second an *in situ* polymerization has to be initiated. A fundamental difference between the use of polymers in solution and polymerizable materials is that with the latter almost the entire amount of consolidant introduced into the wood serves for the stabilization of the object. The amount of consolidant transported into the wood structure by a solvent is by comparison significantly less. The curing process determines how well the impregnated materials are fixed within the wood structure, and what the appearance of the consolidated object will be. The curing process must not have any detrimental effects on the wood, and it is therefore important that in the case of two-part systems for *in situ* polymerization the mixing ratios of polymer and hardener are strictly observed. It is also important that during curing no reaction products are split off which could damage the wood if they remained for extended periods.

In the case of waterlogged wood it is imperative that the water is removed from the wood without collapse of the cell structure with its attendant irreversible changes in form and shape of the object. The primary drying process can be combined with simultaneous consolidation, but carefully dried objects could also later be consolidated with soluble polymers. The water in wood can

be exchanged either directly for water-soluble materials such as PEG, sucrose, or 2-hydroxyethyl methacrylate, or initially for water miscible organic solvents. Most often dewatering of wood is done in a multi-step process with different organic solvents. In the last step the solvent, which is now almost free of water, is exchanged for a solution of polymer in the same solvent, or for a monomer or prepolymer for *in situ* polymerization.

Careful conservation of waterlogged wood without dewatering baths combined with consolidation is possible by artificial or natural freeze-drying or controlled drying in drying chambers or in air. It has been found, however, that partial exchange of water for miscible substances such as PEG types of low relative molecular mass followed by freeze-drying generally leads to better results.

11.4.2 Evaporation Processes

When dry wood is consolidated with solutions of polymers in organic solvents the latter must be allowed to evaporate. The rate of evaporation depends on the particular solvent and technological conditions. In general, solvents should not leave the wood too fast in order to avoid reverse migration of the consolidant and the formation of a shell in the surface layers of the object. The rate of evaporation can be controlled to some extent by covering the impregnated wood with films of different degrees of vapor permeability. However, if rapid removal of solvent is desired, reduced pressure chambers or containers connected to a vacuum pump might be indicated.

Complete evaporation of organic solvents can be very time consuming. Incomplete removal of solvent causes disadvantageous changes in the physical and mechanical properties of the consolidant and consequently the object. Large residues of organic solvents remaining in the core of the wood could subsequently redissolve already solidified consolidant near the surface, e.g. in the case of acrylates. Since most organic solvents give rise to concerns from a toxicological point of view, evaporation must occur under suitable exhaust systems.

11.4.3 Chemical and Physico-Chemical Curing Processes

The polymerization of monomers, oligomers and prepolymers can be initiated by (1) chemicals serving as catalysts, initiators, hardeners, or accelerators; (2) thermal activation; and (3) photochemical activation in the form of gamma or UV radiation.

The above methods may also be used in combination, e.g. in thermocatalytic processes.

Curing by means of chemical substances has the greatest importance for wood consolidation, where a distinction is made between processes at room

temperature or at elevated temperatures. With some synthetics such as epoxy resins the addition of a hardener is sufficient for room temperature curing, but for others such as methyl methacrylate and unsaturated polyester resins an accelerator is required in addition to the initiator. In curing at elevated temperatures the catalyst is activated by the application of heat. In general, room temperature curing is to be preferred for cultural property because, especially in the case of polychrome objects, the application of heat can cause irreversible changes and accelerated aging. With certain consolidants such as methacrylates, their vapor pressure is raised so much by the elevated temperature that, in spite of wrapping, large quantities of consolidant escape from the impregnated object. Although room temperature curing does not require heat application, the reaction is often exothermic, which might cause some damage to the impregnated object. Consolidants to which catalysts or hardeners have been added have a limited pot life during which they remain usable. With some consolidants containing catalysts it is possible to block the curing process, or slow it down significantly, by inhibitors or by temperature reduction. Curing time may be a matter of minutes, hours, or days depending on the consolidant. Heat transfer and bringing the object to temperature in thermo-catalytic processes can be effected in drying chambers, with heating blankets, with flexible heating tapes, or in heating baths containing liquids such as oils. In well-equipped conservation laboratories, in situ polymerization in objects which are not excessively large are definitely possible. For waterlogged wood prior dewatering with non-aqueous solvents is necessary in most cases. In some countries such as France (De Tassigny 1975; Ramière 1975; Tran et al. 1990), Austria (Schaudy 1995) and in Czechoslovakia (Urban et al. 1978) some of the cultural property needing consolidation is or was treated by irradiation. Gamma radiation can kill off wood-destroying organisms and activate in situ polymerization of acrylic and unsaturated polyester resins. In the past, mobile irradiation facilities were available by which in situ polymerization after full impregnation of objects with polymerizable compounds was possible on location. Radionuclides such as ^{60}Co and ^{137}Cs , as well as electron accelerators are possible activators for in situ polymerization. Impregnated objects which are wrapped in film or put into a suitable container are treated in a protective atmosphere such as pure nitrogen or argon at room or slightly elevated temperature. The dosage required ranges from 10 to maximally 100 kGy. The greater the dosage rate capacity of the facility and the higher the temperature, the faster the curing process will be. Irradiated objects do not become radioactive because the applied energy is insufficient to trigger nuclear processes. Excess impregnant remains serviceable because catalysts are not required. Irradiation can be done at room temperature so that, in contrast to thermo-catalytic processes, objects are not subjected to any external thermal load. The costs for establishing, running, and maintaining stationary irradiation facilities are high. Objects must be taken to the facility with the attendant danger of damage to the object during transport. If too

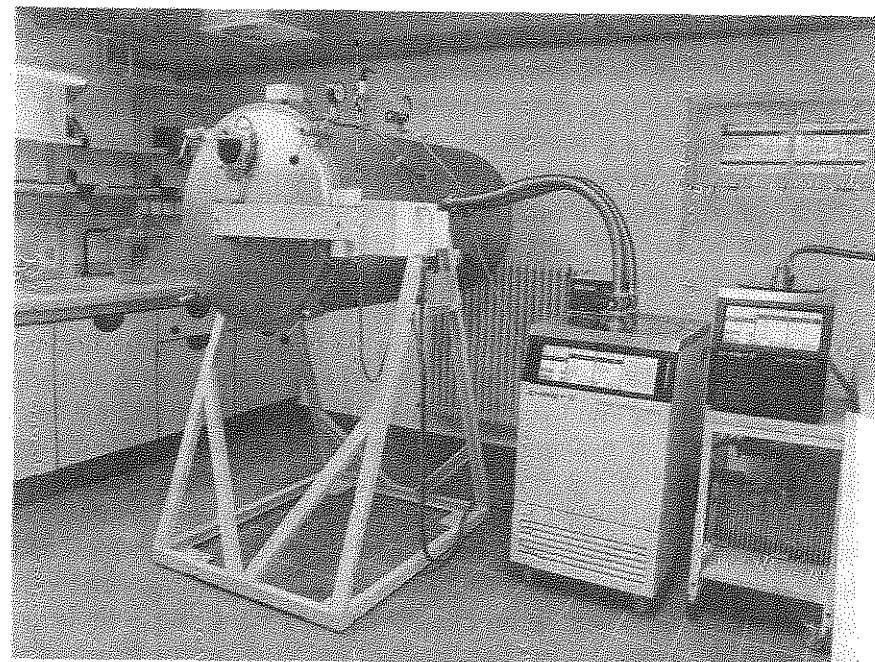


Fig. 11.6. Facility for freeze-drying. (Photograph courtesy of S. Brather)

high a dosage is applied, irreversible damage to the wood and any paint layers can be expected.

11.4.4

Drying Processes for Waterlogged Wood

Dewatering waterlogged wood can be done by freeze-drying (Brown et al. 1994; Fig. 11.6), supercritical drying with carbon dioxide after replacing the water with methanol and 2,2-dimethoxypropane (Kaye and Cole-Hamilton 1995, 1999), controlled drying only (De Jong et al. 1981) or after PEG impregnation (Tran et al. 1997), kiln drying after spraying boron-based fungicides mixed with PEG (Rice and O'Guiness Carlson 1997), and by exchange with solvents (e.g. Jensen et al. 1994). Freeze-drying generally takes place in vacuum, but can also be done at atmospheric pressure or under natural climatic conditions. Waterlogged wood with minor damage is often pretreated with an aqueous solution of about 10% PEG 200 or 400 [cf. Sect. 11.3.6.3, poly(ethylene glycol)s]. Severely damaged wood is treated with a mixture of high relative molecular mass PEG types, or is dewatered with tert-butanol which is then exchanged for a mixture of tert-butanol and PEG 4000. Objects are frozen in a container with solid carbon dioxide or in a freezer chest, before

they are placed on the heating coils in the vacuum chamber of the freeze-drying equipment. The chamber is evacuated with a vacuum pump and the heating coils holding the object are slowly heated under continuous evacuation. The sublimating ice and any pretreatment materials are collected in a condenser. The object is dry when 0°C is reached.

Freeze-drying under vacuum can take several hours, days, but also weeks depending on object size. Objects shrink little and do not warp much. Even poorly preserved, severely degraded wood can be conserved satisfactorily. Color and appearance of the wood surface remain well preserved, inscriptions become more legible, and in the dry condition anatomical studies are possible. Treated objects can be dated by the ^{14}C method, provided that no pretreatment materials had been introduced prior to freeze-drying. Severely degraded, freeze-dried wood is often very light and fragile, so that a subsequent consolidation is necessary. The construction of large freeze-drying facilities is very costly (Kelly 1980), so that usually only small to medium size waterlogged wood finds with a high degree of degradation are treated in this manner. Objects range from rune woods, writing tablets, wooden tools and household utensils, to boat equipment such as paddles, dugout canoe remains, and shipwreck parts. Bark and basketry can also be treated satisfactorily.

Methods and facilities for freeze-drying without vacuum have been introduced by McCawley et al. (1982) and Drocourt and Morel-Deledalle (1983). The latter authors have described the drying of the Roman ship of Marseille, France. The ship timbers are placed on a frame in a drying chamber and cold nitrogen is passed over them, which freezes the water in the wood. An extremely dry air stream is then blown over the wood surface at 20 km/h, removing the ice crystals, which later change into water droplets, by sublimation. The dried objects do not show any noticeable changes in color or structure, and should be stored at low temperature and relative humidity. Lorin and Lemetayer (1999) have improved and simplified this method for practical use.

Natural freeze-drying is a special case of freeze-drying without vacuum. It can be used in locations where winter temperatures are consistently low and strong air currents are common (Grattan and McCawley 1978; Grattan et al. 1980; Grattan et al. 1981; Bergeron 1987; Ambrose 1990; Lu Heng and Zheng Youming 1992). Waterlogged wood is impregnated with 10 or 15% aqueous solutions of PEG 400 and frozen with solid carbon dioxide. The wood is brought outside when temperatures fall below 0°C and placed into a specially constructed shelter or into tents of plastic film with openings. If natural air movement is insufficient, fans may be used. Under the right conditions the objects will dry in 2–3 months, with no more than moderate shrinkage.

In countries without extended periods of low temperatures large, moderately damaged waterlogged wood finds such as shipwrecks can be treated by controlled drying (De Jong et al. 1981). In these cases the wood is slowly air-dried, often after pretreatment with PEG.

Small objects can be dewatered with water-miscible organic solvents such as ethanol, acetone, and tert-butanol, and dried in this manner. Objects of medium size, however, often experience dimensional changes when dewatered with solvents, so that in step-wise exchanges a consolidant is added to the last solvent. Examples are the ethanol-ether-dammar method (Kramer 1979) and the acetone-colophony method (McKerrell et al. 1972). Disadvantages are the health and safety dangers inherent in the use of large amounts of volatile solvents.

11.4.5

Methods of Stabilizing Waterlogged Wood with PEG

PEG serving as a consolidant can be introduced into waterlogged wood in one-step or two-step processes. Early PEG treatments placed the waterlogged wood into an impregnation tank with a single type of PEG, using a batch or a continuous process. PEG 4000 was most common, but PEG 1000, 1450 and 1500 were also used. Examples are the ship timbers of the *Wasa* in Sweden, the Viking ships from the Roskilde-Fjord in Denmark, the *Brown's Ferry Vessel* in the USA and the *Batavia* in Australia. The concentration of the initial aqueous solutions is usually 10–20%, rarely 30% or higher. By slow elevation of temperature to 60–90°C, successive addition of PEG, and evaporation of water, the concentration of PEG is raised to 70–90%, depending on object size, over periods of months or years. Large objects such as the hull of the *Wasa* are sprayed with 10–15% aqueous solutions of PEG 1500 or PEG 4000 (Håfors 1990) or by brushing the surface with the solution. The disadvantage of using a single type of PEG is that in waterlogged wood finds of oak with unevenly degraded regions, uniform impregnation and stabilization are not possible. Hoffmann (1986a,b) therefore recommends a two-step process. In the first step PEG of low relative molecular mass such as PEG 200, is used in the form of 10–15% aqueous solutions, followed by raising the concentration to 40–50% at room temperature. For the second step PEG of high relative molecular mass such as PEG 3000 is used as a 40–50% aqueous solution. By raising the temperature to 60°C, the concentration slowly increases to 70%. The objects are finally air-dried. Hoffmann (1997a) has reported on the status of the conservation of the *Bremen Cog*, which is being treated by the two-step method. Recently, attempts are being made to improve PEG treatments by using supercritical carbon dioxide (Coeuré et al. 1998). It may be possible in this manner to limit treatments to a single type of PEG and still achieve satisfactory stabilization of wood with regions of different degrees of degradation. Ultimately, reductions in treatment times might also be possible. All treatments using PEG, but also those using sugar, require the addition of biocides to the treating solutions to prevent microbial attack, which must be considered a disadvantage in regard to handling and eventual disposal of the solutions.

11.4.6

Methods of Stabilizing Waterlogged Wood/Iron Composites

When waterlogged wood finds have metal parts attached, it is often not possible to treat them separately because the metal is too fragile and the extent of corrosion too great. Sometimes the metal is already completely corroded and the corrosion salt products have been deposited within the wood structure. Iron compounds in the form of chlorides, sulfides, oxyhydroxides and tannates are especially frequent. The iron compounds contained in the wood interfere with PEG treatments and must first be removed as much as possible, and the weakly acidic PEG solutions attack the metal when wood and iron are treated simultaneously, so that corrosion inhibitors must be added.

McKerrell et al. (1972) and Bryce et al. (1975) use 3.5% hydrochloric acid with their acetone/rosin method in order to convert any iron in the wood into chlorides and dissolve them. Neutralization is best achieved with a dilute solution of ammonia. Iron compounds may also be removed by dipping the object into a 5% aqueous solution of the disodium salt of EDTA (Murray 1982), but this leaves iron sulfides practically undissolved. Ramière (1988) also used oxalic acid in addition to Na-EDTA. Grattan and Clarke (1987) list the latter in addition to 1–5% thioglycolic acid; and citric, formic and acetic acids as 9% solutions for the removal of iron corrosion products. According to MacLeod et al. (1991), a clear relationship exists between the degree of degradation and surface pH of the wood, and the formation of iron corrosion products. They use 0.25 M ammonium citrate and ammonium oxalate as complex formers to dissolve the compounds. In the case of ammonium citrate solution, a pretreatment with sodium dithionite strongly reduces surface corrosion products such as FeO(OH) and brings them into solution. MacLeod et al. (1989) had already found that the optimum concentration of PEG 1500 is about 5–10% for the extraction of iron corrosion products and chloride ions. Combining these findings, chlorides of corroded iron can be extracted most effectively by using 2% (w/v) ammonium citrate solutions combined with a 5% (w/v) PEG 400 solution of neutral pH (MacLeod et al. 1994).

In addition to desalting waterlogged wood finds containing iron, the use of corrosion inhibitors before and after PEG treatment is of great interest. Among the corrosion inhibitors tested by Cook et al. (1985) is also Hostacor KS 1, a triethanolamine salt of Hostacor H, an arylsulfonamido-carboxylic acid (Anonymous 1996), which in the amount of 1% added to a 20% aqueous PEG 400 solution is an effective inhibitor without affecting the dimensional stabilization of the wood.

Gilberg et al. (1989) test Hostacor KS 1 on cast iron and steel, and Starling (1989) uses the corrosion inhibitor for metal/wood composites as well as metal/wood/leather composites. The results confirm good inhibitory action without impairing the stabilization of the materials. Long-term tests also gave good results (Binnie 1991; Selwyn et al. 1993). After the manufacturer replaced Hostacor KS 1 by Hostacor IT (triethanolamine salt of an acylamido-

carboxylic acid), Argyropoulos et al. (1999) could show that the new product is also suitable for the conservation of wood/iron composites, and that iron corrosion is prevented by the reaction with the oxygen in the PEG solutions.

When waterlogged wood is treated with PEG without the addition of inhibitor, oxidation of iron sulfides in the wood can lower the pH so much that the wood is attacked. Richards (1990) therefore applies a treatment with gaseous ammonia, to form less aggressive iron oxyhydroxides and ammonium iron sulfates. To stabilize fragile wood, treatment with Luviskol [poly(vinyl pyrrolidone)] is recommended.

11.4.7

Post-treatment Damage by Consolidants and Possible Remedies

Recent times have increasingly seen the discovery of sometimes serious damage in wood objects or waterlogged wood finds which were consolidated decades earlier. The following factors are viewed as causes:

1. Incomplete curing,
2. Residual solvents,
3. Increasing aging of the consolidant, often accompanied by irreversible changes in formerly reversible materials,
4. Effects of secondary components such as impurities from the manufacturing process of the consolidants or intentional additives such as plasticizers,
5. Climatic changes, especially relative humidity fluctuations, which can cause blooming, surface deposits and sweating of consolidants, especially in treated waterlogged wood, and
6. Colonization and attack on consolidants by biological pests.

The most notable cases of damage are the result of long-established use of natural consolidants such as oils, resins and waxes. Especially with linseed oil, alone or in mixtures with other materials, serious damage can occur in treated objects. As is known, linseed oil hardens by reaction with oxygen in the air with an increase in volume. If wood severely damaged by insects has taken up large quantities of consolidants containing linseed oil, the drying or hardening proceeds from the outside to the inside in a process that may go on for years, and later the shell of the object may burst open, allowing consolidant to leak out. The linseed oil inside wood can also be attacked by bacteria, giving the objects the odor of rancid butter. Conifer resins can also cause damage. For example, pearls of the resin have formed on the surface of painted furniture impregnated with resin from *Pinus pinaster* (Fig. 11.7), presumably initiated by the solvent dichloromethane which remained trapped for many years, and furthered by climatic fluctuations (Weidner et al. 1999). Degradation of the semisynthetic consolidants cellulose acetate and cellulose nitrate can be catalyzed by metals. Manufacturing impurities in the product in the form of acetic, sulfuric and nitric acids form salts with the metals which are



Fig. 11.7. Damage to painted furniture after impregnation with resin. (Photograph courtesy of T. Weidner)

then responsible for the gradual degradation of the polymers. A particular example of a synthetic polymer with poor aging characteristics is soluble nylon (cf. linear polyamides). When this is used to stabilize painted objects it can, some time later, cause such stresses that paint particles, together with parts of the wood support, flake off. Further details on aging of conservation materials can be found in Hansen and Bishop (1998). In the area of waterlogged wood conservation, the damage to objects impregnated with alum should be mentioned, which manifest themselves in the form of white blooming on the surface.

As to remedies for damage caused by wood consolidants, these are in their infancy. To date, all efforts have been directed to the removal of the materials with suitable solvents. Often it is only possible to reduce the concentration of the offending substance in the surface layers. Treatment of consolidated polychrome objects is especially difficult, and a very careful choice of solvent is necessary so that the paint layers are neither dissolved nor swelled. Solvent gels can be very helpful in controlling the remedial process. In objects impregnated with as much as 40 or 50% linseed oil or rosin, only some of the material can be removed in a reasonable length of time by extraction with supercritical carbon dioxide with modifier added, because most of the interior void spaces of the wood – cracks, insect tunnels, cell lumina – are filled with the consolidant. Solvents can only penetrate with difficulty, and the time for dissolution and transport of the consolidant becomes very lengthy. In analogy to the wax immersion method of Rosen (cf. beeswax), Hatchfield and Koestler (1987) removed the paraffin wax of a prior consolidation treatment

from archaeological wood with toluene, and consolidated again with acrylic resin in toluene. SEM examination showed that although some of the wax remained, the consolidation with the acrylic resin improved strength and appearance of the wood. However, after extraction with toluene without subsequent consolidation, considerable damage was observed. Even in wood samples first consolidated with acrylic resin which was then extracted, damage was noted. The residual wax appears to prevent dimensional changes during the subsequent treatment with another consolidant. Care must be taken to assure that the old and the new consolidants are compatible. The old consolidant or its components could, for instance, have a plasticizing effect on the new consolidant, which would reduce its strength and that of the treated wood.

References

- Aberle B, Koller M (1968) Konservierung von Holzsulpturen. Probleme und Methoden. Institut für Österreichische Kunstforschung des Bundesdenkmalamtes, Wien (AATA 8-761)
- Aberle B, Koller M (1989) Restauratorische Holzfestigung und die Infusionstränkung. Restauratorenblätter 10:73–78
- Agrawal OP, Bisht AS (1968) Technical examination and conservation of a wooden object. Stud Museol IV:55–58 (AATA 8-1293)
- Alagna P (1977) The construction of the treatment tanks used in the conservation of the wood of the *Marsala* Punic Ship. Stud Conserv 22(3):158–160 (AATA 15-393)
- Albright AB (1966) The preservation of small waterlogged wood specimens with polyethylene glycol. Curator 9(3):228–234
- Ambrose WR (1970) Freeze-drying of swamp-degraded wood. IIC Conference on the Conservation of Stone and Wooden Objects, New York 1970, Preprints, London, vol2, pp 53–57 (AATA 8-742)
- Ambrose WR (1972) The treatment of swamp degraded wood by freeze-drying. ICOM Committee for Conservation, 3rd Triennial Meeting, Madrid 1972, 6/72/1 (AATA 14-95)
- Ambrose WR (1975) Stabilizing degraded swamp wood by freeze-drying. ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/8/4 (AATA 13-257)
- Ambrose WR (1976) Sublimation drying of degraded wet wood. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol1, pp7–15 (AATA 13-893)
- Ambrose WR (1977) Question period following: sublimation drying of degraded wet wood. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol2, pp 39–40 (AATA 14-136)
- Ambrose WR (1990) Application of freeze-drying to archaeological wood. In: Rowell RM, Barbour RJ (eds) Archaeological wood: properties, chemistry, and preservation. American Chemical Society, Washington DC. Adv Chem Ser 225:235–261 (AATA 27-1938)
- Ankner D (1969a) La conservation des objets préhistoriques en bois humide. ICOMOS Symposium on the Weathering of Wood, Ludwigsburg (Germany), 8–11 June 1969, pp 33–39 (AATA 11-548, 13-658)
- Ankner D (1969b) Zur Konservierung vorgeschichtlicher Feuchtholzfunde. Dtsch Kunst Denkmalpflege 27:105–110
- Ankner D (1972) Zur Konservierung vorgeschichtlicher Feuchtholzfunde. Arbeitsbl Restaur 5(1) Gruppe 8:58–67 (AATA 9-621)
- Anonymous (1894) Merkbuch, Alterthümer auszugraben und aufzubewahren (Eine Anleitung für das Verfahren bei Ausgrabungen sowie zum Konservieren vor- und frühgeschichtlicher Alterthümer), Berlin

- Anonymous (1909) Anleitung zur Imprägnierung wurmstichigen Holzes. Mitt KK Zentr Kom 8(9):426-427
- Anonymous (1935) Zeittafel zur Holzkonservierung. Holzmarkt 52:102
- Anonymous (1955) Frage nach dem derzeitigen Stand von Holzverfestigungsmitteln. Maltechnik 61(3):96
- Anonymous (1975) Stabilizing wood with sugar. Paint Manuf 45(2):25; also in Double Liaison 22(234):38 (AATA 13-262)
- Anonymous (1981) Carbowax polyethylene glycols. Union Carbide Corporation, Ethylene Oxide Derivatives, Dunbury, CT
- Anonymous (1983a) Archaeologists experiment with sucrose in preservation of waterlogged wood. Council for Museum Anthropology, Newsletter, Berkeley, p 39 (AATA 21-394)
- Anonymous (1983b) The new "Renaissance" violin. Chem Week 133(20):20-21 (AATA 21-1631)
- Anonymous (1985/1986) Bemalte Holzteile im Freien (Fenster usw.). Restauratorenblätter 8:137-138
- Anonymous (1989) Newsbriefs: the Galilee Boat: a painstaking restoration. Archaeology 42(1):18 (AATA 26-2170)
- Anonymous (1996) Hoechst, Technical Bulletin
- Argyropoulos V, Rameau J-J, Dalard F, De Grigny C (1999) Testing Hostacor IT as a corrosion inhibitor for iron in polyethylene glycol solutions. Stud Conserv 44:49-57
- Arhelger E, Hilbrich V (1992) Kontinuierliche Konzentrationsbestimmung einer Zuckerlösung. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan-I Feb 1991, Freiburg (Germany) 1992, pp 84-86
- Arndt H (1963) Die Wiederherstellungsarbeiten an der thronenden Madonna aus Oberwesel. In: Straub RE (ed) Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich, pp 77-85
- Arthur BV (1972) La conservation des artifacts provenant de l'épave du *Machault*. ICOM Committee for Conservation, 3rd Triennial Meeting, Madrid 1972, 25/72/4 (AATA 14-50)
- Astrup EE (1994) A Medieval log house in Oslo - conservation of waterlogged softwoods with polyethylene glycol (PEG). In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 41-50 (AATA 32-800)
- Augerson C (1998) "Hydlar Z", a nylon-Kevlar product suitable as a reinforcing material in wooden objects. 4th International Symposium on Wood and Furniture Conservation, Rijksmuseum Amsterdam, 10 Dec 1998
- Augusti S (1954) Traitement de conservation des peintures sur panneau. Stud Conserv 1(3):127-130
- Augusti S (1959) Traitement de conservation des quelques objets de fouille en bois. Stud Conserv 4(4):146-151
- Avella-Shaw T (1974) Verfahren zur Dimensionsstabilisierung von Holz und Holzprodukten. German Patent AS 2421446
- Avent RR (1977) Epoxy repair of wood trusses, part II. Behaviour of epoxy repaired full-scale timber trusses. Final report. Mississippi: Department of Civil Engineering, Mississippi State Univ, 1977 (AATA 17-323)
- Avent RR (1986a) Factors affecting strength of epoxy-repaired timber. J Struct Eng 112(2):207-221 (AATA 27-585)
- Avent RR (1986b) Design criteria for epoxy repair of timber structures. J Struct Eng 112(2):222-240 (AATA 27-584)
- Avent RR, Issa A (1984) Effect of fire on epoxy repair timber. J Struct Eng (12):2858-2875 (AATA 23-742)
- Babiński L (1999) The two-step stabilization of the dug-out canoe from Lewin Brzeski. In: Reinprecht L (ed) Reconstruction and conservation of historical wood '99, 2nd International Symposium, 15-17 June 1999, Techn Univ Zvolen, pp 189-194
- Bachmann W (1926/1927) Das Imprägnieren wurmkranker Hölzer. Z Denkmalpflege 1:153-157

- Ballestrem A (1966) Nota over de restauratie van een vergeten 14de-eeuws ge-polychromeerd St. Petrusbeeld (Report on the treatment of an unknown polychromed St. Peter of the XIVth century). Bull Inst Royal Patrimoine Artistique 9:132-137 (AATA 8-1295)
- Balm BV (1973) Verfahren zum Reparieren und Restaurieren von geschichteten Holzträgern, Holzbalken, Monumenten u. dergleichen. German Patent 2340075
- Barclay R (1981) Wood consolidation on an eighteenth century English fire engine. Stud Conserv 26(4):133-139 (AATA 19-338)
- Barclay RL, Grattan DW (1987) A silicone rubber/microballoon mixture for gap filling in wooden objects. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6-11 Sept 1987, vol 1, pp 183-187 (AATA 25-575)
- Barclay R, Mathias C (1989) An epoxy/microballoon mixture for gap filling in wooden objects. J Am Inst Conserv 28(1):31-42 (AATA 27-588)
- Barka G, Hoffmann P (1987) Simultaneous separation of oligomeric and polymeric ethylene glycols (degree of polymerization 1-110) using reversed-phase high-performance liquid chromatography. J Chromatogr 389:273-278
- Barkman L (1962) Konserveringen av *Wasa*. Tidskrift i Sjöväsendet 125: e årg. 10 häftet
- Barkman L (1965) The preservation of the *Wasa*. Wasastudier 5, Statens Sjöhistoriska Museum Stockholm, 19 pp
- Barkman L (1969) The conservation of the wood of the Viking war boat "*Wasa*". ICOMOS Symposium on the Weathering of Wood, Ludwigsburg (Germany), 8-11 June 1969, pp 99-108 (AATA 13-663)
- Barkman L (1977) Further comments on the conservation of waterlogged wood. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol 2, pp 47-60 (AATA 14-140)
- Barkman L, Bengtsson S, Håfors B, Lundvall B (1976) Processing of waterlogged wood. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol 1, pp 17-26 (AATA 13-899)
- Baron M, Wright A (1990) The conservation of waterlogged basketry fragments from the "*William Salthouse*". AICCM Bull 16(3):85-92 (AATA 34-953)
- Barthez J, Ramiere R, Tran QK (1999a) Historic drywood consolidation by in situ resin radio-polymerization. In: Reinprecht L (ed) Reconstruction and conservation of historical wood '99, 2nd international symposium, 15-17 June 1999, Techn Univ Zvolen, pp 155-159
- Barthez J, Hiron X, Arnold B, Marquis B, Velay P (1999b) Historic and conservation treatment of ten Neolithic dug-out canoes from the Bercy site in Paris. In: Reinprecht L (ed) Reconstruction and conservation of historical wood '99, 2nd international symposium, 15-17 June 1999, Techn Univ Zvolen, pp 183-187
- Bateson BA (1936) The shrinkage and swelling of wood-experiments on the influence of sorbitol. Chem Trade J 102:493
- Bateson BA (1938) Sorbitol in wood treatment. Chem Trade J 104:26-27
- Bateson BA (1939) Sorbitol in wood treatment. Chem Trade J 105:93-94
- Baumgartner H, Lanooy R (1982) Eine Methode zur Wassersättigung trockener, fossiler Knochen, Zähne und Hölzer für die Konservierung mit PEG 6000-12000. Präparator 28(2):269-274 (AATA 20-1121)
- Becker A, Kunkel HJ, Potthast I (1992) Konservierung von Naßholz mit Rübenzucker. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan-I Feb 1991, Freiburg (Germany) 1992, pp 87-97
- Becker M (1971) Werkstoff Holz im Kunstwerk. Holzkunde für Restauratoren, Konservatoren und Präparatoren. Schriftenreihe des Instituts für Museumswesen Berlin, vol 2
- Belis J, Josef J, Justa P, Štastný P (1988) Vakuová petrifikace varhannich vzdušnic (Vacuum impregnation of an organ part). Památky a příroda 13(6):346-349 (AATA 27-593)
- Bergeron A (1987) Le séchage à froid en milieu extérieur: évaluation de l'efficacité de l'hiver québécois. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6-11 Sept 1987, vol 1, pp 297-300 (AATA 25-576)

- Bernatova M, Cillikova K, Zilinkova B, Kiimes P (1987) Plastiken. *Renovatio* 5(7):51-54
- Bhatia SK (1988) Technical note. 3: conservation of waterlogged wood. National Research Laboratory for Conservation of Cultural Property (NRLC), Lucknow (AATA 26-2171)
- Biek L, Anstee JW, Cripps ES (1968) A wooden bucket restored. *Mus J* 57:257-261 (AATA 13-173)
- Bill J (1979) Zur Problematik der Naßholzkonservierung. *Z Schweiz Archäol Kunstgesch* 36(2):97-99
- Bilz M, Grattan DW (1997) Strange brew: BHA, PEG and H₂O. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp 385-398
- Bilz M, Dean L, Grattan DW, McCawley JC, McMillen L, Cook C (1994a) A study of the thermal breakdown of polyethylene glycol. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference*, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 167-197 (AATA 32-803)
- Bilz M, Grattan D, Horvath M (1994b) The test treatment of waterlogged wood from the Biskupin archaeological site, Poland. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference*, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 23-40 (AATA 32-804)
- Binnie NE (1991) Corrosion-inhibiting resins for waterlogged wood/metal composites: evaluation of samples six years after treatment. *ICOM Committee for Conservation, Metal Working Group Newslett* (6):4-8
- Birkner L, Boström T, Morén R, Thunell B (1961) Vasa konserveras. *Skogen* 48(4):66-67
- Blackshaw SM (1974) The conservation of the wooden writing-tablets from Vindolanda Roman Fort, Northumberland. *Stud Conserv* 19(4):244-246 (AATA 12-223)
- Blackshaw SM (1976) Comments on the examination and treatment of waterlogged wood based on work carried out during the period 1972-76 at the British Museum. *Pacific Northwest Wet Site Wood Conservation Conference*, Neah Bay (Washington), vol 1, pp 27-34 (AATA 13-901)
- Blackshaw SM (1977) Further comments on the examination and treatment of waterlogged wood based on work carried out during the period 1972-76 at the British Museum. *Pacific Northwest Wet Site Wood Conservation Conference*, Neah Bay (Washington), vol 2, pp 69-75 (AATA 14-142)
- Bockhoff FJ, Guo K-M, Richards GE, Bockhoff E (1984) Infrared studies of the kinetics of insolubilization of soluble nylon. In: Brommelle NS, Pye EM, Smith P, Thomson G (eds) *Adhesives and Consolidants*. International Institute for Conservation, London, pp 81-86
- Borgin K (1978) Appendix 2: progress on evaluating the Thessaloniki process in Mombassa wreck excavation: second preliminary report 1978, by Rubin C.M. Piercy. *Int J Naut Archaeol Underwater Explor* 7(4):314-317 (AATA 16-1343)
- Bosshard ED (1979) Eine Holzfestigung mit Epoxidharz. *Maltechnik Restauo* 85(2):126-128
- Bosshard E, Englisch G (1983) Die Festigung einer bemalten Holzbohlenwand aus dem 16. Jahrhundert. Fach- und Fortbildungstagung "Probleme um den Bildträger Holz" 1982. Selbstverlag der Kunstgewerbeschule Bern, 1983, pp 119-125
- Boucher N (1999) Polyethylene glycol (PEG) in furniture conservation. *Proceedings of the 4th International Symposium on Wood and Furniture Conservation*, Rijksmuseum Amsterdam, 10 Dec 1998, pp 13-21
- Bouis J (1975) La conservation des paléoxyles. Une méthode nouvelle de traitement physico-chimique des objets antiques en bois gorgé d'eau. *ICOM Committee for Conservation, 4th Triennial Meeting*, Venice 75/8/2, pp 1-7 (AATA 13-903)
- Bouis J (1985) La sauvetage de l'épave de l'anse Gerbal a Port-Vendres (Pyrénées-Orientales). *Les Bois Gorgés d'Eau: Étude et conservation*. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble, 28-31 Aug 1984 - Waterlogged wood: study and conservation. *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference*, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble, pp 89-92 (AATA 24-589)
- Boustead W (1966) Conservation of Australian aboriginal bark paintings with a note on the restoration of a New Ireland wood carving. *Stud Conserv* 11(4):197-204 (AATA 6-C3-52)

- Bräker OU (1979) Zum derzeitigen Stand der Naßholzkonservierung. *Z Schweiz Archäol Kunstgesch* 36(2):97-145
- Bratlie E (1981) Use of low-viscosity epoxy resin for the consolidation of fragile wood in the votive ship from Tojömö Church. *Nordisk Konservatorforbunds 9. Kongress Oslo 1981*, preprints of the IIC Nordic Group's 9th Congress, Oslo 1981, pp 135-140 (AATA 18-1245)
- Bratlie E (1983) Råtten tre: stavkirkene-hvorfor og hvordan skal det bevares? (Rotted wood in the stave churches - why and how should it be preserved?). *Hemgrenda* (1983), pp 30-34 (AATA 21-402)
- Brendel G (1966) Ein neues Verfahren zur Konservierung nassen Ausgrabungsholzes. *Muz Közlemények* (3/4):148-155
- Brewer JA (1991) Effect of selected coatings on moisture sorption of selected wood test panels with regard to common panel painting supports. *Stud Conserv* 36(1):9-23 (AATA 28-2248)
- Bright LS (1979) Recovery and preservation of a fresh-water canoe. *Int J Naut Archaeol Underwater Explor* 8(3):261-263 (AATA 20-175)
- Brkić N (1967) Altserbische Ikonen und ihr Bildaufbau. *Maltechnik* 73(4):110-114 (AATA 7-1188)
- Brongers JA, Wijnman HF (1970/1971) The conservation of waterlogged wood in the Netherlands by means of the alcohol-ether-method. *Berichten van de Rijksdienst voor het oudheidkundig. Bodemonderzoek* 20/21:321-322
- Brorson Christensen B (1956) Konservering af Mosetrae ved Hjaelp af Tertiaer Butylalkohol (The conservation of swamp wood with tert-butanol). *Aarbøger for Nordisk Oldkyndighed og Historie*, pp 249-254
- Brorson Christensen B (1970a) The conservation of waterlogged wood in the National Museum of Denmark. *Museumstekniske Studier* 1. National Museum of Denmark, Copenhagen
- Brorson Christensen B (1970b) Developments in the treatment of waterlogged wood in the National Museum of Denmark during the years 1962-69. *IIC Conference on the Conservation of Stone and Wooden Objects*, New York 1970, preprints, London, vol 2, pp 27-44 (AATA 8-749)
- Brown C, Watkins S, White R (1994) Provision for the conservation of waterlogged structural timbers in the United Kingdom. In: Springs JA (ed) *A celebration of wood: proceedings of a conference held by York Archaeological Wood Centre in York, June 1993*, WARP occasional no. 8
- Bruder KT (1987) Gondolatok egy őskori balta famaradványai kapcsán (Meditations over the wooden remains of a prehistoric axe). *Múz Műtárgyvédelem* (16):23-32 (AATA 24-826)
- Bryce T (1980) Conservation of the Walton heathhurdle from the Somerset Levels. *Somerset Levels Pap* (6):72-76
- Bryce T, McKerrell H, Varsanyi A (1975) The acetone/rosin method for the conservation of waterlogged wood and some thoughts on the penetration of PEG into oak. *Maritime Monographs and Reports*, Natl Maritime Mus Greenwich 16:35-44 (AATA 15-400)
- Buchenrieder F (1990) Gefäste Bildwerke. *Arbeitshefte Bayer Landesamt Denkmalpflege München* Nr 40
- Buck RD (1978) The use of moisture barriers on panel paintings. *The Behavior of Wood and the Treatment of Panel Paintings*, Minneapolis. Upper Midwest Conservation Association, Minneapolis Institute of Arts, pp 26-36
- Bucsányi K (1979) A mosonszentjánosi frank vödör restaurálása és rekonstrukciója (Restoration and reconstruction of the Franconian bucket from Mosonszentjános). *Múz Műtárgyvédelem* (6):15-26 (AATA 8-746)
- Bulatov NM (1980) O vozmozhnosti konservacii archeologičeskogo dereva (On possibilities of conservation of archaeological wood). *Voprosy ochrany, restavracii i propagandy pamät-nikov istorii i kultury*, Moskva, pp 43-52
- Byrne A (1976) Conservation of polychrome wood sculpture at the Australian War Memorial. *ICCM Bull* 2(3):5-14 (AATA 14-905)
- Canuti V (1988) Il restauro di due porte lignee intarsiate della chiesa di S. Sigismondo a Cremona. *Kermes* 1(3):34-39 (AATA 28-2253)

- Caple C, Murray W (1994) Characterization of waterlogged charred wood and development of a conservation treatment. *Stud Conserv* 39(1):28–38
- Caprara O (1970) The conservation of wooden objects, particularly in Florence. IIC Conference on the Conservation of Stone and Wooden Objects, New York 1970, preprints London, vol2, pp 97–114 (AATA 8-1765)
- Carlson SM, Schniewind AP (1990) Residual solvents in wood-consolidant composites. *Stud Conserv* 35(1):26–32
- Catalano Fenicia M (1989) Il restauro del pulpito e dell'altare lignei nelle chiesa di S. Antonio ai Cappuccini, Martina Franca (Taranto) (The restoration of the wooden altar and pulpit in the church of San Antonio ai Cappuccini, Martina Franca (Taranto province). In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp 245–246, 350 (AATA 29-2354)
- Cebecauer I, Straková D (1984) Obnova drevených konštrukčných prvkov v historických objektoch (Renovation of wooden construction elements in historic objects). *Památky a příroda* 13(2):13–16 (AATA 21-1642)
- Cebertowicz R, Jasienski D (1951) Elektrokinetyczna metoda petryfikacji drewna oraz mumi-fikacji matewki z prehistorycznego wykopiska w Biskupinie (Electrokinetic method for petrification of mummified wood from the prehistoric site in Biskupin). *Prace i Sesji Naukowej Politechniki Gdańsk*
- Chaumat G, Tran QK, Perre C, Lumia G (1999) Trials of shape recovering from collapsed waterlogged wood by treatment with CO₂ supercritical fluid. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) *Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999*, pp 137–142
- Chen Jinliang, Cui Zhanhua (1994) (Dehydrolyzing and shaping investigation of unearthed waterlogged painted woodemvare at Changtaiguan of Xinyang in Henan). *Wenwu baohu yu kaogu kexue* 6(2):1–6 (AATA 32-2266)
- Choi KN (1988) The conservation of *Shinan* Shipwreck. In: Mills JS, Smith P, Yamasaki K (eds) *The conservation of Far Eastern art: preprints of the contributions to the Kyoto Congress, 19–23 Sept 1988, The International Institute for Conservation of Historic and Artistic Works, London*, pp 101–102 (AATA 26-641)
- Christensen AE Jr (1968) The *Sjøvollen* Ship. Preliminary report on the excavation and reconstruction of a medieval merchantman. *Viking* 32:131–154 (AATA 8-748)
- Ciabach J (1983) Investigation of the cross-linking of thermoplastic resins effected by ultraviolet radiation. In: Tate JO, Tennent NM, Townsend JH (eds) *Proceedings of the symposium on resins in conservation. Scottish Society for Conservation and Restoration, Edinburgh*, pp 5-1 to 5-8
- Clark RW, Gregson C (1987) A large-scale polyethylene glycol conservation facility for waterlogged wood at the National Maritime Museum, Greenwich. In: Grimstad K (ed) *ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6–11 Sept 1987, vol 1*, pp 301–307 (AATA 25-578)
- Clausnitzer K-D (1990) *Historischer Holzschutz. ökobuch, Staufen bei Freiburg*
- Coeuré P, Chaumat G, Tran QK, Perre C (1998) Die Konservierung von Naßholz: Versuche mit Polyethylenglycol in superkritischer Kohlendioxid-Flüssigkeit. *Arbeitsbl Restaur* (1), Gruppe 8, pp 262–265
- Cohen O (1999) The Kinneret Boat: conservation and exhibition. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) *Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999*, pp 182–187
- Coles JM (1989) The world's oldest road. *Sci Am* 261(5):100–106 (AATA 27-1947)
- Cook C, Grattan DW (1985) A practical comparative study of treatments for waterlogged wood, part III: pretreatment solutions for freeze-drying. *Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 Aug 1984 – Waterlogged wood: study and conservation.*

- Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985*, pp 219–239 (AATA 24-607)
- Cook C, Grattan DW (1991) A method of calculating the conservation of PEG for freeze-drying waterlogged wood. In: Hoffmann P (ed) *Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990, Bremerhaven 1991*, pp 239–250
- Cook C, Dietrich A, Grattan DW, Adair N (1985) Experiments with aqueous treatments for waterlogged wood-metal objects. *Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 août 1984 – Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985*, pp 147–159 (AATA 24-606)
- Cooke V, Cooke D, Grattan DW (1994) Reversing old PEG treatments of objects from the Ozette site. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994*, pp 92–109 (AATA 32-810)
- Cott J (1965) Die Konservierung von Feuchthölzern. *Neue Museumskd* 8:329–342 (AATA 13-2160, 6-C3-33)
- Cott J (1968) Erfahrungen mit der Piezap ME/2-Methode nach Abschluß der Holzkonservierung von Oberdorla. *Neue Museumskd* 11:235–238
- Cott J (1992) Arbeitsbericht über die bisherigen Erfahrungen mit der Zuckerkonservierung am Museum für Ur- und Frühgeschichte Thüringens. In: AdR (ed) *Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992*, pp 38–45
- Cott J, Unger A (1991) Resultate einer Naßholzkonservierung mit Zucker – der "Holzgötze" von Oberdorla, Kreis Mühlhausen. *Restauro* 97(6):392–397
- Crisp CFC (1982) Reinforced epoxy and timber beams. *Conference on the protection of the engineering heritage 1982*, pp 36–40 (AATA 19-1340)
- Csere J (1987) A győri mészáros céh ládájának restaurálása (Restoration of the chest of the butchers' guild in Győr). *Műz Műtárgyvédelem* (16):211–226 (AATA 24-611)
- Cuany F, Schaible V, Schiessl U (1989) Studien zur Festigung biologisch geschwächten Nadelholzes. *Kunsttechnol Konserv* 3(2):249–292
- Czajnik M (1968) Srodki i metody konserwacji zabytkowego drewna budowlanego (Composition and methods of conservation for old timber in buildings). *Ochrona Zabytkow* 21(1): 21–29 (AATA 8-754)
- Czakó F (1987) Johanni Schneider németbólyi asztalosmester által 1859-ben készített komód restaurálása (The restoration of the commode made by Johann Schneider, cabinet-maker of Németbóly from 1859). *Műz Műtárgyvédelem* (16):177–194 (AATA 24-613)
- Dalorova A, Brimichova M, Klimes P (1987) Die Tafelgemälde der ehemaligen Flügel des spätgotischen Hauptaltars der Pfarrkirche des Hl. Nikolaus in Presov (Kr. Presov). *Renovatio* 5(7):55–57
- Dean LR, Jones EBG, Jones AM (1994) The stabilization of ancient waterlogged oak with polyethylene glycols. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994*, pp 213–229 (AATA 32-815)
- Decsi G (1987) Acsolt láda restaurálása (The restoration of a timbered chest). *Műz Műtárgyvédelem* (17):115–124 (AATA 24-616)
- De Guichen G, Gäumann T, Mühlethaler B (1966) Méthode de conservation des bois provenant de cites lacustres par diffusion d'un monomère et polymérisation par rayons gamma. Thèse, Ecole Polytechnique Fédérale de Lausanne
- De Jong J (1975a) The conservation of old waterlogged wood from shipwrecks found in the Netherlands. *Ijsselmeerpolders Development Authority, Lelystad, Netherlands*
- De Jong J (1975b) The conservation of waterlogged timber at Ketelhaven (Holland). *ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/8/1* (AATA 13-908)

- De Jong J (1977a) Conservation techniques for old waterlogged wood from shipwrecks found in the Netherlands. In: Walters AH (ed) Biodeterioration investigation techniques. Applied Science Publishers, Essex, pp 295–338 (AATA 15-1291)
- De Jong J (1977b) Conservation of old waterlogged wood. Sources and techniques in boat archaeology. National Maritime Museum, Archaeological series no I; BAR supplementary series 29, Greenwich
- De Jong J (1978) The conservation of shipwrecks. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, 78/7/1 (AATA 16-388)
- De Jong J, Eenkhoorn W, Wevers AJM (1981) Controlled drying as an approach to the conservation of shipwrecks. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/2 (AATA 18-1249)
- De la Baume S (1987) Essais de conservation des bois archéologiques au sucre. VALECTRA/DER/EDF, Saint Denis, pp 162–172
- Delbourgo S (1975) Etude préalable aux procédés de conservation des bois polychromes par polymérisation in situ. ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/18/1 (AATA 14-154)
- Détanger B, Ramière R, De Tassigny C, Eymery R, De Nadaillac L (1974) Application des techniques de polymérisation au traitement des bois gorgés d'eau. Bois For Trop (154):63–68
- Détanger B, Ramière R, De Tassigny C, Eymery R, De Nadaillac L (1976) Application des techniques de polymérisation au traitement des bois gorgés d'eau. International conference on application of nuclear methods in the field of works of art, Venice, 24–29 May 1973, Accademia nazionale dei Lincei, Rome 1976, pp 637–643 (AATA 14-908)
- De Tassigny C (1975) Apport des techniques nucléaires à la conservation des biens culturels. Première Partie. Situation des méthodes nucléaires de conservation en France. Mus Coll Publ France 129(1):19–23, 26
- De Tassigny C, Ginier-Gillet A (1979) La méthode des traitement des bois gorgés d'eau par imprégnation et irradiation gamma. Z Schweiz Archäol Kunstgesch 36(2):138–141
- De Witte E, Terfe A, Vynckier J (1984) The consolidation of the waterlogged wood from the Gallo-Roman boats of Pommeroeul. Stud Conserv 29(2):77–83 (AATA 21-1645)
- Döll M (1997) Methylcellulosen und die Verklebung von Holz. Restauo 103(5):332–336
- Domasłowski W (1958) Zagadnienie konserwacji drewna (Problems concerning conservation of wood). Materiały Zachodnio – Pomorskie Szczecin 4:398–424 (AATA 13-178)
- Domininghaus H (1998) Die Kunststoffe und ihre Eigenschaften, 5th edn. Springer, Berlin Heidelberg New York
- Down JL, MacDonald MA, Tetreault J, Williams RS (1996) Adhesive testing at the Canadian Conservation Institute – an evaluation of selected poly(vinyl acetate) and acrylic adhesives. Stud Conserv 41(1):19–44 (AATA 34-1737)
- Drocourt D, Morel-Deledalle M (1983) The Roman ship of Marseilles: a world première. Museum 137–35(1):49–53
- Dumkow M, Preuss H (1990) Konservierung von Naßholz mit Rübenzucker. Arbeitsbl Restaur 23(1) Gruppe 8, pp 186–192 (AATA 28-655)
- Duval G, Keisser D (1980) La restauration et la consolidation des charpentes en bois. Cab Tech Batiment (27):22–26
- Dyrkova M, Jagielska I (1981) Konserwacja mokrego drewna metoda "Freeze-Drying" w Centralnym Muzeum Morskim w Gdańsku (Conservation of waterlogged wood by freeze-drying in the Central Marine Museum of Gdansk). Ochrona Zabytkow 34(3/4):203–205 (AATA 19-1345)
- Ebert H (1977) Zur Feuchtholzkonservierung. Arbeitsbl Restaur (1), Gruppe 8, pp 78–80
- Elmer JT (1973) Gefriertrocknung neolithischer Gewebe und Geflechte. Arbeitsbl Restaur 6(1), Gruppe 10, pp 17–22 (AATA 12-270)
- Emile-Male G (1976) Gemälde auf Leinwand und Holz. Rembrandt-Verlag, Berlin
- Emmenegger O (1983) Probleme der Holzkonservierung in der Denkmalpflege. Fach- und Fortbildungstagung "Probleme um den Bildträger Holz" 1982. Selbstverlag der Kunstgewerbeschule Bern, 1983, pp 81–87

- Ericks WP, Upson Chemical (1949) Method for treating cellulose and products thereof. US Patent 2,629,674 (7 July 1949)
- Erlor K (1987) Versuche zum Ersatz geschädigter Holzbauteile durch Polyesterbeton und Bewehrung, Teil 1. Internationale Holzbautagung mit RGW-Beteiligung, Dresden 11–12 Dec 1986. Bauakademie der DDR Berlin 204:93–97
- Erlor K (1990) Polyesterharzbeton für die Sanierung von tragenden Holzkonstruktionen, Teil 1 und 2. Bauzeitung 44:81–83, 171–174
- Farrington F (1969) Dissection of a serpent. Galpin Soc J 22:81–96 (AATA 27-609)
- Feller RL (1990) Evaluation of cellulose ethers for conservation. Research in conservation. Getty Conservation Institute, Los Angeles
- Ficke W (1992) Der Einbaum aus der Elbe bei Jasebeck, 1985. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Febr 1991, Freiburg (Germany) 1992, pp 46–52
- Filip J (1951) Konservace dřeva v pudnim prostředí pomoci elektriny (Conservation of wood from sites by electricity). Archeol Rozhledy 3(4):353–354
- Fox LA (1989) The acetone/rosin method for treating waterlogged hardwoods at the Historic Resource Conservation Branch, Ottawa. Conservation of wet wood and metal. In: MacLeod ID (ed) Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals, Fremantle 1987, Western Australian Museum Perth, pp 73–94 (AATA 28-2265)
- Frangulli R (1971/1972) Legni preistorici palustri e loro trattamento conservativo. Sibirium XI:339–346
- Frangulli R, Loda D (1970) Trattamento di repertilignei palafitticoli con un nuovo metodo conservativo. Annali del Museo di Gavarro
- Fries T (1989) Chemické úpravy rezonančního dřeva housli (Chemical treatment of violin resonance wood). Hudební Nástroje 26(5):175–177 (AATA 27-1953)
- Fries T, Šimůnková E, Kubikova J, Zelinger J (1988) Petrifikace smrkového rezonančního dřeva Ethylsilikátem 40 I. (Consolidation of resonant spruce wood by ethyl silicate 40 I) Sb. VŠCHT Praz, Pict Sci Pap S 18:219–233 (AATA 27-1954)
- Gabricevic D (1978) Konservierung und Restaurierung eines Einbaumes von Smedereve, 12. Arbeitstagung der Arbeitsgemeinschaft des Technischen Museumspersonal (ATM), Stuttgart, 18–23 Sept 1978
- Gäumann T, Kowalski TS, Menger A (1988) Application of radiation chemistry for conservation of archaeological waterlogged wood and osteological objects. Radiat Phys Chem 32(2): 275–280 (AATA 26-2174)
- Gäumann T, Haebel S, Kowalski T, Menger A (1989) La conservation d'objets gorgés d'eau par polymérisation d'un monomère sous l'effet de rayons γ. In: Schweizer F, Villinger V (eds) Methoden zur Erhaltung von Kulturgütern. Haupt, Bern, pp 193–197
- Gagen L, Gerasimova N, Sheinina E (1972) Ukreplenie reznoj obuglinnoi drevsesiny (Strengthening of carved charred wood). Soobshcheniya Gosudarstvennogo Hermitage (35):80–83 (AATA 12-865)
- Gambetta A, Orlandi E (1990) Investigations on the resistance of modified wood to biological attack. Folia For Polonica, Ser B, 30:13–19
- Ganiaris H (1990) Examination and treatment of a wooden writing tablet from London. Conservator 14:3–9 (AATA 29-685)
- Garczyński W (1958) Transport i konserwacja wczesnośredniowiecznej łodzi zewsi Czarnowsko, pow. Lebork (Transportation and conservation of the prehistoric boat of Czarnowsko, district Lebork). Muzeum Pomorza Zachodniego, Materiały Zachodnio – Pomorskie Szczecin 4:393–397
- Garrouste L (1965) Procédé de conservation des bois antiques décomposés dans l'eau douce ou l'eau de mer. French Patent 1392835, 7 p
- Gaudel P (1963) Das Polyglycol-Verfahren. Ein Beitrag zur Konservierung großer Feuchtholzobjekte. Präparator 9:202–210 (AATA 13-363)
- Gaudel P (1969) Bibliographie der archäologischen Konservierungstechnik, 2. erw. Ausgabe Ergänzungsband 2. Hessling, Berlin, p 217 (Ref no 1162)

- Gebser J (1955) Die Paraffinmethode, ein vorzügliches Konservierungsmittel für vor- und frühgeschichtliche Holzfundstücke. *Präparator* 1(2):28-31
- Gerasimova NG, Nikitina KF (1975) Konservaciâ mokrogo archeologičeskogo dereva polietilenglikolâmi (Conservation of waterlogged wood with PEG). *Chudožestvennoe Nasledie* 1(31):80-88
- Gerasimova NG, Mikolajchuk EA, Kolosova MI (1981) On the conservation of wet archaeological wood by introduction of waxlike substances into it. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/8 (AATA 18-1255)
- Giachi G, Tordi G (1989) Progetto di restauro di reperti lignei sommersi (A restoration project for underwater wooden finds). In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp 312-317, 342-343 (AATA 29-2381)
- Gilberg M, Grattan D, Rennie D (1989) Treatment of iron/wood composite materials. Conservation of wet wood and metal. In: MacLeod ID (ed) *Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals*, Fremantle 1987, Western Australian Museum Perth 1989, pp 265-270 (AATA 28-2273)
- Gilroy D (1978) Conservation of a pulley shave from the Dutch East Indiaman "Zeewijk", 1727. *ICCM Bull* 4(4):25-27 (AATA 17-340)
- Ginier-Gillet A, Parchas M-D, Ramière R, Tran QK (1985) Méthodes de conservation développées au Centre d'Étude et de Traitement des Bois Gorgés d'Eau (Grenoble - France): imprégnation par une résine radiodurcissable et lyophilisation. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28-31 Aug 1984 - Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 125-137 (AATA 24-638)
- Glastrup J (1997) Degradation of PEG - a review. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp 377-383
- Golubtsova TP, Nikitin MK, Shadrin SA (1977) Use of organosilicate material E-2 in restoration. In: Kharitonov NP, Krotikov VA (eds) *Organosilik Mater, Ikh. Svoistva Opyt Primen Mater Kratkosrochnogo* 1976 (Pub. 1977), Leningrad: Dom Nauchno-Tekh, Propag, pp 32-37
- Gowers HJ (1970) The treatment of ethnographical wood. IIC Conference on the Conservation of Stone and Wooden Objects, New York 1970. Preprints, London, vol2, pp45-52 (AATA 8-756)
- Grant T, Bilz M, de la Cruz V (1997) Conservation of waterlogged cedar basketry and cordage. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp 127-135
- Grattan DW (1980) Consolidants for degraded and damaged wood. *Proc. Furniture and Wooden Objects Symposium*. Canadian Conservation Institute, Ottawa, pp 27-42
- Grattan DW (1982a) A practical comparative study of several treatments for waterlogged wood, part I. *Stud Conserv* 27(3):124-136 (AATA 19-1348)
- Grattan DW (1982b) A practical comparative study of several treatments for waterlogged wood, part II. The effect of humidity on treated wood. *Proceedings of the ICOM Waterlogged Wood Working Group Conference* 1982, pp 243-252 (AATA 21-411)
- Grattan DW (1984) Advances in the conservation of waterlogged wood 1981-1984. ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen 1984, 84.7.8, 8-11 (AATA 21-1652)
- Grattan DW (1988) Treatment of waterlogged wood. In: Purdy BA (ed) *Wet site archaeology*, pp 237-254 (AATA 28-2278)
- Grattan DW (1991) The conservation of specimens from the Geodetic Hills fossil forest site, Canadian Arctic Archipelago. In: Christie RL, McMillan NJ (eds) *Bulletin (Geological Survey of Canada)* 403:213-227 (AATA 30-1262)
- Grattan DW, Barclay RL (1988) A study of gap-fillers for wooden objects. *Stud Conserv* 33(2):71-86 (AATA 26-646)

- Grattan DW, Clarke RW (1987) Conservation of waterlogged wood. In: Pearson C (ed) *Conservation of Marine Archaeological Objects*. Butterworths, London, pp 164-206
- Grattan DW, McCawley JC (1978) The potential of the Canadian winter climate for the freeze-drying of degraded waterlogged wood. *Stud Conserv* 23(4):157-167 (AATA 16-396)
- Grattan DW, McCawley JC, Cook C (1980) The potential of the Canadian winter climate for the freeze-drying of degraded waterlogged wood, part II. *Stud Conserv* 25(3):118-136 (AATA 18-323)
- Grattan DW, McCawley JC, Cook C (1981) The conservation of a waterlogged dug-out canoe using natural freeze-drying. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/3 (AATA 18-1256)
- Grattan DW, Gruchy C, Bilz M, Bigras C (1996) The fossil forest project at the Canadian Conservation Institute. In: Bridgland J (ed) *ICOM Committee for Conservation, 11th Triennial Meeting*, Edinburgh, Scotland, 1-6 Sept 1996. Preprints, pp 776-783 (AATA 34-972)
- Gregson CW (1975) Progress on the conservation of the *Graveney* boat. *Maritime Monographs and Reports*. Natl Maritime Mus Greenwich 16:113-114 (AATA 15-415)
- Grosso GH (1976) Volume processing of waterlogged wood at a remote archaeological site: modification of old techniques, identification of special problems and hopes for their solution. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol 1, pp 35-48 (AATA 13-913)
- Grosso GH (1977) Question period following: volume processing of waterlogged wood at a remote archaeological site: modification of old techniques, identification of special problems and hopes for their solution. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol 2, pp 35-38 (AATA 14-169)
- Grosso GH (1981) Experiments with sugar in conserving waterlogged wood. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/7 (AATA 180-1276)
- Gustafson G (1913) Über die Konservierung der im Vikingerschiffe zu *Oseberg* gefundenen Altertümer. *Chem Z* 37:1599
- Haas A (1964) Erfahrungen und Prüfungsergebnisse zur Feuchtholzkonservierung mittels Arigal C. *Präparator* 10:113-118
- Haas A (1969) Weitere Fortschritte bei der Konservierung von Feuchthölzern mit Arigal C. *Arbeitsbl Restaur* (2), Gruppe 8, pp 16-19 (23) (AATA 8-1299)
- Haas (1979) Die verschiedenen Methoden der Naßholzkonservierung. 1. Methode Lyofix DML. *Z Schweiz Archäol Kunstgesch* 36(2):121-124
- Haas A (1985) Neue Entwicklungen bei der Naßholzkonservierung mit Melamin-Formaldehyd-Kondensaten. *Arbeitsbl Restaur* (1), Gruppe 8, pp 122-127 (AATA 23-774)
- Håfors B (1976) Preliminär rapport angående sockerkonservering. Dimensionstabiliserande verkan av sukros jämförst med PEG 1000. Statens Sjöhistoriska Museum Wasavarvet, Konservings tekniska avd
- Håfors B (1985) The drying pattern of the outer planking of the *Wasa* hull. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28-31 Aug 1984 - Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 313-326 (AATA 24-648)
- Håfors B (1990) The role of the *Wasa* in the development of the polyethylene glycol preservation method. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington DC. *Adv Chem Ser* 225:195-216 (AATA 27-1957)
- Håfors B (1994) Improvements of the conservation programme for tanktreatment with polyethylene glycol at the Vasa Conservation Laboratory. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference*, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 51-62 (AATA 32-827)
- Hamsik M (1978) The flattening and stabilization of soft wood panel paintings by means of a method which respects their original technical structure. *Conservation of wood in painting*

- and the decorative arts. Preprints of the contributions to the Oxford congress 17–23 Sept 1978. IIC; 6 Buckingham Street, London WC 2N 63A, pp 175–177 (AATA 16-399)
- Hansen EF, Bishop MH (1998) Factors affecting the retreatment of previously consolidated matte painted wooden objects. Painted wood: history and conservation. In: Dorge V, Howlett FC (eds) Proceedings of a symposium organized by the Wooden Artifacts Group of the American Institute for Conservation of Historic and Artistic Works and the Foundation of the AIC, held at the Colonial Williamsburg Foundation, Williamsburg, Virginia, 11–14 Nov 1994, Getty Conservation Institute, Los Angeles, pp 484–496
- Hansen EF, Sadoff ET, Lowinger R (1990) A review of problems encountered in the consolidation of paint on ethnographic wood objects and potential remedies. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden 26–31 Aug 1990, vol I, pp 163–168
- Hartwagner S (1956) Die Restaurierung des Gurker Hochaltars. Österr Z Kunst Denkmalpflege 10:72–76
- Hatchfield P (1986) Note on a fill material for water sensitive objects. J Am Inst Conserv 25(2):93–96 (AATA 26-650)
- Hatchfield PB, Koestler RJ (1987) Scanning electron microscopic examination of archaeological wood microstructure altered by consolidation treatments. Scanning Microscopy 1(3):1059–1069 (AATA 25-585)
- Hedlund HP (1997) Acronal D 300 in theory and practice, an evaluation. Nordisk Konservatorforbund XIV Kongress, Konserveringsmidler & Konserveringsmetoder, Consolidants and Conservation methods. NKF-N, Oslo, 20–23 mars 1997
- Heller B (1983) The joining of wood panels with Araldite epoxy system. Abstract of a paper presented at the Paintings Specialty Group, 11th annual meeting of the American Institute for Conservation, Baltimore, 29 May
- Hellwig F (1978) Die besonderen Probleme der Restaurierung alter Musikinstrumente in der nicht spezialisierten Werkstatt. Arbeitsbl Restaur (2), Gruppe 9, pp 88–94
- Herbst CF (1858–60) Om Bevaring af Oldsager af Trae fundne i Tørvemoser. Antiquarisk Tidsskrift Kjöbenhavn, pp 174–176 (1861)
- Heyn C, Petersen K, Krumbein WE (1996) Untersuchungen zum mikrobiellen Abbau in der Denkmalpflege eingesetzter synthetischer Polymere. Kunsttechnol Konserv 10(1):87–105
- Higuchi S (1978) Consolidation and restoration of deteriorated wooden materials with synthetic resins. Conserv Wood Int Symp Conserv Restor Cult Prop, Tokyo 1977. Proceedings 1978, pp 23–32
- Higuchi S (1981) Application of synthetic resin in the restoration of the structural members in old wooden houses. Sci Conserv 20:77–84
- Higuchi S, Nakasato T, Nishiura T (1980) Scientific reinforcing restoration of the structural wooden columns of the Hakogi House. Sci Conserv 19:49–67
- Höring F, Richard H (1997) Erste Erfahrungen mit dem neuen Epoxidharz EP BM 09 in der Praxis der Holzfestigung. Restauratorenblätter 18:20–21
- Hoffmann P (1983) A rapid method for the detection of polyethylene glycols (PEG) in wood. Stud Conserv 28(4):189–193 (AATA 21-413)
- Hoffmann P (1984) Zur Restaurierung mittelalterlicher Daubengefäße mit Polyethylenglycol. Arbeitsbl Restaur (2), Gruppe 8, pp 98–111
- Hoffmann P (1985) On the stabilization of waterlogged oak-wood with PEG: molecular size versus degree of degradation. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 Aug 1984 – Waterlogged Wood: Study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 95–115 (AATA 24-664)
- Hoffmann P (1986a) On the stabilization of waterlogged oak-wood with PEG. II. Designing a two-step treatment for multiquality timbers. Stud Conserv 31(3):103–113 (AATA 24-662)
- Hoffmann P (1986b) The *Bremen Cog* sails a new course. Int J Naut Archaeol Underwater Explor 15(3):215–219 (AATA 24-665)
- Hoffmann P (1988a) On the stabilization of waterlogged oakwood with polyethylene glycol (PEG) III. Testing the oligomers. Holzforschung 42(5):289–294 (AATA 27-628)

- Hoffmann P (1988b) Zur Rückformung feiner mittelalterlicher Drechslerware. Arbeitsbl Restaur 21(1) Gruppe 8, pp 153–170 (AATA 26-651)
- Hoffmann P (1988c) Zur Rückformung mittelalterlicher Drechslerware. Teil 11. Hölzer mit Schwindungsschäden. Arbeitsbl Restaur (2), Gruppe 8, pp 171–185
- Hoffmann P (1989) HPLC for the analysis of polyethylene glycols (PEG) in wood. Conservation of wet wood and metal. In: MacLeod ID (ed) Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals, Fremantle 1987, Western Australian Museum Perth 1989, pp 41–59
- Hoffmann P (1990a) A waterlogged medieval river craft from the Rhine stabilized in a two-step polyethylene glycol treatment. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden, 26–31 Aug 1990, vol I, pp 229–233
- Hoffmann P (1990b) On the stabilization of waterlogged softwoods with polyethylene glycol (PEG). Four species from China and Korea. Holzforschung 44(2):87–93
- Hoffmann P (1991) Sucrose for the stabilization of waterlogged wood. Some investigations into anti-shrink-efficiency (ASE) and penetration. In: Hoffmann P (ed) Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990, Bremerhaven 1991, pp 317–328
- Hoffmann P (1992) Zum Eindringen von Zucker in wassergesättigte Hölzer. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992, pp 9–19
- Hoffmann P (1993) Restoring deformed fine medieval turned woodware. ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 22–27 Aug 1993, vol I, pp 257–261 (AATA 31-534)
- Hoffmann P (1994) Sucrose for stabilizing waterlogged wood. II. Stabilization and the degree of degradation. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 357–379
- Hoffmann P (1995) Das Zuckerschiff. Restauro 101(5):350–354
- Hoffmann P (1996a) Das große Bad. Archäol Deutschl 4(4):6–11 (AATA 34-2204)
- Hoffmann P (1996b) Zur Naßholzkonservierung mit Zucker am Deutschen Schiffahrtsmuseum – eine Bilanz. Arbeitsbl Restaur 29(1), Gruppe 8, pp 231–240 (AATA 34-2205)
- Hoffmann P (1996c) Sucrose for waterlogged wood – not so simple at all. In: Bridgland J (ed) ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland, 1–6 Sept 1996, vol II, pp 657–662 (AATA 34-974)
- Hoffmann P (1997a) The conservation of the *Bremen Cog* – between the steps. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 527–545
- Hoffmann P (1997b) Die Bremer Kogge im 800 000-Liter-PEG-Bad. Restauro 103(4):252–259
- Hoffmann P (1999) Reconstructing a medieval river craft from the Rhine. In: Bridgland J, Brown J (eds) ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, 29 Aug–3 Sept 1999, vol II, pp 609–613
- Hoffmann P, Blanchette RA (1997) The conservation of a fossil tree trunk. Stud Conserv 42(2):74–82
- Hoffmann P, Kühn HJ (1999) The candy ship from Friesland. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 196–203
- Hoffmann P, Wittköpper M (1999) The Kauramin method for stabilizing waterlogged wood. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 163–166
- Hoffmann P, Choi K-N, Kim Y-H (1991) The 14th-century *Shinan Ship*: progress in conservation. Int J Naut Archaeol Underwater Explor 20(1):59–64 (AATA 29-2385)
- Hoffmann P, Pérez de Andrés C, Méndes JLS, Ramière R, Tran QK, Weber U (1994) European interlaboratory study on the conservation of waterlogged wood with sucrose. In: Hoffmann

- P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 309–335
- Hoffmann P, Barthez J, Bernard-Maugiron H, Koefoed IB, Jensen P, Watson J, Jones AM (1999) WOAM 98 comparative study on the stabilization of wet wood lacquerware. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 299–309
- Hopp K (1992) Modellversuche zur Rückformung einer verwölbten Holzplatte. Diplomarbeit, Fachhochschule Köln, Fachbereich Restaurierung und Konservierung, Studienrichtung Holzobjekte
- Horioka K, Higuchi S (1983) Repairing of wooden constructed cultural property with polyurethane resin adhesive. International symposium on the conservation and restoration of cultural property. The Conservation of Wooden Cultural Property, Tokyo and Saitama, 1–6 Nov 1982, Tokyo 1983, pp 173–188 (AATA 22-697)
- Howlett FC (1988) The potential for glycol treatments to counteract warpage in wooden objects. Wooden Artifacts Group, AIC, New Orleans, Louisiana
- Howlett FC (1990) Reducing warpage in wooden objects using low molecular weight glycols. Furniture conservation training program, Williamsburg, Virginia
- Hückel A (1979) Zur Technologie eines Sarkophags aus dem Metropolitan Museum, New York. Arbeitsbl Restaur 2, Gruppe 9, pp 43–50
- Hüllen L (1976) Bergung, Wiederaufbau und Konservierung der Bremer Hansekogge. Arbeitsbl Restaur 9(1), Gruppe 20, pp 40–42 (AATA 14-172)
- Hug B (1979a) Die Methode Arigal C. Z Schweiz Archäol Kunstgesch 36(2):124–127
- Hug B (1979b) Die Methode Carbowachs (PEG)/Gefriertrocknung. Z Schweiz Archäol Kunstgesch 36(2):134–137
- Hug B (1985) Lyophilisation: 10 ans d'expérience. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble, 28–31 Aug 1984 – Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 207–211 (AATA 25-588)
- Hu Jigao (1980) Conservation of waterlogged lacquerwares unearthed in China. 3rd International Symposium on the Conservation and restoration of cultural property, Tokyo 1979, Tokyo National Research Institute of Cultural Properties
- Humphrey BJ (1986) Vapor phase consolidation of books with Parylene polymers. J Am Inst Conserv 25(1):15–29
- Hutchings J (1997) The conservation of the Poole log-boat: sucrose treatment on a large scale. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 281–293
- Ignă A (1978) Restaurarea și conservarea unui fragment de leasă dacică de la șercaia județului Brașov (Restoration and conservation of a hurdle fragment from Dacia, Șercaia, district Brașov). Acta muzei Napocensis, Cluj-Napoca 15:653–658
- Imazu S (1988) The method using mannitol and polyethylene glycol in freeze-drying waterlogged organic material. Kobunkazai No Kagaku 33(2):52–62 (AATA 27-632)
- Imazu S, Morgós A (1997) Conservation of waterlogged wood using sugar alcohol and comparison the effectiveness of lactitol, sucrose and PEG 4000 treatment. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 235–255
- Imazu S, Morgós A (1999a) Lactitol conservation of a 6m long waterlogged timber coffin. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 210–214
- Imazu S, Morgós A (1999b) Lactitol conservation in an open-air environment of large wood elements of a 5th century A.D. dugout pipeline. In: Bridgland J, Brown J (eds) ICOM

- Committee for Conservation, 12th Triennial Meeting, Lyon, 29 Aug–3 Sept 1999, vol II, pp 614–618
- Imazu S, Nishiura T (1990) A new freeze-drying method using mannitol and PEG for the preservation of waterlogged wood. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden, 26–31 Aug 1990, vol 1, pp 234–238
- Inoue M, Ogata S, Nishikawa M, Otsuka Y, Kawai S, Norimoto M (1993) Dimensional stability, mechanical properties, and color changes of a low molecular weight melamine-formaldehyde resin impregnated wood. Mokuzai Gakkaishi 39(2):181–189
- Irwin HT (1977) Question period following: a new method for the preservation of waterlogged archaeological remains: use of tetraethyl orthosilicate. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol 2, pp 61–62 (AATA 14-174)
- Irwin HT, Wessen G (1976) A new method for the preservation of waterlogged archaeological remains: use of tetraethyl orthosilicate. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol 1, pp 49–50 (AATA 13-916)
- Iwasaki T, Higuchi S (1969) Conservation of wooden objects from the ruins of the Heijo Palace. Sci Conserv 5:1–20 (AATA 8-180)
- Iwasaki T, Higuchi S (1970) Conservation treatment of wooden objects (II): synthetic resins for filling and surface trimming of wooden cultural properties. Sci Conserv 6:13–24 (AATA 8-758)
- Jensen J, Sørensen JN, Rieck F, Aistrup MS (1989) Hjortespringbåden genopstillet (The Hjortespring boat reassembled). Nationalmuseets arbejdsarkiv, pp 101–114 (AATA 28-662)
- Jensen P, Bojesen-Koefoed I, Meyer I, Straetkvern K (1994) The Cellosolve-petroleum method. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 523–535 (AATA 32-837)
- Jenssen V, Murdock L (1982) Review of the conservation of *Machault* ships timbers: 1973–1982. In: Grattan DW, McCawley JC (eds) Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa 1981, Ottawa 1982, pp 41–49 (AATA 21-417)
- Jespersen K (1982) Some problems of using tetraethoxysilane (Tetraethyl-orthosilicate: TEOS) for conservation of waterlogged wood. In: Grattan DW, McCawley JC (eds) Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa 1981, Ottawa 1982, pp 203–207 (AATA 21-418)
- Jespersen K (1985) Extended storage of waterlogged wood in nature. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble, 28–31 Aug 1984 – Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 39–54 (AATA 24-670)
- Jespersen K (1986) Konserverwacja drewna wydobytego z wody w Danii od 1859 do 1984 (Conservation of waterlogged wood in Denmark from 1859 to 1984). In: Lehmann J (ed) Proceedings, Ochrona obiektów muzealnych: sympozjum konserwatorskie, Warszawa 2–4.X.1984. Biblioteka muzealnictwa i ochrony zabytków. Seria B, no t 80, pp 27–31 (AATA 28-2292)
- Jiang J (1995) (The reasons for contraction of waterlogged wood in PEG solutions). Wenwu Baohu Yu Kaogu Xue 7(2):57–61 (AATA 33-2579)
- Johnson C, Head K, Green L (1995) The conservation of a polychrome Egyptian coffin. Stud Conserv 40(2):73–81 (AATA 33-1011)
- Jones JB (1988) Rapid silicification of wood artifacts and plant fragments using a silicon chelate. Patent AU 577.788 (AATA 27-1965)
- Jover A (1994) The application of PEG 4000 for the preservation of Palaeolithic wooden artifacts. Stud Conserv 39(3):193–198 (AATA 32-840)
- Kadry A (1986) The Solar Boat of Cheops. Int J Naut Archaeol Underwater Explor 15(2):123–131 (AATA 23-2311)
- Kaenel G (1994) PEG conservation of a Gallo-Roman barge from Yverdon-les-Bains (Canton of Vaud, Switzerland). In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM

- Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 143–165 (AATA 32-842)
- Katzev SW, Katzev ML (1974) Last harbour for the oldest ship. *Natl Geogr Mag* 146(5):618–625 (AATA 13-278)
- Kawagoe M, Ishigaki A (1988) Theoretical considerations on the impregnation process of waterlogged wood with polyethylene glycol (PEG). *Kenkyu Kiyo* (Nara Kogyo Koto Senmon Gakko) (24):83–86 (AATA 28-665)
- Kaye B (1995) Conservation of waterlogged archaeological wood. *Chem Soc Rev* 24(1):35–43 (AATA 33-1013)
- Kaye B, Cole-Hamilton DJ (1995) Conservation of knife handles from the Elizabethan warship *Makeshift*. *Int J Naut Archaeol Underwater Explor* 24(2):147–158
- Kaye B, Cole-Hamilton DJ (1999) Supercritical drying. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) *Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999*, p323 (poster)
- Kazanskaya SY (1973) Konservirujuščie sostavy dlja derevjannyh archeologičeskich izdelij (Preservative compositions for archaeological wood articles). *Modif Drev Sint Polim*, pp 168–173 (AATA 12-869)
- Kazanskaya SY (1979) Voprosy sochaniija archeologičeskoj drevesiny (Questions concerning the maintenance of archaeological wood). *Mat vses nauč-techn konf, Grodno 1979*, Minsk 1979, pp 178–183
- Kazanskaya SY (1992) The different variances of using sucrose in conservation of waterlogged wood by the Minsk method. In: AdR (ed) *Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Febr 1991, Freiburg (Germany) 1992*, pp 59–63
- Kazanskaya SY, Nikitina KF (1985) On the conservation of waterlogged degraded wood by a method worked out in Minsk. *Les Bois Georges d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 Aug 1984 – Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985*, pp 139–146 (AATA 24-674)
- Kazanskaya SY, Nikitina KF (1991) Modification of the Minsk method for conserving wet archaeological wood. In: Hoffmann P (ed) *Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990, Bremerhaven 1991*, pp 259–267
- Kazanskaya SY, Vichrov YV (1982) Sostav dlja konservirovaniâ nasyŝennoj vodoj archeologičeskoj drevesiny (Compositions for conservation of waterlogged archaeological wood). *USSR-Patent 1034903* (8 Jan 1982) (AATA 21-420)
- Kellogg RM (1989) Density and Porosity. In: Schniewind AP (ed) *Concise encyclopedia of wood & wood-based materials*. MIT Press, Cambridge, MA, pp 79–82
- Kelly J (1980) The construction of a low cost, high capacity vacuum freeze-drying system. *Stud Conserv* 25(4):176–177 (AATA 18-132)
- Kenaga DL (1958) Stabilization of wood and wood products with acrylic-like compounds. *US-Patent 3077417*
- Ketelsen A (1959) Konservierung bodenfeuchter Hölzer. *Präparator* 5(1):31
- Kigawa R (1994) Investigation of bacterial and fungal attack in the PEG treatment of excavated wood. *Hozon Kagaku* 33:47–54 (AATA 33-1014)
- Kim SG, Won GD (1974a) Resin treatments for the preservation of the historic remains made of wood: ultraviolet aging of poly (methyl methacrylate) and silicon resins. *Choson Minjujuui Inmin Konghwaguk Kwahagwon Tongbo* 22(2):20–27 (AATA 12-870)
- Kim SG, Won GD (1974b) Resin treatments for the preservation of the historic remains made of wood. Aging of poly (methyl methacrylate) and silicon resins. *Hwahak Kwa Hwahak Kongop* 17(5):249–255 (AATA 12-871)
- Kim SG, Won GD, Chong IY (1975a) Studies on the resin treatments for the preservation of historic remains made of wood. *Choson Minjujuui Inmin Konghwaguk Kwahagwon Tongbo* 23(4):198–201

- Kim SG, Won GD, So JN (1975b) Resin treatments for the preservation of the historic remains made of wood. Hardening of low polymers of poly dimethyl phenylsiloxane and poly phenylsiloxane. *Choson Minjujuui Inmin Konghwaguk Kwahagwon Tongbo* 23(6):22–25 (AATA 13-920)
- Kim SG, Won GD, So JN (1975c) Studies on the resin treatment for the preservation of the historic remains made of wood. 4. Physical properties of silicone resins from mixtures of low polymers of poly dimethyl silicone resins and poly phenyl siloxane. *Hwahak Kwa Hwahak Kongop* 18(3):137–141
- Kim SG, Won GD, Chong IY (1976a) Studies on the resin treatment for the preservation of historic remains made of wood. 6. Microscopic study of silicone resin-permeated wood. *Hwahak Kwa Hwahak Kongop* 19(3):147–152
- Kim SG, Won GD, Han YS (1976b) Studies on the resin treatment for the preservation of the historic remains made of wood. 7. *Hwahak Kwa Hwahak Kongop* 19(6):305–311 (AATA 15-1311)
- Kislov MN, Čistáková ON (1962) Conservation of wooden articles from Novgorod excavations. *Istoriko-archeologičeskij Sbornik. Izdatel'stvo Moskovskogo Universiteta, Moskva*, pp 352–362
- Kiss P (1987) 1756-os szácszláda restaurálása (The restoration of a 1756 furrier's guild chest). *Műz Műtárgyvédelem* 1(6):227–234 (AATA 24-678)
- Kisser J, Pittioni R (1935) Über die Konservierung erdfeuchter urzeitlicher Hölzer. *Museums-kunde* (NF) 7:148–152
- Klapwijk D (1978) Restoration and preservation of decayed timber structures and constructions with epoxies. Conservation of wood in painting and the decorative arts. Preprints of the contributions to the Oxford congress, 17–23 Sept 1978. IIC; 6 Buckingham Street, London WC2 N 63A; 1978, pp 75–76 (AATA 16-414)
- Koch W (1983) Eine Dokumentation historischer Rückseitenbehandlungen von Holztafelgemälden aus Museumsbestand. Fach- und Fortbildungstagung "Probleme um den Bildträger Holz" 1982, Selbstverlag der Kunstgewerbeschule Bern, 1983, pp 88–97
- Koesling V (1992a) Konservierung wassergesättigter Holzdosens mit Zuckerlösungen. In: AdR (ed) *Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992*, pp 98–103
- Koesling V (1992b) Konsolidierung wassergesättigter Naßholzfunde mit heißen Zuckerlösungen. *Arbeitsbl Restaur* 25(2) Gruppe 8, pp 209–212 (AATA 31-1702)
- Koesling V (1993a) Zeittafel zur Kunststoffgeschichte. *Arbeitsbl Restaur* 26(2), Gruppe 16, pp 133–140
- Koesling V (1993b) Zwei Kloben aus der Takelage eines hölzernen Kaffenkahns. *Restaur* 99(4):243–245 (AATA 31-1703)
- Koesling V (1994) Untersuchungen zur Zuckerkonservierung wassergelagerter Hölzer. *Arbeitsbl Restaur* 27(1) Gruppe 8, pp 217–221 (AATA 32-846)
- Kolčín BA (1973) Derevjannoe varenie (Preservatives for wood). *ChimŽizn* (9):14–18 (AATA 13-279)
- Kollmann F (1955) *Technologie des Holzes und der Holzwerkstoffe*, vol 1 and 2. Springer, Berlin Göttingen Heidelberg/Bergmann, München
- Koob SP (1984) The continued use of shellac as an adhesive – why? *Adhesives and Consolidants*, 103 (AATA 21-2355) IIC, London
- Kordač FJ (1964) Konservierung von Bauholz "in situ". *Archeol Rozhledy* 16:881–886
- Kramer W (1979) Die Alkohol-Äther-Harz-Methode. *Z Schweiz Archäol Kunstgesch* 36(2): 127–131
- Kramer W, Mühlethaler B (1967/1968) Über die Erfahrungen mit der Alkoholäther-Methode für die Konservierung von Naßholz am Schweizerischen Landesmuseum. *Z Schweiz Archäol Kunstgesch* 25(2):78–88
- Lachmann M, Nissel D, Peters M, Reichelt L, Unger A (1986) Die Konservierung der Holzbauteile der "Faulen Magd". *Neue Museumskd* 29(4):292–298
- Lan Z (1999) Conservation of an ancient boat using the PEG spray method. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) *Proceedings of the 7th ICOM-CC Working Group on*

- Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 179–181
- Lange W (1996) Natürliche Baumharze – Terpenoide Harze mit geringen Anteilen an etherischen Ölen. Laubholzharze – 3. Mitteilung: Dammar, Cativobalsam und Kopale. Holz-Zentralblatt 122(72):1172, 1174
- Lange W (1997) Natürliche Baumharze – potentielle Erzeugnisse einer forstlichen Nebennutzung. Kiefernhharze – 4. Mitteilung: Kiefernhharze. Holz-Zentralblatt 123(25): 356, 358
- Laures FF (1984) A means of rapid drying of antique wooden material previously saturated with polyethylene glycol (PEG 4000) in a watery solution. Int J Naut Archaeol Underwater Explor 13(4):325–327 (AATA 22-706)
- Laures FF (1986) More details about rapid drying of wood by “frying” it in polyethylene glycol. Int J Naut Archaeol Underwater Explor 15(1):68–69 (AATA 23-2307)
- Lecote O, Oudry S (1990) Traitement du support bois d’une berline du XVIII^e siècle. La conservation du bois dans le patrimoine culturel: Besançon-Vesoul, 8–10 Nov 1990, pp 153–162 (AATA 30-1275)
- Leechman D (1931) Technical methods in the preservation of anthropological museum specimens. National Museums of Canada Annual Report for 1929, Bulletin no 67, Ottawa, pp 127–160
- Lefève R (1958) Alteratie, beschermingen versteviging van hout (Alteration, preservation and stabilization of wood). Bull Inst Royal Patrimoine Artistique 1:111–120
- Lefève R (1961) Conserveringsbehandeling met Polyethyleenglycol van een romeins houten emmertje opgegraven te Wommel. Bull Inst Royal Patrimoine Artistique 4:97–108 (AATA 13-278)
- Lefève R, Vynckier J (1966) Proefbehandeling van nat opgegraven hout met polyethyleenglycol. Bull Inst Royal Patrimoine Artistique 9:206–212 (AATA 8-1769)
- Lehmann J (1962) Konserwacja drewnianych zabytków etnograficznych i archeologicznych (Conservation of ethnographical and archaeological wood items). Ochrona Zabytkow 15: 24–33
- Lehmann J (1975) Badania mozliwosci rownoczesnej stabilizacji i konsolidacji drewna wydobytego z wody przy pomocy roztworu zywicy mocznikowej (Investigations on the possibility of simultaneous stabilization and consolidation of waterlogged wood with a solution of urea resin). Stud Muzealne 11:109–116 (AATA 14-185)
- Leo RF, Barghoorn ESH (1976) Silicification of wood. Bot Mus Leaf Harv Univ 25(1):1–47
- Lill G (1937) Über die Konservierung und Wiederherstellung von plastischen Bildwerken. Dtsch Kunst Denkmalpflege, Deutscher Kunstverlag, Berlin, pp 2–9
- Lodewijks J (1968) Die Härtung mürber Holzbilder und Holzplastiken. Arbeitsbl Restaur (2), Gruppe 8, pp 10–11 (AATA 8-1302)
- Loeken TM (1967) Kristusfigur nr. C 21997. Undersökelse og Konservering (Examination and conservation). Universitetets Oldsaksamlings Årbok 1963–1964, pp 67–78 (AATA 13-924)
- Lorin A, Lemetayer F (1999) La lyophilisation à pression atmosphérique: quoi de neuf? In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 116–119
- Losos L (1958) Petrifikace dřeva umělými pryskyřicemi (Petrification of wood by artificial resins). Památková Péče 18(1/2):12–21
- Lu Heng, Zheng Youming (1992) An experimental study on stabilization of seriously degraded waterlogged wood unearthed from Homutu, Zhejiang province. Wenwu Baohu Yu Kaogu Xexue 4(2):10–18 (AATA 32-2291)
- Lukács MK (1987) Komáromi láda restaurálása (The restoration of a Komárom chest). Műz Műtárgyvédelem (17):75–86 (AATA 24-719)
- Lukowsky D, Peek R-D (1998) Time dependent over-uptake of etherificated melamine resins. IRG/WP/98-40109
- Lukowsky D, Peek R-D, Rapp AO (1998) Curing conditions for a low formaldehyde etherificated melamine resin. IRG/WP/98-40108

- MacLeod ID (1989) Hygroscopicity of archaeological timber: effects of molecular weight of impregnant and degree of degradation. Conservation of wet wood and metal. In: MacLeod ID (ed) Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals, Fremantle 1987, Western Australian Museum Perth 1989, pp 211–213 (AATA 28-2309)
- MacLeod ID (1990) Conservation of waterlogged timbers from the *Batavia* 1629. Bull Austr Inst Mar Archaeol 14(2):1–8 (AATA 28-2310)
- MacLeod ID, Brooke P, Richards V (1991) Iron corrosion products and their interactions with waterlogged wood and PEG. In: Hoffmann P (ed) Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990, Bremerhaven 1991, pp 119–132
- MacLeod ID, Fraser FM, Richards VL (1989) The PEG-water solvent system: effects of composition on extraction of chloride and iron from wood and concretion. Conservation of wet wood and metal. In: MacLeod ID (ed) Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals, Fremantle 1987, Western Australian Museum Perth 1989, pp 245–263 (AATA 28-2311)
- MacLeod ID, Mardikian P, Richards VL (1994) Observations on the extraction of iron and chloride from composite materials. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 199–211
- Madajski S (1952) Sposoby konserwacji drewna w Łódzkim ośrodku archeologicznym (Conservation methods for wood in the archaeological museum of Lodz). Archeol Rozhledy 4:442–448
- Mager-Maag RA (1966) Flüssiges Nylon. Mitt Arbeitsgem Archivrestaur Freib 24:283–284
- Majewski L (1972) On Conservation (of objects made of wood). Mus News 51(2):13–14 (AATA 10-201)
- Makes F, Pühringer J (1987) The protection of wood against moulds from hydrophobics to inhibitors of enzymes. Some strategies. In: Vendl A, Pichler B, Weber J, Banik G (eds). Wiener Ber Naturwiss Kunst 4/5:151–179 (AATA 28–669)
- Manková D (1966) Imprägnieren von Holz mittels einiger synthetischer Stoffe und ihr Einfluß auf die Eigenschaften des Holzes. Monumentorum tutela-Ochrona Pamiątek 1:135
- Marijnissen R-H (1961) O.L. Vrouw ten troost van Vilvoorde, onderzoek en behandeling. Bull Inst Royal Patrimoine Artistique 4:76–95 (AATA 13-281)
- Marijnissen R-H (1967) Degradation, conservation et restauration de l’oeuvre d’art Tome I. Arcade, Bruxelles (AATA 7-710, 14-95)
- Martens M, Unger A (1992) Die Konservierung einer Apostelfigur mit Polyvinylbutyral. Berl Beitr Archäometr 11:207–216
- Masuzawa F, Nishiyama Y (1973) Experiment on the impregnation of waterlogged wood with PEG, part I. Conserv Sci Bull 2
- Masuzawa F, Takada H (1974) Treatment of unearthed wood polymer combinations impregnated with acrylic monomer. Conserv Sci Bull 3:86–89
- Masuzawa F, Kitano N, Ueda N (1993) Dai-shura no Hozonshori (Gaiyo hokoku) [Conservation treatment of a large Shura (wooden sled): preliminary report]. Gangō-ji Bunkazai Henkyū (46):1–13 (AATA 32-856)
- Masuzawa F, Tazawa Y, Okamoto H (1982) Effects of conservation treatments on physical properties and dimensional stability of waterlogged wood. Archaeology and natural science, Nara, 1981 (publ March 1982), vol 14, pp 89–101 (AATA 19-1361)
- Masuzawa F, Ueda N, Inoue M, Kawamoto K (1999) Screening some methods for conserving and restoring about 500 objects of waterlogged Japan ware. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 268–274
- Mateyak M, Sheika E (1984) Rate of change of moisture content and swelling of linden wood impregnated with paraloid and vinacet. Annals of Warsaw Agricultural University – SGGW-AR. For Wood Technol 31:19–23 (AATA 27-643)

- Mavroyannakis EG (1981) Ageing of reinforced ancient materials by gamma ray methods. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/17/1 (AATA 18-985)
- Mavroyannakis EG (1982) Ageing of reinforced ancient waterlogged wood by gamma ray methods. Proceedings of the ICOM Waterlogged Wood Working Group Conference, 1982, pp 263-266 (AATA 21-430)
- McCawley JC (1977) Waterlogged artifacts. The challenge to conservation. JCC1 2:17-26
- McCawley JC, Grattan DW, Cook C (1982) Some experiments on freeze-drying: design and testing of a nonvacuum freeze dryer. In: Grattan DW, McCawley JC (eds) Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa 1981, Ottawa 1982, pp 253-262 (AATA 21-431)
- McKerrell H, Roger E, Varsanyi A (1972) The acetone/rosin method for conservation of waterlogged wood. Stud Conserv 17(3):111-125 (AATA 9-629)
- Mesterházy E (1979) Új-írländi szertartási maszk és óceániai kettős faszobor restaurálása (Restoration of a New-Ireland ceremonial mask and a double wood-carving of Oceania). Múz Műtárgyvédelem (6):125-136 (AATA 17-1181)
- Meyer I (1997) A logboat - from Berne to Brede. The conservation of a Swiss logboat in Denmark. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 269-280
- Michaelsen H (1984) Der Dürerschrank auf der Wartburg. Geschichte, Konservierung, Restaurierung. Neue Museumskd 27(4):260-272
- Mietke H, Martin D (1999) Sugar preservation of the *Friesland* ship. Chemical and microbiological investigations and insights. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 204-209
- Mihailov A (1970a) Conservation of wooden works of art in Bulgaria. IIC Conference on the Conservation of Stone and Wooden Objects, New York 1970, preprints, vol 2, pp 115-136 (AATA 8-768)
- Mihailov A (1970b) Conservation of the wooden elements in the Renaissance houses of the People's Republic of Bulgaria. Stud Conserv 15(3):221-223
- Mihailov A (1975) Conservation of wood which has stayed in water in the P.R. of Bulgaria. ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/8/3 (AATA 13-926)
- Mihailov A (1978) Conservation of a Thracian one-log boat. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, 78/7/2 (AATA 16-426)
- Mihailov A, Ivanova N (1987) Stabilization of wooden museum artifacts. VI. International Restorer Seminar, Veszprem 13-23 July 1987, pp 431-436
- Mihailov A, Savov A, Ivanova N, Palichev A (1974) The conservation of wood and metal ethnographic museum exhibit. National Institute for Cultural Property, Sofia
- Mitanov P, Kabaivanov V (1974) Oпити за укрепване на члудожествени произведениа на дърво или върчу дървечна основа чрез propivane s monomeri i monomerni smesi i posledvaša radiacionna polimerizaciâ (Experiments on the consolidation of art objects made from wood or wood-based materials by impregnation with monomers and monomer mixtures and subsequent radiation polymerization). Muz Pametnicy Kulturata, Sofia 14(4):47-58
- Mitanov P, Kabaivanov V (1975) Obtention de polymères acryliques par la polymérisation de radiation, étude sur les propriétés des films de laque, obtenus des polymères et essais dans le domaine de la consolidation des oeuvres d'art en bois ou sur base de bois par imprégnation avec des monomères et des mélanges de monomères et une polymérisation de radiation subséquente. ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/18/7 (AATA 13-928)
- Mo och Domsjö AB, Centerwall KBS (1952) Improvements in or relating to the preservation of wood. Swedish Patent 157302

- Morén RE, Centerwall KBS (1961) The use of polyglycols in the stabilizing and preservation of wood. Meddelanden från Lunds Universitets Historiska Museum, June 1960 (1961), pp 176-196 (AATA 13-285)
- Morgós A (1987) Nagymértékben hiányos és csökkent szilárdságú fatárgyak restaurálása. Két rossz állapotú ácsolláda restaurálása (Restoration of gravely deteriorated wooden objects - restoration of two timbered chests of poor condition). Múz Műtárgyvédelem (17):159-172 (AATA 24-740)
- Morgós A (1992) Erfahrungen mit der Stabilisierung von Naßholz mit Zucker in Ungarn. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan-1 Feb 1991, Freiburg (Germany) 1992, pp 4-8
- Morgós A (1993a) Régészeti faanyagok konzerválásának története Magyarországon (The history of archaeological waterlogged wood conservation in Hungary). Múz Műtárgyvédelem (22):229-237 (AATA 32-2295)
- Morgós A (1993b) Protection of wooden surfaces by hydrophobisation using silicones. Cultural heritage and restorer in the changing world: 8th international restorer seminar 1993, pp 210-213 (AATA 33-1037)
- Morgós A (1994) A bibliography on the conservation of waterlogged wood using sugars. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 301-308
- Morgós (1999a) The conservation plan of the Iron Age timber structure of the grave chamber at Százhalombatta. Archaeology of the Bronze and Iron Age. In: Jerem E, Poroszlai I (eds) Proceedings of the International Archaeological Conference Százhalombatta, 3-7 Oct 1996. Archaeolingua Budapest 1999, pp 335-341
- Morgós A (1999b) The conservation of large dried out and waterlogged archaeological wooden objects and structural elements - low molecular weight epoxy resin and sucrose, lactitol treatments, part I and II. In: Babiński L (ed) Archaeological Wood Research and Conservation, Symposium Biskupin-Wenecja, 22-24 June 1999, State Archaeological Museum in Warsaw, Museum at Biskupin 1999, pp 135-147 and 149-166
- Morgós A, Czvikovsky T (1987) Composite materials on the basis of wood and silicon acrylate. 6th symposium on wood modification, Poznan, 23-26 June 1987, pp 33-40
- Morgós A, Glatfelder-McQuirk L (1990) The sucrose conservation of 15th-16th century waterlogged wooden finds. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden 26-31 Aug 1990, vol 1, pp 241-242
- Morgós A, Imazu S (1993) A conservation method for waterlogged wood using a sucrose-mannitol mixture. In: Bridgland J (ed) ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC, 22-27 Aug 1993, vol 1, pp 266-272 (AATA 31-539)
- Morgós A, Imazu S (1994) Comparing conservation methods for waterlogged wood using sucrose, mannitol and their mixtures. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 287-300 (AATA 32-857)
- Morgós A, Unger A (1992) Zerstörungsfreie Prüfung von Naßholz mittels Röntgencomputer- und Magnetresonanztomographie. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan-1 Feb 1991, Freiburg (Germany) 1992, pp 78-83
- Morgós A, Glatfelder-McQuirk L, Gondar E (1987) The cheapest method for conservation of waterlogged wood: the use of unheated sucrose solutions. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6-11 July 1987, vol 1, pp 313-319
- Morgós A, Strigazzi G, Preuss H (1994) Microbicides in sugar conservation of waterlogged archaeological wooden finds: the use of isothiazolones. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16-20 Aug 1993, Bremerhaven 1994, pp 463-484

- Morse JD (1970) Conservation of furniture. Country Cabinetwork and Simple City Furniture, University of Virginia Press (papers of the 1969 Winterthur Conference), pp 294–311 (AATA 15-431)
- Moss AA (1952) Preservation of a Saxon bronze-bound wooden bucket with iron handle. *Mus J* 52:175–177 (AATA 13-73)
- Mühlethaler B (1966) CIBA – Arbeitstechnische Hinweise. Araldit bei der Erhaltung von Altertümern. CIBA-Publication, Basel, 34 197, 22 pp
- Mühlethaler B (1966/1967) Araldit bei der Erhaltung von Altertümern. CIBA-Aspekte, Sondernummer, p10
- Mühlethaler B (1969a) L'état actuel dans le domaine de la conservation du bois humide. ICOMOS Symposium on the Weathering of Wood, Ludwigsburg (Germany), 8–11 June 1969, pp 41–52 (AATA 11-568)
- Mühlethaler B (1969 b) Über den heutigen Stand der Feuchtholzkonservierung. *Dtsch Kunst Denkmalpflege* 27:111–116
- Mühlethaler B (1973) Kleines Handbuch der Konservierungstechnik. Haupt, Bern (AATA 10-676 u. 13-585)
- Mühlethaler B (1977) Das Verfestigen und Konservieren von porösen organischen Materialien. Araldit – ein Beitrag zur Erhaltung von Kulturgut. CIBA-GEIGY, Basel, pp 20–24
- Mühlethaler B, Barkman L, Noack D (1973) Conservation of waterlogged wood and wet leather. ICOM Travaux et Publications, no 11. Edition Eyrolles, Paris
- Müller HG, Thieme J (1966) Zur Reinigung und Festigung mittelalterlicher Holz- und Gewebefunde. *Neue Museumskd* 9:63–75
- Mueller-Beck H, Haas A (1959) Holzkonservierung mit Arigal C (Ciba). *Jahrb Bern Histor Mus* 37/38:260–271
- Mueller-Beck H, Haas A (1960) A method for wood preservation using Arigal C. *Stud Conserv* 5:150–157(8) (AATA 13-248)
- Mueller-Beck, H, Haas A (1961) Ein neues Verfahren zur Konservierung von Feuchthölzern. *Präparator* 7:157–168
- Munnikendam RA (1967) Conservation of waterlogged wood using radiation polymerization. *Stud Conserv* 12(2):70–75 (AATA 7-290)
- Munnikendam RA (1971) Conservering van houten en stenen voorwerpen. *Chem Weekblad* 67:K23–K26 (AATA 9-176, 13-796)
- Munnikendam RA (1972a) Low molecular weight epoxy resins for the consolidation of decayed wooden objects. *Stud Conserv* 17(4):202–204 (AATA 13-848)
- Munnikendam RA (1972b) The conservation of waterlogged wood with glycol methacrylate. ICOM Committee for Conservation, 3rd Triennial Meeting, Madrid 1972, 6/72/6 (AATA 14-115)
- Munnikendam RA (1973) The conservation of waterlogged wood with glycol methacrylate. *Stud Conserv* 18(2):97–99 (AATA 13-892)
- Munnikendam RA, Wolschrijn TJ (1969) Further remarks on the impregnation of porous materials with monomers. *Stud Conserv* 14(3):133–135 (AATA 13-697)
- Murdock L (1977) Construction details of a tank for polyethylene glycol treatment. Pacific Northwest Wet Site Wood Conservation Conference, Neah Bay (Washington), vol2, pp 67–68 (AATA 14-190)
- Murray H (1982) The conservation of artifacts from the *Mary Rose*. In: Grattan DW, McCawley JC (eds) Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa 1981, Ottawa 1982, pp 13–18 (AATA 21-1191)
- Murray H (1985) The use of mannitol in freeze-drying waterlogged organic material. *Conservator* (9):33–35
- Nacsá M (1987) Csalikulacs restaurálása (Restoration of a csalikulacs (double flask)). *Műz Műtárgyvédelem* (17):151–158 (AATA 24-744)
- Nakasato T (1975) Reinforcement and conservation treatment on "Igi" of lacquered wooden saddle: property of the Kashina Shrine. *Sci Conserv* 14:77–82 (AATA 12-873)

- Nakasato T (1994) Conservation of wooden panels used as ornamental members of roof decoration. *Hozon Kagaku* 33:55–66 (AATA 33-1039)
- Nakasato T, Higuchi S (1973) Conservation treatment of members in the removal rebuilding of the Jo-an, a national treasure. *Sci Conserv* 10:109–117 (AATA 10-677)
- Nakhla SM (1986) A comparative study of resins for the consolidation of wooden objects. *Stud Conserv* 31(1):38–44
- Natchinkina J, Cheinina E (1981) Conservation d'objets de l'Egypte ancienne en bois polychromé au Musée de l'Ermitage d'Etat. ICOM Committee for Conservation, 6th Triennial Meeting Ottawa 1981, 81/5/1 (AATA 18-1275)
- Netherlands National Commission for Unesco (1981) Conservation of waterlogged wood. International Symposium on the Conservation of large objects of waterlogged wood. Ministry of Education of Science (Netherlands), The Hague
- Nicholas DD (1972) Characteristics of preservative solutions which influence their penetration into wood. *For Prod J* 22(5):31–36
- Nicholas DD, Williams AD (1987) Dimensional stabilization of wood with dimethylol compounds. *IRG/WP/3412*
- Niedzielska M (1992) Konserwacja rzeźby "Krol Kazimierz Wielki" z Muzeum UJ (Conservation of the sculpture King Casimir the Great from the Jagiellonian University Museum). *Ochrona Zabytkow* 45(3):225–231 (AATA 31-542)
- Nielsen H-O (1985a) The treatment of waterlogged wood from the excavation of the *Haithabu* Ship. Les Bois Gorgés d'Eau: étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 août 1984 – Waterlogged wood: study and conservation. Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 299–312 (AATA 24-747)
- Nielsen H-O (1985b) Die Konservierung des Wikingerschiffes und der Naßholzfunde aus dem Hafen von Haithabu. *Arbeitsbl Restaur* (1), Gruppe 8, pp 128–136
- Nikitina KF, Gerasimova NG, Kolosova MI (1974) O sohrannosti i konservacii mokroj archeologičeskoj drevesiny (On the maintenance and conservation of waterlogged wood). *Konservacija i restavracija pamatnikov kul'tury i iskusstva*. Scientific conference, Ermitage, Leningrad 21–25 Jan 1974, pp 39–40
- Nishiura T, Imazu S (1989) Shutsudo-suishin-mokuzai no hozonshori go no anteisei (Dai 1 ppou) Kankyō-shitsudo-henka niyoru sunpōhenka (1) [Stability of waterlogged wood after preservation treatment (1). Behavior against change of ambient humidity (1)]. *Hozon Kagaku* 28:63–72 (AATA 27-654)
- Nishiura T, Imazu S (1990) Stability of waterlogged wood after preservation treatment, 2. Behavior against change of ambient humidity, 2. *Sci Conserv* 29:59–68 (AATA 28-2322)
- Nishiura T, Imazu S (1991) Experimental study on the dimensional change of highly degraded waterlogged wood according to ambient humidity after preservation treatment. In: Hoffmann P (ed) Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990, Bremerhaven 1991, pp 107–118
- Noack D (1965) Der gegenwärtige Stand der Dimensionsstabilisierung von Holz und Schlußfolgerungen für die Konservierung der Bremer Kogge. *Brem Jahrb* 50:43–72
- Noack D (1969) Some remarks on the processes used for the conservation of the "*Bremen Cog*". ICOMOS Symposium on the Weathering of Wood, Ludwigsburg (Germany), 8–11 June 1969, pp 89–97 (AATA 11-570)
- Nogid IL, Podzdnák AI (1965) Konservacija mokroj archeologičeskoj drevesiny (Conservation of wet archaeological wood). *Sovjet Archeol* (3):277–279 (AATA 8-771)
- Noldt U (1994) Termite bioassay of sucrose-treated waterlogged archaeological wood. In: Hoffmann P, Daley T, Grant T (eds) Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 337–356
- Oellermann E (1978) The working methods of the studio in Bernt Notke illustrated by the crucifix in Lübeck Cathedral, 1477. Conservation of wood in painting and the decorative arts.

- Preprints of the contributions to the Oxford congress 17–23 Sept 1978. IIC; 6 Buckingham Street, London WC 2N 63 A, 1978, pp 85–87 (AATA 13-433)
- O'Guinness Carlson M, Harvey RS, Singley K (1999) Conservation of waterlogged laquered wooden sculptures from the Warring States Period of China (476–221 BC). In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 275–283
- Organ RM (1959) Carbowax and other materials in the treatment of water-logged paleolithic wood. *Stud Conserv* 4(3):96–105 (AATA 13-212)
- Paciorek M (1993) Badania wybranych tworzyw termoplastycznych stosowanych do impregnacji drewna (A study of some thermoplastic resins used for wood impregnation). *Studia i Materiały Akademii Sztuk Pięknych w Krakowie*, Tom III, Wydawnictwo Literackie, Krakow 1993
- Packard E (1970) Consolidation of decayed wood sculpture. IIC Conference on the Conservation of Stone and Wooden Objects, New York 1970, proceedings, London, pp 13–17 (AATA 8-772, 13-751)
- Padfield T, Winslow J, Pedersen WB, Glastrup J (1990) Decomposition of polyethylene glycol (PEG) on heating. ICOM Committee for Conservation, 9th Triennial Meeting, Dresden, 26–31 Aug 1990, vol 1, pp 243–245
- Pang JTT (1981) The treatment of waterlogged oak timbers from a 17th century Dutch East Indiaman, *Batavia*, using polyethylene glycol. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/6 (AATA 18-1276)
- Parrent JM (1983a) The conservation of waterlogged wood using sucrose. Master's Thesis Texas, A and M University, College Station, Texas USA
- Parrent JM (1983b) The conservation of waterlogged wood using sucrose. Paper presented to the joint CUA/SHA Meeting, Denver, Colorado, Jan 1983
- Parrent JM (1985) The conservation of waterlogged wood using sucrose. *Stud Conserv* 30:63–72
- Paterakis A (1987) Synthetikes Ritines gia tin Stereosi tou Xilou (Synthetic resins for the consolidation of wood). *Anastylosis, restoration, protection, monuments and complexes B*: 371–374 (AATA 26-669)
- Paterakis A (1996) Sintirisi Templou i. Naou Evagelismou tis Teotokou sti Nazaret (Conservation of the sculpted wooden iconostasis in the Holy Church of the Annunciation in Nazareth). *Archéologia* 59:83–86 (AATA 34-989)
- Paul O (1979) Kunststoffprothesen für schadhafte Deckenbalkenköpfe im BETA-Verfahren. *Bautenschutz Bausanierung* 2:70–72
- Paul O (1981) 400 Jahre alter Fachwerkgiebel entdeckt und gerettet. *Bautenschutz Bausanierung* 4:45–48
- Payton R (1984) The conservation of an eighth century BC table from Gordion. In: Brommelle NS, Pye EM, Smith P, Thomson G (eds) *Adhesives and Consolidants*. International Institute for Conservation, London, pp 133–137 (AATA 21-1675)
- Payton R (1987) The conservation of artefacts from one of the world's oldest shipwrecks, the Ulu Burun, Kas shipwreck, Turkey. Recent Advances in the Conservation and Analysis of Artifacts, Jubilee Conservation Conference, Univ London, Institute of Archaeology, pp 41–49
- Peralta JT (1980) Ancient mariners of the Philippines. *Archaeology* 33(5):41–48 (AATA 18-338)
- Perleberg J, Unger A (1985) Zum Problem der Neuvergoldung von mit Methylmethacrylat konsolidierten Kunstobjekten aus Holz. *Neue Museumsdkd* 28(4):277–278
- Peters KM (1981) The conservation of a living artefact – a Maori meeting house at Makahae. A preliminary report. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/3/10 (AATA 18-1806)
- Peters K (1984) The Chatham Island dendroglyphs – conservation and survival. ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen, 1984, 84.3.10–84.3.12 (AATA 21-2343)
- Petersohn HR (1989) Die Restaurierung eines Tafelgemäldes aus der Werkstatt des Hans Leonhard Schäuflerin. *Restaurio* 95(1):14–21

- Petrovski Z (1987) A gyulai ácsok és kőművesek legényládájának restaurálása (The restoration of the carpenter and mason journeymen's chest from Gyula). *Műz Műtárgyvédelem* (16):289–316 (AATA 24-765)
- Phillips MW, Selwyn JE (1978) Epoxies for wood repairs in historic buildings. US Dept. Interior, Heritage Conservation and Recreation Service, Washington, DC
- Pirling R, Buchwald G (1974) Ein Schiff aus karolingischer Zeit und seine Konservierung. *Naturwissenschaften* 61:396–398
- Pittioni R (1952) Die Präparation der Holztröge von der Kelchalpe bei Kitzbühel. *Nachr-BI Österr Ur Frühgeschichtsforsch* 1(1/2):9–10
- Plenderleith HJ (1954) The conservation of the sword and scabbard. In: Wheeler M (ed) *The Stanwick fortifications, North Riding of Yorkshire* (Repts Res Committee Soc Antiquaries). Oxford Univ Press, London, pp 45–47 (AATA 13-109)
- Plenderleith HJ (1956) The conservation of antiquities and works of art. Oxford Univ Press, London, part 1/5, pp 116–143 (Wood)
- Pluska I (1970) Czesciowe usuniecie zniszczonego drewna nzezby polichromowanej i zastapieme go skorupa z tworzyw sztucznych (Partial removal of degraded wood from the inside of a polychromed sculpture and its replacement by synthetic resins). *Ochrona Zabytkow* 23(2): 101–105 (AATA 8-1306)
- Pokrovskaya EN, Melnikova IN, Sidorov VJ (1994) Ispolzovanie oligo furfuriolsiloksana dlya povisheniya prochnosti degradirovannoi drevesini (Application of oligo furfuryloxysiloxane to increase the strength of degraded wood). *Khimia Drevesiny* 1994(1):42–45 (AATA 34-992)
- Pothast I (1996) Untersuchungen an zuckerkonserviertem Naßholz. *Kunsttechnol Konserv* 10(1):173
- Pouliot B (1988) Research on the conservation of African camwood: a project realized in a small conservation laboratory. In: Barclay R, Gilberg M, McCawley JC, Stone T (eds) *Symposium 86. The care and preservation of ethnological materials: proceedings*. Canadian Conservation Institute, Ottawa, pp 215–221 (AATA 26-673)
- Pournou A, Moss ST, Jones AM (1999) Preliminary studies on polyalkylene glycols (PAGs) as a pre-treatment to the freeze-drying of waterlogged archaeological wood. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 104–109
- Powell W (1904) US Patent 755,240, 22 March
- Prandstetten R (1989) Zwei Verfahren zur Sanierung von Bauholz: Aussteifung durch 2-Komponentenharze ("Beta-Verfahren")/Konservierung mittels Heißluft. *Restauratorenblätter* 10:80–82
- Prange C (1990) Problems of restoration and conservation of wooden lighters. *Transport Mus: Yearb Int Assoc Transport Mus* 15/16:20–25 (AATA 29-2415)
- Preißler H (1989) Naßholzkonservierung und Behandlung deformierter Holzfundstücke. In: Möller H (ed) *Restaurierung von Kulturdenkmälern: Beispiele aus der niedersächsischen Denkmalpflege, Berichte zur Denkmalpflege in Niedersachsen*. Beiheft no 2, pp 321–323 (AATA 28-2325)
- Preuss H (1992) Mit Zucker Naßholz konservieren? In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992, pp 64–69
- Rama Rao N, Pandit Rao V (1990) Conservation of an old wooden bullock cart. *Indian J Chem Sci* 4:69–71 (AATA 29-697)
- Ramière R (1975) Apport des techniques nucléaires à la conservation des biens culturels – description de cas précis de conservation par des méthodes nucléaires et des problèmes qui s'y rattachent. *Mus Coll Bull France* 129(1):27–30
- Ramière R (1988) Les traitements du bois gorgés d'eau par lyophilisation et par imprégnation/polymérisation gamma. *Konservierung und Restaurierung von Kulturgütern*, 2. Teil, Praktische Anwendung von Kunststoffen 1, Seminar 20–22 Nov 1986 in Bern. Schweizerischer Verband für Konservierung und Restaurierung. Haupt, Bern, pp 63–66

- Ramseyer D, Vonlanthen D (1987) Archaeology and waterlogged wood. *Museum* 39(1):18–25 (AATA 26-2183)
- Rapp AO, Peek R-D (1995) New principles for the protection of wood: impregnation with waterborne resins. IRG/WP/95-40047
- Rapp AO, Peek R-D (1996) Melamine resins as preservatives: results of biological testing. IRG/WP/96-40061
- Rathgen F (1904) Das Zapon und seine Verwendung zur Konservierung von Sammlungsgegenständen. *Prometheus* 15, no 485 and 499
- Rathgen F (1910) Über Mittel gegen Holzwurmfraß. *Museumskunde* 6:27
- Rathgen F (1924) Die Konservierung von Alterthumsfunden, Teil II und III. De Gruyter, Berlin, pp 133–149 (Wood)
- Reid NKM, MacLeod ID, Sander N (1984) Conservation of waterlogged organic materials: comments on the analysis of polyethylene glycol and the treatment of leather and rope. ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen 1984, preprints, vol I, 84.7.16–84.7.20 (AATA 21-2350)
- Reinprecht L, Varinska S (1999) Bending properties of wood after its decay with *Coniophora puteana* and subsequent modification with selected chemicals. IRG/WP/99-40146
- Rice JT (1990) Gluing of archaeological wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington DC. *Adv Chem Ser* 225:373–397 (AATA 270-1986)
- Rice RW, O'Guinness Carlson M (1997) Stabilization of the SNOW SQUALL using a lumber drying kiln. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp 47–55
- Richards VL (1990) The consolidation of degraded deacidified *Batavia* timbers. *AICCM Bull* 16(3):35–52 (AATA 34-994)
- Riens R (1988) Zur Stabilisierung wassergesättigter archäologischer Laubhölzer durch Gefriertrocknung nach Vorbehandlung. Diplomarbeit, Univ Hamburg, Fachbereich Biologie, Studiengang Holzwirtschaft
- Ringgaard M (1989) Hjortespringbåden: historien om den gamle konservator Gustav Rosenberg udgravnings-og konserveringsmetoder (The *Hjortespring* find: excavation and conservation methods used by Gustav Rosenberg). *Meddelelser Konserv* 4(3):110–121 (AATA 28-677)
- Robson MA (1993) Early advances in the use of acrylic resins for the conservation of antiquities. In: Seymour RB, Porter RS (eds) *Manmade fibers: their origin and development*. Univ Southern Mississippi, Dept Polymer Science, pp 208–213 (AATA 31-1227)
- Rosen D (1950/1951) The preservation of wood sculpture: the wax immersion method. *J Walters Art Gallery* 13/14:45–71
- Rosenqvist AM (1957) Nypreparering av tresakene i *Oseberg* fundet. *Museumsnytt* 3:112–116
- Rosenqvist AM (1959) The stabilizing of wood found in the Viking Ship of *Oseberg*, part I and II. *Stud Conserv* 4(1):13–22 (part I), 4(2):62–72 (part II) (AATA 13-216)
- Rosenqvist AM (1969a) The *Oseberg* Find, its conservation and present state. ICOMOS Symposium on the Weathering of Wood, Ludwigsburg (Germany), 8–11 June 1969, pp 77–87 (AATA 11-574, 13-707)
- Rosenqvist AM (1969b) Der Osebergfund, seine Konservierung und gegenwärtiger Stand. *Dtsch Kunst Denkmalpflege* 27:121–129
- Rosenqvist AM (1973) Versuche zur Konservierung von Naßhölzern durch Gefriertrocknung. *Arbeitsbl Restaur* 6(2), Gruppe 8, pp 69–74 (AATA 12-242)
- Rothe A, Marussich G (1998) Florentine structural stabilization techniques. The structural conservation of panel paintings. In: Dardes K, Rothe A (eds) *Proceedings of a Symposium at the J. Paul Getty Museum*, 24–28 April 1995. Getty Conservation Institute, Los Angeles, pp 306–315
- Rowell RM (1990) Chemical modification of cell wall polymers as potential treatments of archaeological wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties,*

- chemistry, and preservation. American Chemical Society, Washington DC. *Adv Chem Ser* 225:421–431
- Rowell RM, Ellis WD (1984) Reaction of epoxides with wood. *Res Pap For Prod Lab (US)*, FPL 451, 41 pp
- Rumâncev EA (1958) Stabilizaciã nasyŝennoj vlagoj drevesiny, najdennoj pri archeologičeskich raskopkach (The conservation of wet wood from archaeological excavations). *Kratkie soobŝeniã o dokladach i polevyh issledovaniãh instituta istorii material'noj kul'tury*, Moskva, 72: 96–99
- Rumi A (1987) "Prágai ku Jézus" ábrázolású, három dongából álló faragott hordófenék restaurálása (The restoration of a tub bottom made of three staves, with the delineation of the Infant Jesus). *Műz Műtárgyvédelem* (16):235–244 (AATA 24-784)
- Ryu JY, Imamura Y, Takahashi M, Kajita H (1993) Effects of molecular weight and some other properties of resins on the biological resistance of phenolic resin treated wood. *Mokuzai Gakkaishi* 39(4):486–492
- Ryu JY, Takahashi M, Imamura Y, Sato T (1991) Biological resistance of phenol-resin treated wood. *Mokuzai Gakkaishi* 37(9):852–858
- Sachse T (1956) Holzkonservierung bei Trockenfäule. *Maltechnik* 62(4):114–115
- Saeterhaug R (1985) Investigations concerning the freeze-drying of waterlogged wood conducted at the University of Trondheim. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble, 28–31 Aug 1984 – Waterlogged wood: study and conservation. *Proceeding of the 2nd ICOM Waterlogged Wood Working Group Conference*, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 195–206 (AATA 24-787)
- Sailer M, Rapp AO, Peek R-D (1998) Biological resistance of wood treated with waterbased resins and drying oils in a mini-block test. IRG/WP/98-40107
- Sakuno T, Schniewind AP (1987) Mokuzai rekka boshiyo jushi no shogeki setchakuryoku (Impact adhesive strength of resins used to treat deteriorated wood). *Book of abstracts*, 37th Annual Meeting of the Japan Wood Research Society, p 308
- Sakuno T, Schniewind AP (1990) Adhesive qualities of consolidants for deteriorated wood. *J Am Inst Conserv* 29(1):33–44
- Sanchez Ledesma A, Castro Boch J, Martinez Outorino P (1990) Experiencia cubana en la consolidación de maderas arqueológicas deterioradas por el agua empleando azúcar de caña: estudio microbiológico. *Documentos Grupo de Información Esfera de las Artes Visuales* 2/3:1–17 (AATA 30-1293)
- Sawada M (1978) Conservation of waterlogged wooden materials from the Nara Palace Site. *Conserv Wood Int Symp Conserv Restor Cult Prop Tokyo 1977 (Proceedings 1978)*, pp 49–58 (AATA 17-356)
- Sawada M (1981a) A modified technique for treatment of waterlogged wood employing the freeze-drying method. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/4 (AATA 18-1810)
- Sawada M (1981b) Zur Konservierung eines bemalten japanischen Lackgefäßes. *Arbeitsbl Restaur* (1), Gruppe 11, pp 31–34
- Sawada M (1985) Some problems of setting of PEG 4000 impregnated in wood (Contraction of impregnated PEG solutions upon setting and its effects on wood). Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 août 1984 – Waterlogged wood: study and conservation. *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference*, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 117–124 (AATA 24-790)
- Sawada M (1990) Conservation of waterlogged wood. *Mokuzai Kogyo* 45(517):173–176 (AATA 28-680)
- Sawada M (1992) Conservation of archaeological materials. *Kagaku To Kyoiku (Chemical education)* 40(1):22–25 (AATA 32-876)
- Schaffer E (1971) Consolidation of softwood artifacts. *Stud Conserv* 16(3):110–113 (AATA 9-177, 13-804)

- Schaffer E (1974) Consolidation of painted wooden artifacts. *Stud Conserv* 19(4):212–221 (AATA 12-243, 13-954)
- Schaffer E (1976) The preservation and restoration of Canadian ethnographic basketry. *Stud Conserv* 21(3):129–133 (AATA 14-631)
- Schaffer E (1978) Water soluble plastics in the preservation of artifacts made of cellulosic materials. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, 78/3/7 (AATA 16-186)
- Schaible V (1983) Zur Festigung der beidseitig bemalten Altarflügel des "Bocksdorfer Altares" von 1524 aus dem Konstanzer Münster. Fach- und Fortbildungstagung "Probleme um den Bildträger Holz" 1982. Selbstverlag der Kunstgewerbeschule Bern, 1983, pp 126–140
- Schaudy R (1995) Zur Problematik der festigenden Holzkonservierung. In: Schreiner M (ed) *Naturwissenschaften in der Kunst*, Böhlau, Wien, pp 155–159
- Schaudy R, Kies A (1978) Strahlenchemische Konservierung von Holz aus der späturnenfelderzeitlichen Wallanlage von Stillfried (Vorläufiger Bericht). Veröffentlichung der Österreichischen Arbeitsgemeinschaft für Ur- und Frühgeschichte, Wien, vol 10. *Forsch Stillfried* 3:91–93
- Schaudy R, Knoll H (1988) Zur Konservierung von Nassholz durch Gefriertrocknung und Harztränkung. Teil 2: Konzentrationsvariation in der Vorbehandlung, Tränkung mit Harzlösungen und Klimaversuche. Österreichisches Forschungszentrum Seibersdorf, OEFZS Ber nr 4483 (AATA 28-2336)
- Schaudy R, Slais E (1983) Konservierungsversuche mit strahlungshärtbaren Imprägniermitteln an intakten und künstlich abgebauten Holzproben. Österreichisches Forschungszentrum Seibersdorf, OEFZS Ber nr 4198
- Schaudy R, Slais E (1986) Zur Konservierung von Naßholz durch Gefriertrocknung und Harztränkung, Teil 1: Einfluß der Vorbehandlung auf das Trocknungsergebnis. Österreichisches Forschungszentrum Seibersdorf, OEFZS-Ber nr 4350
- Schaudy R, Eibner C, Slais E (1985) Conservation of a medieval climbing stem by freeze-drying and resin impregnation. Österreichisches Forschungszentrum Seibersdorf, OEFZS Ber nr 4341
- Schaudy R, Wendrinsky J, Kalteis H, Grienauer W (1982a) Strahlungshärtbare Imprägniermittel für die Konservierung archäologischer Holzfunde. Österreichisches Forschungszentrum Seibersdorf, OEFZS Ber nr 4165 (AATA 21-446)
- Schaudy R, Wendrinsky J, Kalteis H, Greinauer W (1982b) Strahlungshärtbare Imprägniermittel für die Konservierung archäologischer Holzfunde (Teil 2). Österreichisches Forschungszentrum Seibersdorf, OEFZS Ber nr 4195
- Scheinring J (1987) 19. Századi fiókos irókomód restaurálása (Restoration of a 19th-century bureau). *Műz Műtárgyvédelem* (16):161–176 (AATA 24-792)
- Schiessl U (1984) Historischer Überblick über die Werkstoffe der schädlingsbekämpfenden und festigkeitserhöhenden Holzkonservierung. *Maltechnik Restaura* 90(2):9–40
- Schiessl U (1989) Probleme der Konservierungsstoffe und Festigkeitserhöhung von degradiertem Holz. In: Bilfinger M, Meili D (eds) *Konservierung von Holzbauten*. Haupt, Bern, pp 91–114
- Schiweck H (1996) Zucker/Saccharose – seine anwendungstechnisch relevanten Eigenschaften bei der Naßholzkonservierung. *Arbeitsbl Restaur* 29(2) Gruppe 8, pp 241–246 (AATA 34-2224)
- Schlabow K (1961) Der Moorleichenfund von Peiting. Förderverein Textilmuseum Neumünster, Neumünster, vol 2, 55pp
- Schmitt U, Noldt U (1994) Scanning electron microscopic observation on sucrose impregnation of waterlogged archaeological wood. In: Hoffmann P, Daley T, Grant T (eds) *Proceedings of the 5th ICOM Group on Wet Organic Archaeological Materials Conference*, Portland, Maine, 16–20 Aug 1993, Bremerhaven 1994, pp 381–390
- Schneider A (1969) Beiträge zur Dimensionsstabilisierung des Holzes mit Polyäthylenglykol. Erste Mitteilung: Grundlegende Untersuchung zur Dimensionsstabilisierung des Holzes mit Polyäthylenglykol. *Holz Roh Werkst* 27(6):210–224

- Schniewind AP (1985) Old cultural property and wood. *J Wood Conserv* 1(1):1–11
- Schniewind AP (1988) On the reversibility of consolidation treatments of deteriorated wood with soluble resins. *Wooden Artifacts Group Preprints*, New Orleans Meeting, 5 June 1988. American Institute for Conservation of Historic and Artistic Works, Washington, DC
- Schniewind AP (1990a) Consolidation of dry archaeological wood by impregnation with thermoplastic resins. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington DC. *Adv Chem Ser* 225:361–371
- Schniewind AP (1990b) Solvent and moisture effects in deteriorated wood consolidated with soluble resins. *Holz Roh Werkst* 48(1):11–14
- Schniewind AP (1991) Mokuzai rekka boshiyo jushi shori ni tsuite (On consolidation treatments for deteriorated wood). *Preprints of the 41st Annual Meeting of the Japan Wood Research Society*. Nihon Mokuzai Gakkai, Tokyo, Japan
- Schniewind AP (1998) Consolidation of wooden panels. *The Structural Conservation of Panel Paintings*. In: Dardes K, Rothe A (eds) *Proceedings of a symposium at the J. Paul Getty Museum*, 24–28 April 1995. Getty Conservation Institute, Los Angeles, pp 87–107
- Schniewind AP, Eastman PY (1992) Consolidant distribution in deteriorated wood treated with soluble resins. *Wood Artifacts Group Preprints*, Buffalo Meeting, American Institute for Conservation of Historic and Artistic Works, Washington, DC, 11 pp
- Schniewind AP, Eastman PY (1994) Consolidant distribution in deteriorated wood treated with soluble resins. *J Am Inst Conserv* 33(3):247–255
- Schniewind AP, Kronkright DP (1984) Strength evaluation of deteriorated wood treated with consolidants. In: Brommelle NS, Pye EM, Smith P, Thomson G (eds) *Adhesives and Consolidants*. *Preprints of the contributions to the Paris Congress*, 2–8 Sept 1984. International Institute for Conservation of Historic and Artistic Works, London, pp 146–150
- Schröder E (1959) Methode der Holzhärtung im Unterdruck. *Präparator* 5(1):30
- Schuldt E (1960) Neue Versuche zur Konservierung von Fundstücken aus Holz. *Ausgrabungen Funde* 5(4):161–163
- Scott A (1921) The cleaning and restoration of museum exhibits. Department of Scientific and Industrial Research, British Museum, first report
- Scott A (1923) The cleaning and restoration of museum exhibits. Department of Scientific and Industrial Research, British Museum, second report
- Scott A (1926) The cleaning and restoration of museum exhibits. Department of Scientific and Industrial Research, British Museum, third report
- Sease C (1981) The case against using soluble nylon in conservation work. *Stud Conserv* 26(3):102–110 (AATA 18-1704)
- Seborg RM, Inverarity RB (1962) Conservation of 200 year-old waterlogged boats with polyethylene glycol. *Stud Conserv* 7:111–119 (AATA 13-332)
- Seekamp H (1950) Der Schutz des Holzes gegen leichte Entflammbarkeit. In: Liese J (ed) *Mahlke-Troschel Handbuch der Holzkonservierung*. Springer, Berlin Göttingen Heidelberg, pp 400–417
- Seifert B, Jagels R (1985) Conservation of the Ronson ship's bow. *Les Bois Gorgés d'Eau: Étude et conservation*. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 Aug 1984 – Waterlogged wood: study and conservation. *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference*, Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 269–297 (AATA 24-798)
- Seifert K (1960) *Angewandte Chemie und Physikochemie der Holztechnik*. Fachbuchverlag, Leipzig
- Sekino M (1973a) Development of artificial resin application methods in the conservation and restoration work of wooden materials of the Rakando in the former Fukiji Temple, an important cultural property, and the Jo-an, a national treasure. *Sci Conserv* 10:118 (AATA 10-685)
- Sekino M (1973b) New applications of synthetic resins for the conservation and restoration of wooden parts in structures. *Sci Conserv* 10:119–122
- Selwitz C (1988) Cellulose nitrate in conservation. *Research in conservation*. Getty Conservation Institute, Los Angeles

- Selwitz C (1992) Epoxy resins in stone conservation. Research in conservation, vol7. Getty Conservation Institute, Los Angeles
- Selwyn L (1993) Treatments for waterlogged wood-metal composites. CCI Newslett (11):12
- Selwyn LS, Rennie-Bisaillon DA, Binnie NE (1993) Metal corrosion rates in aqueous treatments for waterlogged wood-metal composites. Stud Conserv 38:180-197
- Semczak C (1975) Waterlogged wood preservation with tetraethyl-orthosilicate. Problems of the conservation of waterlogged wood, Maritime Monographs and Reports, Natl Maritime Mus, Greenwich, 16: 151-152
- Semczak C (1977) Waterlogged wood preservation with tetraethyl-orthosilicate. Papers from the First Southern Hemisphere Conference on Maritime Archaeology, Oceans Society of Australia Perth 1977, Melbourne 1977, pp 151-152 (AATA 15-1330)
- Serck-Dewaide M (1990) Le retable de Sainte Colombe à Deerlijk XVIe siècle: étude et restauration. La conservation du bois dans le patrimoine culturel: Besançon-Vesoul, 8-10 Nov 1990, pp 113-124 (AATA 30-1297)
- Siau JF (1984) Transport processes in wood. Springer, Berlin Heidelberg New York
- Simpson E, Payton R (1986) Royal wooden furniture from Gordion. Archaeology 39(6):40-47 (AATA 24-810)
- Šimůnková E (1983) Metoda vakuové impregnace v obalu z polyethylenové fólie a vliv zpevňovacích prostředků na rozměrovou stabilitu dřeva (Method of vacuum impregnation in a bubble of PE-foil and the effect of consolidant on dimensional stability of wood). 6. Celostátní Konference Ochrana Dřeva, Zvolen 11-13 Oct 1983. Dom Techniky ČSVTS Bratislava 1983, pp 164-173
- Šimůnková E (1986) Prostriedky na zpevňovanie pamätkových objektov z dreva (The means for wood objects consolidation). Památky Příroda 15(3):99-100 (AATA 25-605)
- Šimůnková E (1988) Radiační metody pro zpevňování dřevěných památek (Radiation methods used for consolidation of wooden monuments). In: Justa P (ed) Conference proceedings. Nové metody muzejní konzervace, Národní technické muzeum, Praha 1988, pp 75-86 (AATA 26-679)
- Šimůnková E (1990) Petrifikace dřeva radiační polymerací monomerů (The petrification of wood by polymerization of monomers). Památky Příroda 15(6):346-350 (AATA 28-2343)
- Šimůnková E, Josef J (1987) Impregnace a zpevňování dřeva v památkách (Impregnation and consolidation of wood from monuments). 7. Celostátní Konference, Pisek 3-5 Nov 1987. ČSVTS Dum techniky, pp 129-145
- Šimůnková E, Josef J (1988) Petrifikace dřeva v závislosti na polaritě použitých rozpouštědel (The dependence of wood consolidation on the polarity of the impregnation solvent). Památky Příroda 13(5):283-285 (AATA 26-2184)
- Šimůnková E, Josef J (1989) Petrifikace dřeva v závislosti na polaritě použitých rozpouštědel. 2. Odolnost proti změně vlhkosti a mechanická pevnost (The dependence of wood consolidation on the polarity of the impregnation solvent. Part 2: the resistance of wood to humidity changes and its mechanical strength). Památky Příroda 14(1):27-29 (AATA 28-2344)
- Šimůnková E, Kozany P (1993) Petrifikace dřeva s polychromii radiační polymerací metylmetakrylátu (Petrification of polychrome wood using gamma ray polymerization of methyl methacrylate). Zprávy Památkové Péče 53(4):159-161 (AATA 31-546)
- Šimůnková E, Škvaril L (1985) Metody impregnace památkových objektů ze dřeva (Method of impregnation of historical wood objects). Sb. VŠCHT Praze, Pict Sci Pap S13:63-68
- Šimůnková E, Zelinger J (1981) Zpevňování dřeva roztoky polymerů a polymerací monomerů v objektu (The consolidation of wood by polymer solutions and polymerization of monomers in situ). Sb. VŠCHT Praze, Pict Sci Pap S6:35-58 (AATA 18-341)
- Šimůnková E, Zelinger J (1983) Dimensional stability of polymer-reinforced wood. Sb. VŠCHT Praze, Pict Sci Pap S10:61-72
- Šimůnková E, Šmejkalová Z, Zelinger J (1981) Konzervace dřeva nasyceného vodou (The conservation of waterlogged wood). Sb. VŠCHT Praze, Pict Sci Pap S6:59-72 (AATA 18-342)
- Šimůnková E, Šmejkalová Z, Zelinger J (1983) Consolidation of wood by the method of monomer polymerization in the object. Stud Conserv 28(3):133-144 (AATA 20-1708)

- Šimůnková E, Stasova K, Fries T (1993) Radiační roubování metylmetakrylátu na dřevo (Radiation grafting of methyl methacrylate on wood). Sb. VŠCHT Praze, Pict Sci Pap, pp 143-154 (AATA 32-884)
- Šimůnková E, Fries T, Justa P, Zelinger J (1988) Petrifikace dřeva radiační polymerací monomerů v podmínkách o zařovny Středočeského muzea (The consolidation of wood by radiation polymerization upon the condition of the irradiation chamber at Bohemian Central Museum). Sb. VŠCHT Praze, Pict Sci Pap S18:35-51 (AATA 27-666)
- Singley KR (1981) Design of a large-scale PEG treatment facility for the Brown's Ferry Vessel. ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa 1981, 81/7/5 (AATA 18-1287)
- Slánský B (1956) Technika Malby. Díl II. Průzkum a restaurování obrazu. (Technique of painting, part II: investigation and restoration of painting.) Státní Nakladatelství, Krásné Literatury, Hudby u umění, pp 255-266
- Soldenhoff B (1981) Wzmocnianie drewna żywicami termoplastycznymi (The reinforcement of wood with thermoplastic resins). Chemia w Konserwacji Zabytków Informatów PKZ, pp 48-53 (AATA 20-468)
- Speersneider CA (1858-60) Behandling of Oldsager af Trae fundne i Tørvemoser. Antiquarisk Tidsskrift Kjøbenhavn, pp 176-178 (1861)
- Spurlock D (1978) The application of balsa blocks as a stabilizing auxiliary for panel paintings. Conservation of wood in painting and the decorative arts. Preprints of the contributions to the Oxford Congress 17-23 Sept 1978, IIC, 6 Buckingham Street, London WC 2 N 63 A 1978
- Stadler J (1987) Die Restaurierung einer Wappentruhe des frühen 17. Jahrhunderts. Arbeitsbl Restaur 20(2) Gruppe 12, pp 34-41
- Stamm AJ (1937) Treatment with sucrose and invert sugar. Ind Eng Chem 29(7):833-835.
- Stamm AJ (1956) Dimensional stabilization of wood with carbowaxes. For Prod J 6(5):201-204
- Stamm AJ (1959) Effect of polyethylene glycol on the dimensional stability of wood. For Prod J 9(10):375-381
- Stark BL (1976) Waterlogged wood preservation with polyethylene glycol. Stud Conserv 21(3):154-158 (AATA 14-202)
- Starling K (1987) The conservation, reconstruction, and dendrochronology of a medieval waterfront revetment from London. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6-11 Sept, vol 1, pp 321-324 (AATA 25-607)
- Starling K (1989) The conservation of wet metal/organic composite archaeological artefacts at the Museum of London. Conservation of wet wood and metal. In: MacLeod ID (ed) Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals, Fremantle 1987, Western Australian Museum Perth 1989, pp 215-221 (AATA 28-2346)
- Stawicka K (1981) Prace konserwatorskie przy trzech XVII-wiecznych stropach polichromowanych z kanonii Św. Michała we Fromborku (The conservation of three 17th century ceilings in St. Michael's canonry in Frombork). Przyczynki, Problemy Konserwacji Malarstwa, Warszawa 1981, pp 6-14 (AATA 19-1383)
- Stehlik M (1968) Restaurování Madony z Brankovic (Restoration of the Madonna from Brankovice). Památková Péče 2:37-40 (AATA 8-779)
- Stone TG (1996) Artifacts revisited: the evaluation of old treatments. In: Bridgland J (ed) ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland, 1-6 Sept 1996, vol II, pp 643-649
- Storch PS (1987) The analysis and conservation of an historic wooden gate. Recent advances in the conservation and analysis of artifacts, jubilee conservation conference, University of London, Institute of Archaeology, Summer Schools Press, pp 257-262
- Storch PS (1994) Fills for bridging structural gaps in wooden objects. J Am Inst Conserv 33(1):71-75 (AATA 32-889)
- Straub R (1962) Neues und altes über Holztafeln. Bericht von der IIC Konferenz in Rom, September 1961. Maltechnik 68(1):16-19

- Straub RE (1963) Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich
- Strigazzi G (1992) Zucker in der Naßholzkonservierung/Zucker-Aceton-Methode, Verwendung anderer Zuckersorten, Konservierung der Zuckerlösung. In: AdR (ed) Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992, pp 53–58
- Strigazzi G (1997) Naßholzkonservierung eines Einbaumschiffes der Bronzezeit. Arbeitsbl Restaur (1), Gruppe 8, pp 258–261
- Strigazzi G (1998) Saccharide und Netzmittel in der Naßholz-Konservierung. Arbeitsbl Restaur (1), Gruppe 8, pp 266–269
- Strigazzi G, Koberstein A (1997) Nonionic surfactants in sucrose solutions and highly concentrated glucose sirup for waterlogged woods. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceeding of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 257–268
- Stumes P (1978) Structural rehabilitation of deteriorated timber in historic buildings. Conserv Wood Int Symp Conserv Restor Cult Prop, Tokyo 1977, Proceedings 1978, pp 33–47
- Stumes P (1979) WER-system manual. Association for Preservation Technology, Ottawa
- Šujanova O (1972) O konservovani dreva (On conservation of wood). Konservátorské praktikum, pp 27–34 (AATA 15-448)
- Suthers T (1975) The treatment of waterlogged oak timbers from *Ferriby* Boat III using polyethylene glycol. Maritime Monographs and Reports, Natl Maritime Mus, Greenwich 16: 115–119
- Szalay Z (1980) Ujabb eredmények a nedves fa konzerválásában (New results in the conservation of waterlogged wood). Műz Műtárgyvédelem 7:108–112 (AATA 18-344)
- Takano M (1980) Wood treatment. Jpn Kokkai Tokkyo Koho 8049204
- Tamer MH (1958) An essay on the conservation of wood. Ann Archaeol Mus Istanbul 8:88–90
- Tampone G (ed) (1989a) Il restauro del Legno, vol 1, 2e Congresso Nazionale Restauro del Legno, Firenze, 8–11 Nov 1989. Nardine Editore – Centro Internazionale del Libro, Firenze (AATA 29-2426)
- Tampone G (ed) (1989b) Legno e restauro: ricerche e restauri su architetture e manufatti lignei. Messaggerie toscane, Firenze (AATA 29-2427)
- Thielker A (1970) The consolidation of a Spanish polychromed wood sculpture of the thirteenth century. IIC-American Group Technical Papers. From 1968 Through 1970, New York June 1970, pp 167–169 (AATA 9-179)
- Thunell B (1985) Moisture conditions in PEG-treated wood from the warship *Wasa*. Xylorama. In: Kučera LJ (ed) Trends in wood research. Wood Tech Processing, Royal Inst Tech, Stockholm, pp 192–197 (AATA 24-828)
- Tiemann HD (1951) Wood technology, 3rd edn. Pitman, New York
- Tintori L, Rothe A (1978) Observations on the straightening and cradling of warped panel paintings. Conservation of wood in painting and the decorative arts. Preprints of the contributions to the Oxford Congress 17–23 Sept 1978. IIC; 6 Buckingham Street, London WC 2N 63 A, 1978, pp 179–180 (AATA 16-457)
- Tomashevich GN (1969) The conservation of waterlogged wood. Problems of Conservation in Museums, Centre International d'Etudes pour la conservation et la restauration des biens culturels. Travaux Publ 8:165–186
- Tomaszewski K, Wieczorek K, Chrzanowski A (1990) Z badań nad opracowaniem kitó do uzupełniania ubytków w drewnie zabytkowym na bazie żywicy pochodzenia krajowego (Studies on the preparation of domestically made resin-based putty to fill in missing fragments in ancient wood). Rocznik przedsiębiorstwa Państwowego Pracowni Konserwacji Zabytków 1986, (1), pp 259–283 (AATA 29-2428)
- Tran QK, Gelas A, Mordant D (1999) Remise en forme de la pirogue carolingienne de Noyen-sur-Seine après son traitement au PEG à saturation. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999, pp 188–195

- Tran QK, Hiron X, Damery E (1997) Treatment of a Neolithic dugout canoe from Paris-Bercy: Controlled drying after PEG impregnation and attempt at modelling of the drying process. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 569–582
- Tran QK, Ramière R, Ginier-Gillet A (1990) Impregnation with radiation – curing monomers and resins. In: Rowell RM, Barbour RJ (eds) Archaeological wood: properties, chemistry, and preservation. American Chemical Society, Washington DC. Adv Chem Ser 225:217–233 (AATA 27-2000)
- Triboulot M-C (1998) The study of the properties of polyethylene glycol. 4th International Symposium on Wood and furniture conservation, Rijksmuseum, Amsterdam, 10 Dec 1998
- Tripp G (1953) Zur Restaurierung gotischer Schnitzaltäre in Oberösterreich. Ein technischer Bericht. Österr Z Kunst Denkmalpflege 7:96–107
- Troschel E (1916) Handbuch der Holzkonservierung. Springer, Berlin
- Turner WS (1978) Conservation of the finds. Int J Naut Archaeol Underwater Explor 7:317–319 (AATA 16-1150)
- Ueda N, Inoue M (1994) Syutsudo-mokuzai no PEG-syoriho no minaoshi to soreni kawaru yakuzai no kaiatsu (1) (A reconsideration of the PEG 4000 treatment for waterlogged wood and development of alternative treatment methods, part 1). Gangō-ji Bunkazai Kenkyū 51: 1–8 (AATA 33-2605)
- Ueda N, Matsuda T, Inoue M (1990) Preservation of archaeological wood artifacts with cationic surfactants and polyethylene glycol. Jpn Kokai Tokkyo Koho JP-Patent 0222,004 (AATA 28-2356)
- Ujszaszy A (1987) 19. század eleji fa patikaláda és gyógyszergyűjtemény restaurálása (The restoration of a pharmacy chest and medicine collection from the beginning of the 19th century). Műz Műtárgyvédelem (16):245–272 (AATA 24-841)
- Ullmann F (1919) Enzyklopädie der technischen Chemie, vol 7. Urban & Schwarzenberg, Berlin
- Unger A (1988) Holzkonservierung. Schutz und Festigung von Kulturgut aus Holz. Fachbuchverlag, Leipzig
- Unger A, Perleberg J (1987) X-ray computer tomography (XCT) in wood conservation. In: Grinstead K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6–11 Sept 1987, vol 1, pp 99–105
- Unger A, Unger W (1987) Holzfestigung im musealen und denkmalpflegerischen Bereich. Holztechnologie 28(5):234–238
- Unger A, Planitzer J, Morgós A (1988) Röntgencomputer- und Magnetresonanztomographie zur Charakterisierung von archäologischem Naßholz. Holztechnologie 29(5):243–250
- Unger A, Reichelt L, Nissel D (1981a) Zur Konservierung von Holz mit organischen Verbindungen. Verfestigung alter Pistolenschäfte mit Platten. Neue Museumskd 24(1):58–65 (AATA 19-381)
- Unger A, Reichelt L, Nissel D (1981b) Zur Konservierung von Holz mit organischen Verbindungen. Entwicklung und Möglichkeiten. Neue Museumskd 24(2):118–128
- Unger A, Schiessl U, Unger W (1996) Widersteht gefestigtes, insektenzerstörtes Holz von Kunstwerken einem erneuten Insektenangriff? Kunsttechnol Konserv 10(2):308–314
- Unger A, Reichelt L, Bär M, Reinhardt J, Nissel D (1982) Erfahrungen bei der strahlenchemischen Konservierung von Holz mit Methylmethacrylat. Neue Museumskd 25(3):202–206
- Unger A, Reichelt L, Lachmann M, Nissel D, Peters M (1984) Zur Verfestigung der hölzernen Lafette der „Faulen Magd“ mit Methylmethacrylat. Holztechnologie 25(5):242–243
- Unger W, Doblinski M (1976) Zur Biostabilität von Polyurethan- und Polystyrol-Schaumstoffen. Holzindustrie 10:311–314
- Unger W, Unger A (1984) Zur Termitenresistenz von Platten und Elasten. Plaste Kautschuk 31(7):241–247
- Unger W, Unger A (1995a) On the bioresistance of waterlogged wood impregnated with sucrose. Mat Org 29(3):231–240
- Unger W, Unger A (1995b) Die biologische Korrosion von Konsolidierungsmitteln für Kunst- und Kulturgut aus Holz. Kunsttechnol Konserv 9(2):377–384

- Unger W, Fritsche H, Unger A (1996) Zur Resistenz von Malmaterialien und Stabilisierungsmitteln für Kunst- und Kulturgut gegenüber holzerstörenden Insekten. *Kunsttechnol Konserv* 10(1):106–116
- Urban J, Santar I, Sedláčková J, Pipota J (1978) Use of gamma radiation for conservation purposes in Czechoslovakia. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, 78/17/4 (AATA 16-463)
- Urban B (1971) Eine Einrichtung für die Konservierung feuchter Hölzer mit Polyglycol (mit Diskussion). *Arbeitsbl Restaur* 4(2) Gruppe 8, pp 50–57 (AATA 9-180)
- Vámosi L (1987) Egy avarkori favödör restaurálása (Restoration of a kit from the Avar period). *Műz Műtárgyvédelem* (16):57–68 (AATA 24-843)
- Vandyke-Lee DJ (1977) The conservation of some carved wooden war shields from the Tifalmin Valley, Papua New Guinea. *Mus J* 77(2):77 (AATA 15-454)
- Verdu J, Kleitz MO, Djoud F, Valot H (1990) Le rayonnement gamma et la désinfection des sculptures polychromes. La conservation du bois dans le patrimoine culturel: Besançon-Vesoul, 8–10 Nov 1990, pp63–80 (AATA 30-167)
- Vere-Stevens L, Crawshaw A, Panter I, Spriggs JA (1999) Further research into the copper/silver ion sterilisation system as applied to the treatment of archaeological waterlogged oak wood in PEG solutions. In: Bonnot-Diconne C, Hiron X, Tran QK, Hoffmann P (eds) *Proceedings of the 7th ICOM-CC Working Group on Wet Organic Archaeological Materials Conference, Grenoble/France 1998, ARC-Nucléart, Grenoble 1999*, pp 95–103
- Vichrov VE, Paul EE, Vichrov YV, Kazanskaya SY (1972) Stostav dlja konservacii i stabilizacii archeologičeskich nachodok iz degradirovannoj drevesiny (Compositions for conservation and stabilization of archaeological finds from degraded wood). *USSR-Patent* 329006 (9 Feb 1972)
- Vichrov VE, Vichrov YV, Borisov VA (1974) Pickling old boats in alcohol. *New Sci* 63(904):27 (AATA 11-582)
- Vichrov YV, Borisov VA, Kazanskaya SY, Piščik II (1978) Sostav dlja konservirovanii i upročnenii (Compositions for conservation and stabilization). *USSR-Patent* 620373 (25 Aug 1978)
- Von Derschau D, Unger A (1998) Epoxidharz-Restaurierungen. Zum Problem der Entfernung. *Restauro* 104(7):486–493
- Von Imhoff HC (1978) Reinforcing a thin panel painting. Conservation of wood in painting and the decorative arts. Preprints of the contributions to the Oxford Congress 17–23 Sept 1978. IIC; 6 Buckingham Street, London WC 2N 63A, 1978, pp157–163 (AATA 16-407)
- Von Stokar W (1939) Ein neues Verfahren zur Konservierung von Moorhölzern. *Nachrichtenbl Dtsch Vorzeit* 15(5/6):145–149
- Vynckier J (1973/1974) Een verbeterde techniek ter bereiding van microscopische preparaten van broos hout. *Bull Inst Royal Patrimoine Artistique* 14:128–131 (AATA 12-887)
- Vynckier J (1982/1983) De behandeling van nat opgegraven hout volgens de alcohol-etherlanoline methode. *Bull Inst Royal Patrimoine Artistique* 19:63–73 (AATA 21-1689)
- Wächter O (1994) Zur Alterungsmethodik für synthetische Festigungs- und Klebmittel, die Prophylaxe auf dem Prüfstand. *Restauratorenblätter* 15:193–196
- Wagner T, Chavannis JP (1986) Le traitement nucléaire des bois anciens. *L'Estampille* (190):28–37 (AATA 24-849)
- Wang Liqin, Wang Huizheng, Song Disheng (1994) The anticorrosive and reinforcing treatment of ancient wooden objects. *Wenwu Baohu Yu Kaogu Kexue* 6(2):16–19 (AATA 32-2307)
- Wang Y, Schniewind AP (1985) Consolidation of wood with soluble resins. *J Am Inst Conserv* 24(2):77–91
- Waterhouse M (1981) Restoration of structural timber. *British Wood Preserving Association Annual Convention, Paper 4, London* (AATA 20-1715)
- Watson J (1985) Research into aspects of freeze-drying hardwoods between 1982 and 1984. Les Bois Gorgés d'Eau: Étude et conservation. Actes de la 2^e conférence du groupe de travail "Bois Gorgés d'Eau" de l'ICOM. Grenoble 28–31 Aug 1984 = Waterlogged wood: study and conservation. *Proceedings of the 2nd ICOM Waterlogged Wood Working Group Conference,*

- Centre d'Étude et de Traitement des Bois Gorgés d'Eau, Grenoble 1985, pp 213–218 (AATA 24-856)
- Watson J (1993) Dover Bronze-Age boat: assessment for conservation. Technical report. Ancient Monuments Laboratory reports, no 47/93, English Heritage, London, 25 p (AATA 33-11059)
- Watson J (1997a) Freeze-drying highly degraded waterlogged wood. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997*, pp 9–23
- Watson J (1997b) Conservation of the Bronze-Age boat from Dover: an interim report. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997*, pp 555–567
- Wazny J (1970) Badanie wpływu impregnacji Vinoflexem MP-400 na właściwości techniczne drewna wystroju rzeźbiarskiego wież pałacu w Wilanowie (The examination of the effect of impregnation with Vinoflex MP-400 on the technical properties of wooden carved decoration on the towers of the palace of Wilanow). *Ochrona Zabytkow* 23(2):83–88 (AATA 8-1316)
- Weber UM, Rosenthaler KJ (1994) Wet archaeological wood treated with sucrose: preliminary test series. *Z Schweiz Archäol Kunstgesch* 51(1):1–8 (AATA 33-2610)
- Weber UM, Rosenthaler KJ (1996) Desinfektion von Zuckerlösungen für die Naßholzkonservierung: eine erste Versuchsreihe. *Arbeitsbl Restaur* 29(2), Gruppe 8, pp 247–257 (AATA 34-2241)
- Weidman D, Kaenel G (1974) La barque romaine d'Yverdon. *Helv Archaeol* 19/20(5):66–81
- Weidner S (1992) Zur Bestimmung der Zuckerverteilung im getränkten Naßholz. In: AdR (ed) *Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992*, pp 70–77
- Weidner T, Eichner U, Heck G, Unger A (1999) Die "Harzlösung Sommerfeld" – ein Berliner Holzfestigungsmittel der dreißiger Jahre. *Restauro* 105(6):453–459
- Weihls F (1963) Über die Restaurierung von Holzbildwerken. In: Straub RE (ed) *Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich*, pp 59–73
- Wermuth JA (1990) Simple and integrated consolidation systems for degraded wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood, properties, chemistry, and preservation. American Chemical Society, Washington DC. Adv Chem Ser* 225:301–359
- Werner AEA (1958) Technical notes on a new material in conservation. *Chron Egypte* 33:273–278
- Werner AEA (1959) Chemistry in the preservation of antiquities. *Nature* 184(4686):585–587
- Werner AEA (1961) Consolidation of fragile objects. *Stud Conserv* 6(4):133–135 (AATA 13-397, 15-1140)
- Werner AEA (1963) Einige wissenschaftliche Gesichtspunkte zum Problem der Konservierung von Kunstwerken. In: Straub RE (ed) *Über die Erhaltung von Gemälden und Skulpturen. Fretz & Wasmuth, Zürich*, pp 13–17
- Werner AEA (1969) Neue Werkstoffe für Konservierungszwecke. *Maltechnik* 75(4):100–106
- Werner G (1983) Konservering av medeltida trädörr med järnbeslag och lås av järn. *Konserveringstekniska studier, Civiltryck AB, Stockholm*, pp 80–82 (AATA 22-763)
- Wieczorek K (1992) The conservation of waterlogged wood from excavation at Pultusk – the comparison of different treatment methods. In: AdR (ed) *Proceedings of the Conference: Konservierung von archäologischem Naßholz mit Zucker, Stade (Germany), 31 Jan–1 Feb 1991, Freiburg (Germany) 1992*, pp 20–37
- Wielicka M (1959/60) Prace i konserwacja drewna pochodzącego z wykopalisk w Biskupinie i Gdańsku (Research for the protection of wood from the excavations in Biskupin and Gdańsk). *Wiadomości Archeologiczne* 25:288–296
- Wittköpper M (1998) Der aktuelle Stand der Konservierung archäologischer Naßhölzer mit Melamin/Aminoharzen am Römisch-Germanischen Zentralmuseum. *Archäol Korrespondenzbl* 28(4):637–645
- Wojciechowska A (1964) Metody i przebieg konserwacji łodzi Lednickiej (Method and progress of conservation of the boat at Lednickiej). *Wiadomości Archeologiczne* 30:481–488
- Wolbers RC, McGinn M, Duerbeck D (1998) Poly(2-ethyl-2-oxazoline): a new conservation consolidant. Painted wood: history and conservation. In: Dorge V, Howlett FC (eds) *Proceedings*

- of a symposium organized by the Wooden Artifacts Group of the American Institute for Conservation of Historic and Artistic Works and the Foundation of the AIC, held at the Colonial Williamsburg Foundation, Williamsburg, Virginia, 11–14 Nov 1994, Getty Conservation Institute, Los Angeles, pp 514–527
- Wolters C (1961) Treatment of warped panels by plastic deformation; moisture barriers, elastic supports. *Stud Conserv* 6:141
- Wolters C (1998) Zusammenfassung der auf die Rundfrage der Bayer. Staatsgemäldesammlungen vom März 1952 eingegangenen Berichte über die Behandlung hölzerner Bildträger. *Kunsttechnol Konserv* 12(2):292–304
- Wróblewska K, Tomaszewski K, Wieczorek K (1991) Conservation of waterlogged wood from excavation at Pultusk. The comparison of different treatment methods. In: Hoffmann P (ed) *Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990*, Bremerhaven 1991, pp 281–316
- Wrubel FT (1977) Conservation of a seven-foot wooden lady. Papers presented by Cons. Students, 3rd annual conference of art conservation training programs, Queen's Univ, Kingston (Canada) 1977, pp 27–39 (AATA 16-475)
- Xu Y (1983) Gudai baoshui muqi he qiqi chuli fangfa zongshu (The methods for conservation treatment of waterlogged archaeological lacquer and wood works). *Kaogu Yu Wenwu* (3):104–109 (AATA 25-612)
- Yashvili N (1975) Conservation of the archaeological wood with transparent silicon organic polymers. ICOM Committee for Conservation, 4th Triennial Meeting, Venice 1975, 75/8/5 (AATA 13-935)
- Yashvili N (1978) Testing new transparent siliconorganic and some organic polymers for conservation of archaeological wood. ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, 78/7/3 (AATA 16-477)
- Yin S (1985) Polyethylene glycol treatment of wood. II. A test on preserving ancient wood. *Nanjing Linxueyuan Xuebao* (3):51–60
- Young G, Wainwright I (1982) A study of waterlogged wood conservation treatment at the cellular level of organization. In: Grattan DW, McCawley JC (eds) *Proceedings of the ICOM Waterlogged Wood Working Group Conference, Ottawa 1981, Ottawa 1982*, pp 107–116 (AATA 21-460)
- Ypey J (1964) Zusammenhänge zwischen der Konservierung während der Grabung und der Behandlung der Funde im Labor. *Präparator* 10:39–47
- Zhang Lan (1995) A note on the conservation of a thousand-year-old boat. *Stud Conserv* 40:189–193 (AATA 33-1062)
- Zillich I (1991) Über das Begradigen von Holztafelgemälden. Diplomarbeit, Staatliche Akademie der Bildenden Künste, Stuttgart
- Zillich I (1994) Über das Begradigen von Holztafelgemälden. Holz in der restauratorischen denkmalpflegerischen Praxis. 2. Fortbildungsveranstaltung für Restauratoren am 11. März 1994 in Hannover. Niedersächsisches Landesverwaltungsamt, Institut für Denkmalpflege
- Zurowski T (1953) Doświadczenia nad elektrokinetyczną konserwacją drewna (Experiences with the elektrokinetic conservation of wood). *Ochrona Zabytkow* 6(4):224–227

12 Adhesives and Gap Fillers

12.1

Adhesives

12.1.1

Adhesives for Wood Conservation

Adhesives are non-metallic materials which join solids (adherents) to each other by adhesion and cohesion, without causing any significant changes in the solids to be joined. The cohesion derives from internal, intermolecular forces and the molecular size of the adhesive. The adhesion refers to the molecular forces between the solid surfaces of the adherents and a second phase, the adhesive, which may consist of individual particles such as droplets or powders, or a continuous liquid or solid film. The adhesion of adhesives is effected primarily by Van-der-Waal's forces, but also by electrostatic forces.

In the conservation of wood, adhesives should meet the following requirements:

1. Reversibility of the adhesive and the adhesive joint
2. Absence of darkening or color changes of the joined pieces
3. Compatibility of the adhesive with wood preservatives and consolidants
4. Adequate strength of the adhesive joint
5. Permanence and flexibility of the joint, i.e., the adhesive and the joint must have acceptable aging characteristics
6. Resistance of the adhesive to pests
7. Evidence of adhesive joints in objects after conservation treatments

Reversibility of the adhesive joints is especially important where old, open joints are to be readhered, or where a new and different adhesive is to be used for an old joint, so that the adherents will not be damaged further. Industrial practice strives for joints that are stronger than the wood itself, but for conservation the strength of adhesive joints should be slightly less than the adherents, so that a possible failure will take place in the adhesive rather than in the wood. Failure in the wood means a loss of originality and of original substance. Permanently elastic adhesives can absorb some of the swelling and

shrinking of the wood in response to climatic changes and thus avoid cracks in the adhesive joint.

Practical examples of joining wooden parts with adhesives can be classified in various ways. Moisture content, for instance, can be used to classify wood as dry, wet or waterlogged. Wet or waterlogged wood does not respond well to adhesives, and this problem has not been solved completely. The usual method for dealing with wet or waterlogged wood from archaeological digs is to first dry it carefully, possibly in combination with the simultaneous impregnation of dimensional stabilizers and consolidants.

If wooden parts that have been damaged biologically are to be joined, the nature of the damage, e.g., by insects, fungi, or marine borers, and the degree of deterioration from mild to heavy will determine the final result. Density and strength of the deteriorated wood are reduced, but permeability and capacity for absorbing adhesives are increased. Greatly increased permeability of the wood can lead to excessive absorption of adhesive or 'starved joints' when the adhesive tends to disappear into the interior of the wood. This can make corrections or newer joining with or without removing the old adhesive more difficult.

In many cases, dry wood with much damage by insects or fungi, or archaeological waterlogged wood must first be consolidated and treated for dimensional stability before it is possible to join it with adhesives. Consolidants already present in the wood will noticeably reduce its permeability, possibly leading to reduced joint strength. If the consolidant is also present in the surface layers, compatibility problems with the adhesive can arise, e.g., use of waterborne adhesive systems on wood consolidated with acrylic resins, leading to insufficient adhesion. In order to use traditional adhesives such as animal glues, the consolidant would then have to be reduced or largely removed. This also applies to waterlogged wood treated with PEG or sugar. It is, of course, also possible to use the same substance not only for consolidating and stabilizing, but also for gluing wood, since many consolidants have adhesive qualities. Much depends on the formulation, especially as regards viscosity, since low viscosity will favor penetration of consolidant, while higher viscosity is better for adhesives to avoid excessive absorption into wood.

The wood, as well as the adhesive, must meet a number of requirements to make stable adhesive joints possible. The pieces of wood should not differ too much in their anatomic and structural characteristics. Joining parts of different species, or different degrees of decomposition or destruction increases the danger of premature joint failure, because permeability, density, and strength can differ significantly from each other. Grain direction can also have a significant effect. Cross-sectional surfaces of wood generally absorb adhesives faster and in greater quantities, which can lead to poor joints, while side grain joints are usually stronger and more stable. Density and strength of the wood are also important factors, since the stronger the wood, the stronger the joint must be. Woods of higher density will take up less adhesive

than low density woods, and the latter may even take up too much. Generally, woods of higher density are more difficult to adhere than less dense ones. Wood moisture content is a decisive factor in determining a stable and durable bond. When gluing dry wood with traditional adhesives its moisture content should be in the range of 2–16%. Wood with a moisture content that is too high will delay adhesive setting and leads to weaker joints. Wood extractives such as resins, waxes, or fats can interfere with adhesion and prevent penetration of adhesive into the wood. In such cases a partial extraction of these substances is indicated. Further influencing factors, especially in the case of greatly damaged wood, are the creation of suitable adhesion surfaces, e.g., by the use of gap fillers, and in using gentle pressure when the joint is formed. The actual condition of adhesive joints can be evaluated by means of nondestructive holographic interferometry (Szava et al. 1994).

Adhesives can be classified according to various points of view, such as chemical composition and origin, type of setting, manner of use, and end use. Most commonly it is done on the basis of origin (inorganic and organic) or of chemical nature (natural, semisynthetic or synthetic) as well as according to whether it sets physically or by chemical reaction. Physically setting adhesives which are usually single-component can be free of solvents (e.g., hot-melt adhesives) or contain solvents (protein glues, and solvent-based, dispersion, pressure sensitive, and contact adhesives). Adhesion is achieved by changing from a liquid to a solid phase, or by evaporation of solvent either before or during the process of adhesion. Chemically setting adhesives consist of one or more reactive components which harden by chain polymerization such as methacrylates and cyanacrylates, polycondensation such as phenol, urea or melamine formaldehydes, or polyaddition such as epoxy resins and polyisocyanates plus polyols. Among both physically and chemically setting adhesives are systems which harden at room temperature and/or at elevated temperatures. In the future the number of adhesives which contain organic solvents will be reduced in favor of solvent-free or waterborne adhesives.

Adhesion processes can be classified according to the process, e.g., pressure-sensitive or contact adhesive; the state of the adhesive at the time of gluing, e.g., wet or melted adhesive; the temperature, e.g., cold, warm or hot; the applied pressure, e.g., with or without; and the wood surface of the adherents, e.g., flat, edge, or end-grain surfaces.

Detailed information on the properties of adhesives and their use in conservation can be found in Newey et al. (1983), Brommelle et al. (1984) and Horie (1987). Down et al. (1996) investigated 27 poly(vinyl acetate) and 25 acrylic adhesives, beginning in 1983, with respect to their pH values, emission of dangerous volatile components, their flexibility and strength, and their yellowing after aging with and without exposure to light. Gluing of wood has been discussed by Kollmann (1975), Grattan and Clarke (1987), Rice (1990), Williams (1998) and Pizzi (2000).

Since most of the adhesives have the same chemical basis as the consolidants already discussed in Chapter 11, descriptions of their chemical and physical characteristics have been dispensed with in favor of emphasis on their use in conservation.

12.1.2

Natural Adhesives

12.1.2.1

Proteins

Among the protein adhesives are casein; albumin from blood or chicken eggs; animal glues from bones, hides, leather or fish; and gelatins.

Casein was used 10,000 years ago as a pigment binder in cave paintings and therefore may have been used for gluing wood early on as well, making it probably the oldest wood adhesive. An early written recipe for the preparation of casein adhesive for altar panels, which in principle is still valid today, is from the book of techniques by the Benedictine monk Theophilus Presbyter of the twelfth century. Blood albumin adhesive reportedly was also used already in antiquity. Albumin is the adhesive substance in both white and yolk of the chicken egg, and egg white is mentioned in the Leyden Papyrus of the sixth century B.C. as an adhesive for gilding.

About 3500 B.C. the Sumerians obtained an animal glue called *se gin* by boiling animal hides (Römpf 1995). A wall painting in the tomb of Prefect Rekhmara of Theben dating to 1470 B.C. also shows preparation of animal glues. Bars of glue that hardly differ from those of today have been recovered from other tombs (Schramm and Hering 1989). Other finds from tombs verify the use of glue for making glued and veneered objects. In Theophrastus' (371–286 B.C.) writings on plants are directions for the use of 'taurocolla' – glue made from bulls' ears – for gluing wood. Plinius the Elder (23–74 A.D.) reported on the preparation of glue from bull hides and fish bladders ('ichtyocolla'). From the Middle Ages we have directions for glue preparation by Theophilus Presbyter and Cennini. Bone glue was discovered by D. Papin about 1700. Following this, the first industrial production of animal glues began in France. A systematic description of the production of glues can be found in Duhamel de Monceau's book on arts and crafts published in 1771 (Schramm and Hering 1989). Not until the 1930s did the development of synthetic resin adhesives largely displace protein adhesives in the industrial sector. Lately, however, there has been a resurgence of interest in adhesives based on renewable natural resources.

Casein adhesive hardens chemically and has high adhesive strength. After hardening it is resistant to moisture and heat, but it is a poor gap filler and can be removed only mechanically. Casein glues have been and are used for edge-gluing boards to form painting supports (Castelli et al. 1991) and have found use in glued-laminated structural wood members.

Water-resistant blood-albumin glues were made from fresh blood in antiquity. The discovery of a method for making dry blood-glue in the first third of the twentieth century led to a renaissance of its use in plywood production. Early paintings on plywood and early airplanes contained plywood glued with blood-albumin (Williams 1998). Animal glues (cf. Chap. 11) are warm adhesives which must be used warm. The collagen contained in the animal raw materials can break down at lower or higher temperatures so that glues of different adhesive strength are formed. Glues from mammal products can be distinguished from fish glue by high performance liquid chromatography (HPLC) (Sinkai et al. 1992). Animal glues swell in water and become soluble upon heating, which gives them the reversibility desired by conservators and was probably one of the reasons for their use over the centuries. Animal glues are hygroscopic and sensitive to climatic influences, which affects the stability and strength of glue lines. Whereas too low a relative humidity embrittles the glue, it will soften when there is too much moisture in the air, the latter also favoring an attack by mold fungi. It is well known that some larvae of wood-destroying insects prefer food sources containing proteins (cf. Chap. 5), so that glue lines will be attacked preferentially. Since some animal glues lack sufficient flexibility, glycerol or sorbitol are sometimes added as plasticizers. If the swelling of the glue in moist air is to be reduced or prevented entirely, the glue must be hardened. Addition of alum serves for prehardening, whereas posthardening can be done with chromates (customary in the past), tannin or formaldehyde in the form of formalin. However, the hardening causes a loss of thermoplasticity and the glue becomes irreversibly cross-linked and therefore insoluble.

Wood damaged by insects or fungi that has been stabilized by the polymerization of acrylic monomers *in situ* can be glued with animal glues, because the monomers in the surface layers tend to evaporate during polymerization and thus will not form a water-repellent barrier.

12.1.2.2

Carbohydrates

Adhesives from plant sources are mostly carbohydrates such as starch from rice, wheat, rye, or potatoes; gums such as gum arabic, tragacanth, or fruit-tree gum; and agar-agar. Dextrins, shorter chain decomposition products of starch, are also used as adhesives. Carbohydrate adhesives are not used for gluing dry wood because of their low adhesive strength and swelling tendency, but do find application in gluing paper and papyrus. Waterlogged wood that has been treated with sugar can be glued with the customary wood glues, whereby the highly concentrated sugar solution of the treatment already offers considerable adhesion. Dowels inserted into moist wood treated with sugar, for example, will hold without additional application of adhesive (Hoffmann 1995).

12.1.2.3

Waxes

Among the natural waxes are beeswax, carnauba wax and montan wax, but paraffin wax will also be included here even though it is of synthetic origin. The use of beeswax in Egypt was known from a papyrus from the time of Ramses II (Schramm and Hering 1989), and Plinius the Elder described its use in painting. Waxes do not offer sufficient adhesive strength to use them for gluing load-bearing parts. Wooden objects which have been consolidated with beeswax or paraffin wax (cf. Chap. 11) must have the wax leached from the faying surfaces before they can be glued with hide glues, but even then the bond will be weak. Jespersen (1979) used a mixture of five parts beeswax and four parts dammar to glue wood treated with PEG 3350.

12.1.2.4

Resins

Just as the adhesive qualities of tree resins were utilized 6000 years ago, it is probable that India rubber and the plant resins amber, copal, dammar, mastic, sandarac, and colophony as well as the animal secretion shellac were used for gluing in early times, although the resins were used mainly for the preparation of lacquers and varnishes. Colophony and shellac were known in antiquity. During the Baroque period, colophony was used as the adhesive for fastening stone mosaics to their base. Although colophony and shellac are relatively resistant to heat and chemical attack, they do not have sufficient flexibility or adhesive strength for a permanent adhesive bond in wood. According to Koob (1984), shellac will cross link, becomes increasingly brittle with age, produces high stresses in the adherents and discolors them, and can only be removed with difficulty.

12.1.2.5

Wood Tar, Bitumen, and Asphalt

Wood tar is obtained by destructive distillation (pyrolysis) of wood, especially birch and pine. Bitumen and asphalt are oxidation and polymerization products of petroleum under the influence of microorganisms. Wood tar and the pitch derived from it were used in Europe during the middle Paleolithic Age. They were used to shaft stone or flint blades with wood, bones, or antlers, or were used for filling cracks in building timbers. An example of the use of pitch derived from wood or bark of birch (Betulaceae) to shaft an ax and arrows was found with the glacier mummy 'Ötzi' dating to the Neolithic Age (Sauter et al. 1992). Excavations in Syria yielded artifacts from the middle Paleolithic Age which were shafted using bitumen occurring naturally in the vicinity (Boëda et al. 1996).

12.1.2.6

Adhesives Derived from Wood

In a broader sense, the natural adhesives also include lignins which are by-products of the pulping process (Marutzky 1998). They are sometimes used as extenders for synthetic adhesives. Pure lignin adhesives can be obtained by special condensation processes or by the addition of cross-linking agents. Furthermore, materials for the production of adhesives can be obtained by plasticization or liquefaction of wood (Shiraishi 1993).

12.1.3

Semisynthetic Adhesives

12.1.3.1

Cellulose Ether: Methyl Cellulose

The cellulose ethers produced in the first third of the twentieth century have not attained much importance in the conservation and gluing of wood. A survey of American conservators made in the late 1980s showed that only 4.5% of all users had used cellulose ethers for gluing wood (Feller and Wilt 1990). According to an investigation by Döll (1997), the use of 7–10% solutions of methyl cellulose yielded adhesive strengths superior to those of 15% aqueous solutions of bone glue. However, compared with Ponal, a poly(vinyl acetate) adhesive, bond strength was 35–40% less. The high viscosity of methyl cellulose makes it very suitable for fixing and gluing small wooden parts and replacement pieces. Normal variations in relative humidity will not loosen the bonds, but data on long-term behavior are not available. Park (1997) uses a 2.5% (w/v) solution of Klucel G in distilled water as an adhesive for freeze-dried waterlogged wood.

12.1.3.2

Cellulose Ester: Cellulose Nitrate

Beginning at the end of the nineteenth century and continuing into the 1930s, cellulose nitrate was used initially in the form of Zapon, a cellulose nitrate/camphor solution in amyl acetate, and later in other forms of application, for coating, gluing, and consolidating the most diverse materials. Trade names for cellulose nitrate adhesives are Duco Cement, Durofix HMG, Waterproof Adhesive and UHU Hart. However, early in its usage its instability and tendency to discolor objects was noted. According to Koob (1982) the causes of the instability are to be found in the presence of traces of acid from production, the eventual loss of volatile plasticizer, and environmental conditions. Selwitz (1988) lists three mechanisms for the primary decomposition of cellulose nitrate: (1) acid catalyzed ester splitting, (2) breaking the

nitrogen-oxygen bond by UV radiation, for example, and (3) ring splitting. The formation during the initial breakdown phase of nitrogen oxides, which act as catalysts, accelerates further decomposition (secondary phase). Cross-linking reactions do not occur with cellulose nitrate, so that its solubility and thus its reversibility is largely maintained even in an aged condition. This is probably the reason that cellulose nitrate which is soluble in organic solvents is used to a limited extent in conservation adhesives even today. However, for gluing wood it is not very suitable. Small fragments of wood which have been consolidated by the alcohol-ether-rosin method of Kramer (1979) can be rejoined readily using 'Karlsons-Klister', a cellulose-derived adhesive.

12.1.4

Synthetic Adhesives

12.1.4.1

Phenol/Resorcinol-Formaldehyde Resins

Although Baekeland applied for the first patent for phenol formaldehyde (PF) resin at the beginning of the twentieth century (cf. Chap. 11), the resin has been used in the gluing of plywood for airplane construction and for glued-laminated timbers only since the 1930s. Resorcinol formaldehyde (RF) resins were first used in the USA for gluing wood in 1943. PF resins are used in the form of aqueous solutions of precondensate, which are then hardened with the addition of acid or alkaline catalysts and evaporation of the water. By variations in temperature, reaction time, catalyst type, and the quantities and proportions of the initial components, adhesives with a range of properties can be obtained. During early uses of PF resins, acid catalysts were used which produce strong bonds at room temperature, but acid catalysts are hardly used anymore because of concerns over long-term damage to the wood by residual acid and corrosion of fasteners and associated metallic hardware. PF resins are now used almost entirely as alkaline precondensates (resols) and require a curing temperature above 100 °C in order to achieve sufficient cross-linking. The alkalinity of these resins interferes with application of veneers, laminates, or coatings to particleboard, so that they are hardly used in furniture production. PF resins have a relatively low reactivity but very high thermal and hydrolytic stability, which explains their use for building timbers with potential exposure to moisture (Marutzky 1998). Gluing of wooden objects stabilized by acrylic monomers polymerized in situ can be done not only with animal glues but also with PF adhesives, where the latter give higher bond strength. According to Stamm (1959), wood treated with PEG can be glued with a high-temperature curing phenolic resin. Stable adhesive bonds can only be obtained if the PEG is largely extracted first from the surface layers (Grattan and Clarke 1987). Adhesive strength can be increased by adding 15% PEG to the PF resin. Noack (1969) carried out gluing experiments on PEG-treated wood using PF, RF, and urea formaldehyde (UF) resins, and

obtained glue bond shear strengths of about 2.5 MPa. The reactivity of PF resins can be increased by copolymerization with resorcinol (Steiner 1990). Adhesives which can be cured at room temperature are also very moisture and temperature resistant and are used for glued-laminated timbers and finger joints. They are the preferred adhesives for wood used in shipbuilding and airplane construction. Generally, PF and RF adhesives are not suitable for works of art because they cross-link during curing and therefore can only be removed with difficulty if retreatment should be necessary.

12.1.4.2

Urea-Formaldehyde Resins

In 1929, 10 years after the first patent for the production of condensation resins of urea and formaldehyde was applied for, an acid-curing UF resin with the trade name Kaurit glue found use in the gluing of plywood and similar products. Today about 50% of plywood, 85% of particleboard, and almost all medium density fiberboard (MDF) are made with UF resins (Marutzky 1998). UF resins are water based, colorless adhesives of high reactivity which can be produced much less expensively than PF and RF resins. The resistance of the resin to moisture and temperature is limited, and therefore the materials made with it are used primarily for interior applications and furniture.

UF resins are cured at room or elevated temperatures in a weakly acid medium by the addition of acid-reacting salts or by the natural acidity of woods such as oak or cedar. UF resins tend to emit formaldehyde under the influence of moisture and heat. In order to obtain bonds that are more moisture resistant and largely free of formaldehyde emissions copolymers with melamine (MUF resins) are used, which are sometimes further fortified with phenol (MUPF resins). Another disadvantage of unmodified urea resins is their high shrinkage during curing compared with, for instance, epoxy resins. As a matter of principle, UF resins, just like PF resins, do not have much importance for the conservation of cultural property because as a result of cross-linking the bonds are irreversible. One possible use is in the treatment of wood members of excavated historical buildings (cf. PF, UF, and MF resins in Chap. 11).

12.1.4.3

Melamine-Formaldehyde Resins

The first use of aqueous melamine formaldehyde (MF) adhesives for gluing wood dates to the time shortly before World War II. Pure MF resins are highly moisture and temperature resistant, but they are relatively expensive so that they are used in the wood industry only as facing materials. Waterlogged wood stabilized by the Arigal C or Lyofix methods with MF resin (cf. Chap. 11) is not glued with MF resin but with a common wood glue, probably hide glue or poly(vinyl acetate) adhesive (Haas 1979).

12.1.4.4

Poly(vinyl acetate)

The thermoplastic poly(vinyl acetate) (PVA) adhesives were first produced in 1928, and after World War II found widespread use in gluing wood. They are known generically as white glues and yellow or carpenter's glues. PVA was already being used in 1932 as a binder and an adhesive in the transfer of a fresco (Horie 1987). Nowadays, PVA adhesives are put to such industrial uses as fastening laminates and edges to wood-based materials, and for the assembly of furniture parts. The aqueous emulsions have trade names such as Elmer's White Glue, Evertite, Titebond, Elmer's Carpenter's Glue, Vinylite, Gelva, Elvacet, Vinavil, Planatol, Ponal and Mowicoll. PVA is colorless and lightfast, compatible with plasticizers and has good adhesion to all kinds of adherents. It is also soluble in various solvents and therefore reversible, in principle. It has been possible, for instance, to dissolve it from objects after 30–40 years (Horie 1987). Loss of reversibility can be prevented by the addition of methyl cellulose (Wächter 1995). However, PVA has limited resistance to moisture and temperature, is subject to creep (cold flow) and has a low softening point. The emulsions are very stable and have a long shelf life but are subject to mold. Mold can also be a problem for PVA coatings and glue lines on objects in spaces with high relative humidity, so that biocides are often added. Next to hide glues, PVA adhesives are the ones most often used in conservation, for instance for wooden painting supports (Nicolaus 1998; Rothe and Marussich 1998) and organs (Miller 1988). The adhesive strength of a commercial PVA emulsion was, according to Sakuno and Schniewind (1990), greater than that of 15% solutions of Acryloid B72, Butvar B98, and the PVA resin AYAT, although even the last yielded acceptable values. Among the adhesives tested by Down et al. (1996), PVAs were more acidic than acrylics, and PVA homopolymers had higher pH values than PVA copolymers. PVA adhesives liberate noticeable amounts of acetic acid only during curing. They tend to yellow at twice the rate of acrylic adhesives when exposed to light. Among the PVA copolymers, vinyl acetate/ethylene copolymers exhibited especially advantageous properties (Down 1995).

Wood treated with PEG can be glued with PVA adhesives, whereby the addition of small amounts of PEG to the PVA improves the bonding (Grattan and Clarke 1987).

12.1.4.5

Poly(vinyl acetal)s

Poly(vinyl formal) was used in the early 1960s for the consolidation of textiles, and poly(vinyl acetal) from the 1930s to the 1960s for the conservation of excavated bones and for ivory (Horie 1987). Later, these were replaced by poly(vinyl butyral, PVB) sold under the trade names Butvar and Mowital. Barclay (1981) and Nakhla (1986), who consolidated air-dry

wood objects with PVB, pointed out the possibility of also using it to bond fractured pieces. Sakuno and Schniewind (1990) tested the adhesive strength of Butvar B98 in some detail and found that the glue line impact shear strength was higher than could be obtained with Acryloid B72 and AYAT, but less than the values for a PVA emulsion. Watson (1987) reported that freeze-dried wet wood can be glued with a solution of Butvar B79 in amyl acetate and acetone.

12.1.4.6

Acrylic Compounds

Although acrylic polymers in aqueous emulsion which were first produced in 1928 have good adhesive properties like PVA, they are actually not being used as adhesives in the wood industry. However, they have gained a firm place in the conservation of cultural property because of many possible variations in their composition. In connection with wood, the trade products Primal AC 33 (Rhodoplex in North America) and Plextol B 500 and D 360 should be mentioned. Horie (1987) gives many literature references on the properties, aging characteristics, and the associated losses in reversibility for acrylic emulsions. Detailed data on 25 different acrylic resin adhesives have been presented by Down et al. (1996). Acrylic resin emulsions have found use not only for air-dry wood but also for wet wood. Nakasato (1994) used thixotropic acrylic resin emulsions for the point-wise gluing of wood panel reliefs for a roof. Waterlogged wood that was pretreated with acrylic resin emulsion and then freeze dried could be glued with a hot-melt adhesive (Zumpe 1989).

The group of acrylic compounds also includes the cyanoacrylates, which are used without solvent and as a single-component adhesive. They react with the film of moisture on the adherent surfaces and therefore belong to the group of adhesives which cure by chemical reaction. Their short reaction time, low adhesive strength with wood, and unsatisfactory aging characteristics (Williams 1998) would seem to make them unsuitable for conservators. Furthermore, these resins sometimes cross-link during curing and can only be removed with difficulty by using special solvents such as dimethyl formamide or nitromethane (Horie 1987). Smaller fragments of wet wood that have been stabilized with PEG can be glued with cyanoacrylate (trade name Fimofix; Zumpe 1981).

Wooden objects which have been consolidated with acrylates can be bonded better with acrylic polymers in organic solvents than with aqueous emulsions of PVA, where possible problems with solvent retention must be considered. For example, wood decayed by brown rot and consolidated with Plexigum PQ 610 can readily be glued with a 45% solution of the same polymer in aliphatic white spirit (Isopar E; Ruhnau 1995). Gluing of wooden objects consolidated by in situ polymerization of acrylic monomers has been discussed under proteins in Section 12.1.2.

12.1.4.7 Epoxy Resins

Epoxy resins were first mentioned as adhesives in a patent of the Swiss Castan in 1938, and adhesives and consolidants suitable for conservation have been on the market since the 1950s (Horie 1987). Epoxy resin (trade names Araldite, Rütapox) adhesives cure by chemical reaction taking place in situ and will form strong secondary bonds with the adherents. Once cured they are irreversibly cross-linked and can no longer be dissolved, but can be caused to swell in certain solvents such as 1,2-dichloromethane and 1,3-dioxolane. Curing at room temperature takes place without significant shrinkage, and it forms strong bonds which are sometimes too strong for fragile objects. Epoxy resins are used as a wood adhesive only in special applications, the repair of structural timbers being an important example. Phillips and Selwyn (1978), Avent and Issa (1984) and Avent (1986a,b) have dealt in detail with development of methods, with criteria affecting bond strength, and resistant to fire when structural repairs are made with epoxy resins in wood buildings. There are numerous examples of Hungarian conservators' use of epoxy resins (trade names Eporapid, Eporezit FM 20, UHU Plus Endfest 300) for gluing parts to wood objects in museums (cf. Chap. 11, epoxy resins). Epoxy resins are also often used in Italy to glue wood and to close up open joints (Gianelli 1989). Down (1984, 1986) has published detailed investigations of the aging (yellowing) of epoxy resins. The resins are also used to glue wood treated with PEG (Grattan and Clarke 1987; Terfve 1997).

12.1.4.8 Polyurethanes (Polyisocyanates)

Polyurethane adhesives were first used in the 1940s to glue wood in airplane construction, and in the early 1970s they came into use in particleboard production. At present mainly polymeric diphenylmethane diisocyanate (PMDI) is used as a reactive adhesive, usually in the form of an aqueous emulsion, for the production of formaldehyde-free particleboard (Marutzky 1998). Polymeric toluene diisocyanate (PTDI) can also be used as an adhesive and for making modified wood. According to Horie (1987), Xylamon LX Hardening N, often used in the 1950s to consolidate fragile objects, probably contained an isocyanate in a petroleum distillate solution which formed a polyurethane by reacting with moisture in air and wood. Hoffmann (1988) used an isocyanate adhesive for gluing parts of a wooden goblet that had been treated with PEG, because the UHU-coll express normally used did not adhere well or did not harden completely. In 1965, Noack presented a method for gluing PEG-treated wood with a polyurethane (cf. Chap. 11). Industrial adhesive bonds with polyisocyanates such as PMDI have high strength, high resistance to moisture and temperature, but are costly. After curing, the polyurethane

systems are irreversibly cross-linked and can be removed only by swelling and mechanical means.

12.2 Gap Fillers

12.2.1 Types of Gap Fillers

Gap fillers are kneadable to highly viscous masses which can be divided into gap-filling adhesives and fillers (Römpf 1995). Gap-filling adhesives are adhesives which can be deformed plastically at normal temperatures, contain only volatile or no solvents and fill materials, and are used to bridge thick glue lines. No special demands are made on fillers in regard to adhesive strength and flexibility, and they are used to fill and seal hollows and thicker joint openings. Both groups can be subdivided on the basis of their hardening mechanism into hot-melt, evaporation, and reaction gap fillers. Hot-melt fillers are normally solid and must be melted for use. Resin, wax, asphalt, and pitch with added fill materials of pure sulfur, quartz or glass powder, or iron dust belong to this group. Evaporation fillers contain binders dissolved in volatile solvents which evaporate during hardening, often accompanied by some shrinkage. Examples would be animal glue, shellac in alcohol, and celluloid in amyl acetate with added fill materials such as wood flour. Reaction fillers are doughy mixtures which cure into hard solids by chemical reactions. Epoxy resins, polyurethanes, polysulfides, and silicon resins as well as inorganic fillers belong to this group.

12.2.2 Gap Fillers for Wood Conservation

Gap fillers used in the conservation of wooden objects to fill cracks, splits, holes such as insect exit holes, and for loss compensation should meet the following requirements:

1. Good adhesive strength, but this should only be high enough so that any failure during swelling and shrinking of the wood will be in the filler and not in the wood,
2. Cohesive strength commensurate with that of the wood, to prevent excessive resistance during swelling and shrinkage which might lead to damage to both wood and filler (Ruhnau 1995; Mintrop 1997),
3. Sufficient permeability to water vapor,
4. Long-term flexibility,
5. Good lightfastness,
6. Good aging characteristics and reversibility,

7. Receptivity to in-painting or coloring,
8. Adequate pot life,
9. Adequate shelf life and lack of separation of components,
10. No swelling of the wood by solvents in the filler, and no stress cracks in the filler upon evaporation of solvent,
11. Can be worked with a spatula, and sanded after curing without creating toxic dust.

12.2.3

Organic Gap Fillers

Although gap fillers may be subdivided into two groups based on the type of binder used, namely into inorganic and organic gap fillers, the organic gap fillers are the most important for use in conservation, and will be the only ones discussed in more detail.

12.2.3.1

Natural Substance Fillers

Protein Glue Fillers. These often-used gap fillers can incorporate various hide glues such as bone, rabbit skin, and fish glues, or casein as binders. Fill materials may be inorganic such as chalk or gypsum or organic such as sawdust, wood flour (especially of balsa wood), *Lycopodium* spores, and cork granules. Protein glue fillers are often used in conservation treatments of panel paintings and sculptures (Koller 1986), and for loss compensation of valuable parts of pipe organs (Caputi Jambrenghi 1989) and ancient Egyptian objects as for example the Solar Boat of Cheops (Kadry 1986). *Lycopodium* filler (*Lycopodium* spores, chalk, fish glue, and glycerol) has been used to close exit holes of wood-destroying insects.

Oil-Based Fillers. Often-used components of such gap fillers are linseed oil and whiting. They have been used preferentially to seal gaps in the joints of window frames.

Wax-Based Fillers. Fillers consisting of beeswax and/or paraffin wax, which are sometimes stiffened by the inclusion of natural resins, are particularly suitable for closing exit holes of wood-destroying insects in furniture and sculptures.

12.2.3.2

Synthetic Resin Fillers

Cellulose Nitrate Fillers. Fillers of this type became known as 'liquid wood'. They consist of cellulose nitrate dissolved in the customary solvents, with filler materials added depending on the particular case. Information on the use of such gap fillers has been published by Decsi (1987) and Nacsá (1987).

Poly(vinyl acetate) Fillers. Gypsum and sawdust are added to aqueous emulsions of PVA to produce a gap filler suitable for filling cracks, open joints, and exit holes of wood-destroying insects (Schleicher 1984).

Poly(vinyl butyral) Fillers. Dry furniture parts excavated in Gordion and dating to the eighth century B.C. were consolidated with Butvar B98 in toluene/ethanol, and repairs were made with a paste prepared with glass microspheres and Butvar B98 solution, with dry pigment added. This gap filler proved to be appropriate because of its moderate strength, unobtrusive appearance, and light weight (Simpson and Spirydowicz 1999).

Acrylic Resin Fillers. These fillers are based on acrylic resins either in aqueous dispersions or dissolved in organic solvents. As a compensatory filler for window frames (Anonymous 1985/1986) and to close cracks in a sarcophagus (Formica 1989), for example, a mixture of Primal AC 33 with fill materials such as wood flour can be used. Mintrop (1997) has investigated in detail the suitability of the acrylate dispersion Plextol B 500 for the preparation of thermoplastic gap fillers. Hatchfield (1986) recommended the use of Acryloid B72 extended with glass microspheres for water-sensitive objects such as mummy masks. The white, powdery glass microspheres have a diameter of $\leq 177 \mu\text{m}$ and a density of $150\text{--}400 \text{ kg/m}^3$. The gap filler is prepared by mixing equal volumes of a 15% solution of Acryloid B72 in acetone/ethanol (1:1) and 3 M C15/250 microspheres. The hardened filler can be carved and sanded, and can readily be dissolved again. Stappel (2000) used a 35% solution of Plexigum PQ 610 in Shellsol/acetone extended with cork flour to fill cubical fractures of brown rot in a wooden coat of arms.

Epoxy Resin, Polyurethane, and Silicone Rubber Gap Fillers. In the early 1980s, Grattan and Barclay (1984), Fuller (1985) and Tomaszewski et al. (1986) began systematic investigations of various gap filler systems, with emphasis on those based on epoxy resins, polyurethanes, and silicone rubbers. Since all three types contain binders which will cross-link irreversibly upon hardening they will be discussed together.

Fuller (1985) followed up the work of Grattan and Barclay (1984) and studied the suitability of silicones compared with other elastomers for filling cracks in wooden objects. Mixtures of silicone rubber and phenolic resin microballoons were prepared in various proportions, and the best results were obtained for a silicone rubber/microballoon ratio of 1:2. This work was continued by Barclay and Grattan (1987), who discussed the pros and cons of using different silicone rubbers, and pointed out that the red-brown phenolic microballoons can be replaced with white glass microballoons. Storch (1994) examined how the experience with silicone resins gained at the Canadian Conservation Institute translated to practical applications for architectural elements of wood. He believed that above all the flexibility of the resin he used was an advantage, and estimated a lifetime under exterior exposure of at least 10 years.

Mintrop (1997) distinguished between thermoplastic and elastomeric gap fillers. Binders can be the thermoplastic acrylate dispersion Plextol B 500 and the elastomeric silicone rubber Dow Corning 7091, to which inorganic (glass microballoons, chalk, pumice or quartz flour, mica, kaolin, bentonite, attapulgite) or organic (pulp fibers, wood flour, cork, polyacrylic fibers) fill materials are added in various proportions. Whereas the flexibility of the thermoplastic gap fillers is influenced especially by the fill materials, the binder is the dominant factor for systems containing elastomers. Elastomeric gap fillers based on silicone rubber are superior to thermoplastic gap fillers with respect to their capacity for compression and extension under repeated loading, whereby organic fill materials which are also highly flexible, such as cork, have an especially advantageous influence on the extensibility of the gap fillers. A disadvantage of silicone rubber gap fillers is their low permeability to water vapors and endangerment of the object by penetrating silicone oils.

In addition to the silicone rubber/microballoon gap fillers, Grattan and Barclay (1988) and Barclay and Mathias (1989) also investigated epoxy resin/microballoon gap fillers, based on the epoxy resin Araldite AW 106/HV 953 and glass microballoons. Gap fillers of that type produce good adhesion and have high compressibility. They should be used if the objects to be treated are exposed to air of stable relative humidity; otherwise gap fillers with wax or with silicone rubber and microballoons, which exert only low resistance to compression when the wood swells, are to be preferred (Grattan and Barclay 1988). Barclay and Mathias (1989) tested several gap fillers using Araldite AZ 3456 with HY 3456 hardener and phenolic resin microballoons, the proportions of resin/microballoons ranging from 0.5:1 to 2:1. The epoxy resin contains furfuryl alcohol as a solvent which gives it low viscosity and the capacity for taking up large quantities of microballoons. The short curing time of 3 h reduces the probability that the resin will penetrate into the wood. Using phenolic resin rather than glass microballoons results in an appearance better adapted to the damaged wood, and the cured gap filler can be carved and painted. Tensile and compression tests have shown that the use of the fill material decreases the pressure on the wood and the adhesion on the wood surfaces after curing, which improves the reversibility of the gap filler. For gaps which do not exceed a thickness of 20 mm it is not expected that there will be ill effects on the wood by the heat developed during the exothermic curing reaction of the epoxy resin.

Whereas the studies cited so far used glass or phenolic resin microballoons, Tomaszewski et al. (1986) used mainly wood fibers or wood flour in amounts ranging from 5–30% as fill materials in their study of 29 gap fillers with epoxy resins and polyurethanes. After testing thickness swelling, resistance to compression, cohesion and adhesion, susceptibility to vibration and deformation, and permeability to water vapor, none of the epoxy resin and PUR systems had ideal characteristics, according to tests made on fresh gap fillers and those which had undergone thermal and hydrolytic aging. The PUR gap fillers had

acceptable permeability to water vapor, but their swelling behavior and compression strength were unsatisfactory. The epoxy resin gap fillers, on the other hand, had sufficient stability under pressure, but the permeability to water vapor was unsatisfactory.

Petersohn (1989) made wedge-shaped cuts into the edges of a panel painting and filled them with a mixture of Araldite AW 134/HY994 and balsa-wood flour, in order to further stabilize the object and prevent insect attack. Rama Rao and Pandit Rao (1990) also used a gap filler of epoxy resin with wood flour for the conservation treatment of an ox cart. Further applications of epoxy resin gap fillers have been described by Csere (1987), Dalorová et al. (1987), Kiss (1987), and Vámosi (1987), with Araldite SV 427 being the preferred resin.

References

- Anonymous (1985/1986) Bemalte Holzteile im Freien (Fenster usw.). Restauratorenblätter 8:137–138
- Avent RR (1986a) Factors affecting strength of epoxy-repaired timber. *J Struct Eng* 112(2):207–221 (AATA 27–585)
- Avent RR (1986 b) Design criteria for epoxy repair of timber structures. *J Struct Eng* 112(2):222–240 (AATA 27–584)
- Avent RR, Issa CA (1984) Effect of fire on epoxy repair timber. *J Struct Eng* (12):2858–2875 (AATA 23–742)
- Barclay R (1981) Wood consolidation on an eighteenth century English fire engine. *Stud Conserv* 26(4):133–139 (AATA 19–338)
- Barclay RL, Grattan DW (1987) A silicone rubber/microballoon mixture for gap filling in wooden objects. In: Grimstad K (ed) ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, 6–11 July 1987, preprints vol 1, pp 183–187 (AATA 25–575)
- Barclay RL, Mathias C (1989) An epoxy/microballoon mixture for gap filling in wooden objects. *J Am Inst Conserv* 28(1):31–42 (AATA 27–588)
- Boëda E, Connan J, Dessort D, Muhesen S, Mercier N, Valladas H, Tisnerat N (1996) Bitumen as a hafting material on Middle Palaeolithic artefacts. *Nature* 380:336–338
- Brommelle NS, Pye EM, Smith P, Thomson G (eds) (1984) Adhesives and Consolidants. Preprints of the contributions to the Paris Congress, 2–8 Sept 1984. The International Institute for Conservation of Historic and Artistic Works, London
- Caputi Jambrenghi E (1989) Il restauro della cassa armonica dell'organo della chiesa di S. Maria Vetere di Andria (Bari) [The restoration of the soundbox of the organ in the church of Santa Maria Vetere in Andria (Bari)]. In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp 228–230. (AATA 29–2350)
- Castelli C, Parri M, Santacesaria A (1991) Il supporto: costruzione, stato di conservazione e intervento di restauro (The support: construction, state of conservation, and restoration treatment). In: Chiarini M, Ciatti M, Padovani S (eds) *Raffaello a Pitti: "La Madonna del balzacchino": storia e restauro* Firenze, Palazzo Pitti, 23 July–15 Sept 1991, pp 73–77 (AATA 32–2265)
- Csere J (1987) A györi mézszaros céh ládájának restaurálása (Restoration of the chest of the butchers guild in Győr). *Műz Műtárgyvédelem* (16):211–226 (AATA 24–611)
- Dalorová A, Brimichová M, Klimeš P (1987) Die Tafelgemälde der ehemaligen Flügel des spätgotischen Hauptaltars der Pfarrkirche des Hl. Nikolaus in Prešov (Kr. Prešov). *Renovatio* 5(7):55–57
- Decsi G (1987) Ácsolt láda restaurálása (The restoration of a timbered chest). *Műz Műtárgyvédelem* (17):115–124 (AATA 24–616)

- Döll M (1997) Methylcellulosen und die Verklebung von Holz. *Restauro* 103(5):332–336
- Down JL (1984) The yellowing of epoxy resin adhesives: report on natural dark ageing. *Stud Conserv* 29:63–76
- Down JL (1986) The yellowing of epoxy resin adhesives: report on high-intensity light ageing. *Stud Conserv* 31:159–170
- Down JL (1995) Adhesive projects at the Canadian Conservation Institute. In: Wright MM, Townsend JH (eds) *Resins ancient and modern*. Preprints of the SSCR's 2nd Resins Conference held at the Department of Zoology, University of Aberdeen, 13–14 Sept 1995, pp4–12
- Down JL, MacDonald MA, Tétreault J, Williams RS (1996) Adhesive testing at the Canadian Conservation Institute – an evaluation of selected poly(vinyl acetate) and acrylic adhesives. *Stud Conserv* 41(1):19–44 (AATA 34–1737)
- Feller RL, Wilt M (1990) Evaluation of cellulose ethers for conservation. *Research in conservation* 3. The Getty Conservation Institute, Los Angeles
- Formica L (1989) Intervento di conservazione di sarcofagi fenici (Conservation of Phoenician sarcophagi). In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp303–306, 342 (AATA 29–2379)
- Fuller RD (1985) An investigation of the physical and tensile properties of selected elastomeric gap-fillers for wood. MAC Thesis, Queen's University, Kingston, Ontario
- Gianelli I (1989) Il restauro del Cristo ligneo attribuito a Michelozzo di Bartolommeo nella chiesa di San Niccolò Oltrarno (The restoration of the crucifix attributed to Michelozzo di Bartolommeo in the church of San Niccolò Oltrarno in Florence). In: Tampone G (ed) *Legno e restauro: ricerche e restauri su architetture e manufatti lignei*, pp276–278, 340–341 (AATA 29–2382)
- Grattan DW, Barclay RL (1984) Gap fillers for wood. *IIC Can Group Newslett* 12:9–10
- Grattan DW, Barclay RL (1988) A study of gap-fillers for wooden objects. *Stud Conserv* 33(2):71–86 (AATA 26–646)
- Grattan DW, Clarke RW (1987) Conservation of waterlogged wood. In: Pearson C (ed) *Conservation of marine archaeological objects*. Butterworths, London, pp164–206 (AATA 28–2275)
- Haas (1979) Die verschiedenen Methoden der Naßholzkonservierung. 1. Methode Lyofix DML. *Z Schweiz Archäol Kunstges* 36(2):121–124
- Hatchfield P (1986) Note on a fill material for water sensitive objects. *J Am Inst Conserv* 25(2):93–96 (AATA 26–650)
- Hoffmann P (1988) Zur Rückformung feiner mittelalterlicher Drechslerware. *Arbeitsbl Restaur* 21(1) Gruppe 8, pp153–170 (AATA 26–651)
- Hoffmann P (1995) Das Zuckerschiff. *Restauro* 101(5):350–354
- Horie CV (1987) *Materials for conservation. Organic consolidants, adhesives and coatings*. Butterworth-Heinemann, Oxford
- Jespersen K (1979) Conservation of waterlogged wood by use of tertiary butanol, PEG and freeze-drying. In: De Vries-Zuiderbaan LH (ed) *Conservation of waterlogged wood, international symposium on the conservation of large objects of waterlogged wood*. Netherland National Commission for UNESCO, The Hague, pp69–76
- Kadry A (1986) The Solar boat of Cheops. *Int J Underwater Archaeol Underwater Explor* 15(2):123–131 (AATA 23–2311)
- Kiss P (1987) 1756-os szücsláda restaurálása (The restoration of a 1756 furrier's guild chest). *Műz Műtárgyvédelem* (16):227–234 (AATA 24–678)
- Koller M (1986) Studien zur gefaßten Skulptur des Mittelalters in Österreich: 2 romanische Kruzifixe aus Salzburg. *Österr Z Kunst Denkmalpflege* 40(3/4):127–134 (AATA 25–593)
- Kollmann FF (1975) *Principles of wood science and technology, vol II: wood based materials*. Springer, Berlin Heidelberg New York
- Koob SP (1982) The instability of cellulose nitrate adhesives. *Conservator* (6):30–34
- Koob SP (1984) The continued use of shellac as an adhesive – why? *Adhesives and Consolidants*. In: Brommelle NS, Pye EM, Smith P, Thomson G (eds) *Preprints of the contributions to the*

- Paris Congress, 2–8 Sept 1984. International Institute for Conservation of Historic and Artistic Works London, p 103 (AATA 21–2355)
- Kramer W (1979) Die Alkohol-Äther-Harz-Methode. *Z Schweiz Archäol Kunstges* 36(2):127–131
- Marutzky R (1998) Holzwerkstoffe und Klebstoffe für den Möbelbau. *Holz-Zentralblatt* 124(7):82
- Miller T (1988) The restoration of the Fonthill Organ. *Conservator* (12):38–43 (AATA 26–666)
- Mintrop B (1997) Elastische Kitte in der Holzrestaurierung. *Kölner Beitr Restaur Konserv Kunst Kulturgut* 9. Siegl, München
- Nacsa M (1987) Csalikulacs restaurálása (Restoration of a csalikulacs (double flask)). *Műz Műtárgyvédelem* (17):151–158 (AATA 24–744)
- Nakasato T (1994) (Conservation of wooden panels used as ornamental members of roof decoration.) *Hozon Kagaku* 33:55–66 (AATA 33–1039)
- Nakhla SM (1986) A comparative study of resins for the consolidation of wooden objects. *Stud Conserv* 31:38–44
- Newey C, Boff R, Daniels V, Pascoe M, Tennent N (1983) *Adhesives and Coatings*. Science for Conservators 3. Crafts Council, London
- Nicolaus K (1998) *Handbuch der Gemälderestaurierung*. Könemann, Köln
- Noack D (1965) Der gegenwärtige Stand der Dimensionsstabilisierung von Holz und Schlußfolgerungen für die Konservierung der Bremer Kogge. *Brem Jahrb* 50:43–72
- Noack D (1969) Zur Verfahrenstechnik der Konservierung des Holzes der Bremer Kogge. *Die Bremer Hanse-Kogge*. Röver, Bremen, pp127–156
- Park J (1997) The Barton-on-Humber project. A large collection of waterlogged wood: data, retrieval, storage, pre- and post-treatment methods. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) *Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference*, York 1996, Bremerhaven 1997, pp503–516
- Petersohn HR (1989) Die Restaurierung eines Tafelgemäldes aus der Werkstatt des Hans Leonhard Schäufler. *Restauro* 95(1):14–21
- Phillips MW, Selwyn JE (1978) *Epoxies in wood repairs for historic buildings*. Heritage Conserv Recreat Service Publ 1, US Department of the Interior, Washington, DC
- Pizzi A (2000) Tannery row – The story of some natural and synthetic wood adhesives. *Wood Sci Technol* 34:277–316
- Rama Rao N, Pandit Rao V (1990) Conservation of an old wooden bullock cart. *Ind J Chem Sci* 4:69–71 (AATA 29–697)
- Rice JT (1990) Gluing of archaeological wood. In: Rowell RM, Barbour RJ (eds) *Archaeological wood: properties, chemistry, and preservation*. American Chemical Society, Washington, DC, Adv Chem Ser 225:373–397
- Römpf H (1995) *Chemie-Lexikon*. Falbe J, Regitz M (eds) Thieme, Stuttgart
- Rothe A, Marussich G (1998) Florentine structural stabilization techniques. In: Dardes K, Rothe A (eds) *The structural conservation of panel paintings*. Proceedings of a symposium at the J. Paul Getty Museum, 24–28 April 1995. The Getty Conservation Institute, Los Angeles, pp306–315
- Ruhnau B (1995) Die Stabilisierung braunfaulen Holzes. *Kölner Beitr Restaur Konserv Kunst Kulturgut* 1. Siegl, München
- Sakuno T, Schniewind AP (1990) Adhesive qualities of consolidants for deteriorated wood. *J Am Inst Conserv* 29(1):33–44
- Sauter F, Jordis U, Hayek E (1992) Chemische Untersuchungen der Kittschäftungs-Materialien. In: Höpfel F, Platzer W, Spindler K (eds) *Der Mann im Eis, vol 1. Bericht über das Internationale Symposium 1992 in Innsbruck*. Eigenverlag der Universität Innsbruck, Innsbruck, pp435–441
- Schleicher B (1984) Relazione sul restauro della cornice (Report on the restoration of the frame) Il Tondo Doni di Michelangelo e il suo restauro, pp71–76 (AATA 24–793)
- Schramm H-P, Hering B (1989) *Historische Malmaterialien und ihre Identifizierung*. Deutscher Verlag der Wissenschaften, Berlin
- Selwitz C (1988) Cellulose nitrate in conservation. *Research in conservation* 2. The Getty Conservation Institute, Los Angeles

- Shiraishi N (1993) Plasticization of wood and its application. In: Shiraishi N, Kajita H, Norimoto M (eds) Recent research on wood and wood-based materials. Curr Jpn Mater Res (11):155–167 (AATA 33–1050)
- Simpson E, Spirydowicz K (1999) Gordion wooden furniture. Museum of Anatolian Civilizations, Ankara
- Sinkai T, Nagasawa I, Shida T, Sugisita R (1992) Analysis of binding media and adhesives in Buddhist wooden statues. Sci Pap Jpn Antiques Art Crafts (37):1–11
- Stamm AJ (1959) Effect of polyethylene glycol on the dimensional stability of wood. For Prod J 9(10):375–381
- Stappel M (2000) Holzergänzung im Außenbereich. Restauro 106(1):42–47
- Steiner PR (1990) Adhesives for wood: an update. In: Cahn RW (ed) Encyclopedia of materials science and engineering, suppl vol 2. Pergamon Press, Oxford, pp 655–660
- Storch PS (1994) Fills for bridging structural gaps in wooden objects. J Am Inst Conserv 33(1):71–75 (AATA 32–889)
- Szava I, Curtu I, Rosca C, Romulus C (1994) Devices for wood joints analysis using holographical interferometry. Proc 1st European Symposium on Nondestructive evaluation of wood. University of Sopron, Sopron, Hungary, 21–23 Sept, vol 1, pp 26–33
- Terfve A (1997) Bilan et perspectives du remontage des barques de Pommeroeul. In: Hoffmann P, Grant T, Spriggs JA, Daley T (eds) Proceedings of the 6th ICOM Group on Wet Organic Archaeological Materials Conference, York 1996, Bremerhaven 1997, pp 517–526
- Tomaszewski K, Wieczorek K, Chrzanowski A (1986) Z badań nad opracowaniem kitó do uzupełniania ubytków w drewnie zabytkowym na bazie żywic pochodzenia krajowego (Studies on the preparation of domestically made resin-based putty to fill in missing fragments in ancient wood). Rocznik przedsiębiorstwa państwowego Pracowni Konserwacji Zabytków (1):259–283 (1990) (AATA 29–2428)
- Vámosi L (1987) Egy avar kori favödör restaurálása (Restoration of a kit from the Avar period). Múz Mútagyvédelem (16):57–68 (AATA 24–843)
- Wächter O (1995) Zur Alterungsmethodik für synthetische Festigungs- und Klebemittel, die Prophylaxe auf dem Prüfstand. Restauratorenblätter 15:193–196
- Watson J (1987) Suitability of waterlogged wood from British excavations for conservation by freeze-drying. Recent advances in the conservation and analysis of artifacts, jubilee conservation conference, University of London, Institute of Archaeology, Summer Schools Press, pp 273–276
- Williams DC (1998) A survey of adhesives for wood conservation. In: Dardes K, Rothe A (eds) The structural conservation of panel paintings. Proceedings of a symposium at the J. Paul Getty Museum, 24–28 April 1995. The Getty Conservation Institute, Los Angeles, pp 79–86
- Zumpe R (1981) Die Konservierung von Feuchtholz mit Polyethylenglycol (PEG). Neue Museumskd 24:129–137
- Zumpe R (1989) Bergung und Konservierung der Fundgegenstände aus organischen Materialien vom mesolithisch-neolithischen Moorfundplatz Friesack, Kr. Nauen. Veröffentl Museum Ur Frühgesch Potsdam 23:29–40

Appendix

Table 1. Chronology of wood preservative use

ca. 4000 B.C.	Old Testament: God tells Noah to use tar in building the Ark
ca. 2000 B.C.	Gilgamesh Epic: tar is poured over wood
ca. 484–424 B.C.	Herodotus: alum (aluminum potassium sulfate) used as a fire retardant. Describes extraction of oils, tars, and resins for the preservation of organic materials. Touches on the embalming of Egyptian mummies
356–323 B.C.	Alexander the Great: Decrees that pilings and other parts of bridges are to be treated against decay with olive oil
33–14 B.C.	Vitruvius Pollio: ten books on the art of building. Refers to the practice of preserving wood by charring or coating with residue from olive oil production
23/24 to 79 A.D.	Plinius Secundus: <i>Naturalis historia</i> in 37 volumes. Wood treated with cedar oil is reputed to be resistant to decay and insects. The wooden statue of Diana in Ephesus is impregnated with nard oil
Fourth century	Palladius: wood preservation with saltwater
1445	Frankenspiegel: timber for a church is boiled in brine
1452–1519	Leonardo da Vinci: backs of panel paintings and wood carvings are coated with mercury(II) chloride and arsenic(III) oxide
1469–1524	Vasco da Gama: has shipbuilding timber charred against shipworm
ca. 1500	The Franciscan monks of San Domingo control termites with mercury(II) chloride and arsenic(III) oxide
1666	<i>Journal des Savans</i> : compilation of many wood preservation methods
1705	W. Homberg (1652–1715): Report to the Academie des Sciences in Paris on the use of mercury (II) chloride in the South of France to protect wood floors from insects
1718	Hiarne awarded a patent by King Carl XII of Sweden for a wood balm based on copper or iron sulfate. It is the first commercially prepared wood preservative, available since 1720
1720	The <i>Royal William</i> is built in England with charred timber
1735	Zedler's <i>Universal Encyclopedia</i> : bark borers are controlled with pepper, laurel, and myrrh in wine; also with ox urine and vinegar
1756	Use of plant tars and extracts as wood preservatives in England and America
1767	De Boissieu and Bordenare: recommend copper sulfate for wood preservation
1770	Sir John Pringle: the first list of wood preservatives is published in England
1784	Royal Society of Arts: promise of a gold medal for the discovery of the cause and control of decay in buildings
ca. 1800	Pyrethrum is known as an insecticide
1812	Kyan: starts experiments with mercury(II) chloride as a wood preservative
1815	Thomas Wade: zinc chloride as wood preservative

1825	Faraday: discovery of hexachlorocyclohexane (HCH)
1832	Kyan: British patent 6.253 for vat treatment with mercury(II) chloride in aqueous solution. The beginning of modern wood preservation
1836	Franz Moll: patent for wood preservation with coal tar creosote, coining the term creosote
1838	John Bethell: pressure impregnation with "creosote oil"
1838	Boucherie: French patent for a sap replacement process with copper sulfate
1840	Anna Rosauer: Dalmatian insect powder; pyrethrum (<i>Chrysanthemum cinerariifolium</i>) as insecticide
1841	Erdmann: synthesis of pentachlorophenol (PCP)
1863	Great Britain: last major use of mercury(II) chloride; because of its toxicity it is replaced by other chemicals
1874	O. Zeidler: synthesis of DDT
1881	Conservation at the Belvedere in Vienna: use of copper sulfate for the back of a Gothic winged altar
1881	Pyrethrum is used in California against grasshoppers. Pyrethrum cultivation is introduced to Japan
1887	Thompson: French patent for impregnation of wood with fluor compounds
1888	Avenarius: patent introducing the designation "Carbolineum"
1901	Malenkovic: patent for the preservation of wood with fluor compounds
1912/1913	Chromium compounds as components of non-leachable wood preservatives
1915	First use of 1,4-dichlorobenzene against wood borers
1916/1918	Councillor Boile: the Kefermarkt altar in Austria is coated annually with petroleum and hexachloroethane
1920	Mono- and dichloronaphthalene are suggested as wood preservatives
1923	A patent for chloronaphthalenes under the designation "Xylamon" is applied for. The oily liquids are also often used for cultural property
1933	A British patent for boron compounds is applied for
1935	Hartfield (USA): research on the fungicidal effectiveness of chlorophenols
1936	Production of pentachlorophenol (PCP) in the USA, and its use in the wood industry
1939	P. Müller (Switzerland): discovery of the insecticidal effect of DDT
1945	Lindane (γ -HCH) and DDT used as insecticides in Great Britain
1947–1953	Lindane and PCP used as biocides in Germany
1948	Production of a synthetic pyrethroid in the USA
1959	Tributyltin oxide (TBTO) used as a fungicide in Great Britain
1976/1978	Testing of the effectiveness of synthetic pyrethroids against wood-destroying insects in Great Britain

Table 2. Chronology of the use of volatile and gaseous substances on wood

About 900 B.C.	Homer's Odyssey lists sulfur dioxide as a disinfectant
About 700 B.C.	Hesiodos: wood can be preserved by smoke from the stove
80 A.D.	Wood is treated with the smoke from the slaves' bath
ca. 1225–1287	Konrad von Megenbach: beech wood exposed to smoke does not deteriorate easily
1812	First attempt by Lukin at the Woolwich dockyard to treat wood with resinous vapors, but the apparatus exploded
1835	Moll: wood is treated with creosote vapors
1848	Lecour: wood is exposed to heated ammonium chloride and pyroligneous acid
After 1850	Patents, which recommend impregnation of wood with ozone or carbon dioxide
1880	Control of plant and stored products pests with prussic acid in the USA

ca. 1900	Wood infested with insects is treated in fumigation chests with carbon disulfide and tetrachloromethane
1915	Kemner: successful fumigation of anobiid larvae with prussic acid
1921	Control of Anobiidae in the royal castle in Kalmar, Sweden, with hydrogen cyanide
	Nagel: gaseous hydrogen cyanide does not kill anobiid larvae
1924	Rathgen warns against use of prussic acid because of its erratic efficacy and its toxicity
1928	Control of wood borers (<i>Hylotrupes bajulus</i>) in the Emmaus Church in Copenhagen with prussic acid
	The lethal effect of ethylene oxide on insect pests in wood becomes known
1929	Fumigation of the carved Gothic altar of the parish church in Kefermarkt, Austria, with the hydrogen cyanide preparation Zyklon B
1932	Le Goupil discovers the insecticidal effect of bromomethane (methyl bromide)
1936	Delicia process for fumigating stored cereals. Hydrogen phosphide is produced by hydrolysis of aluminum phosphide
Since 1950	Increased use of bromomethane against wood-destroying insects
1951	Fumigation of infected wood with ethylene oxide
1957	In the United States, Kenaga describes the insecticidal effect of sulfuryl fluoride, and Stewart uses it to control termites
1980	Use of carbon dioxide to control pests in stored products
1984	Fumigation of three Norwegian stave churches with hydrogen phosphide
1987	Control of wood-destroying insects with carbon dioxide by Paton and Creffield
1989	Gilberg controls insect pests in museum objects by displacing oxygen with nitrogen
1992	First fumigation of a German church infested with Anobiidae with sulfuryl fluoride

Table 3. Chronology of physical methods to control insect pests

1784	The physicist Bertolon develops a method to control wood borers in forests with electricity
1796	Wood which is being attacked by insects should be dried in an oven or by other application of heat
1848	Baudet: control of insect pests in wood by heating in an oven to 80–100 °C
ca. 1900	Rathgen: use of heat to control wood borers
1908	Haupt: control of wood borers by well-fired baking oven for several hours
Since 1930	Hot air is used in Denmark to control wood borers in attics
1947	Attempts by Parfentiev to kill anobiid larvae in wood by low temperatures
1957	Bletchly and Fisher: use of gamma radiation to kill wood-destroying insects
1959	Thomas and White use microwaves to sterilize wood with insect infestation
1961	According to Schmidt, X-rays do not destroy wood borer larvae inside wood
Since 1972	Irradiation of art objects infested with insects at the French nuclear research center in Grenoble
1978	Toskina: anobiid larvae in icons can be killed by prevailing winter temperatures in Russia
1979	Urban and collaborators: establishment of a conservation laboratory for radiation treatment of art objects at the Bohemian Central Museum in Roztoky near Prague
1987	Florian makes extensive studies of the application of low temperatures to insect-infested cultural property

Table 4. Overview of consolidation in art conservation

Eighteenth/nineteenth centuries	Consolidation by soaking in glue
1852–1855	Adalbert Stifter: use of table salt solution and copal varnish for treating the Kefermarkt altar in Austria. In his book <i>Nachsommer</i> , a model program for the restoration of carved Gothic altars is recommended for the first time
1898	Rathgen publishes a book on the conservation of finds from antiquity
Before 1900	Wooden objects are soaked in kettles with hot linseed oil
About 1900	Frequent use of hot glue with added fungicidal substances to stabilize wood
	Cellulose nitrate (zapon varnishes) and cellulose acetate are used as wood consolidants
1902	C. Gurlitt soaks deteriorated wood objects in hot wax and resin solutions
1924	Rathgen uses Chinese tung oil as well as paraffin, dammar resin and rosin for the consolidation of objects severely deteriorated by insects
About 1925	Treatment of deteriorated wooden objects with a mixture of linseed oil, amber varnish and camphor oil at the Saxony Institute for Conservation (Sächsisches Landesamt für Denkmalpflege)
1934	A Gothic winged altar is consolidated with shellac
1934–1940	Use of resin emulsions containing methyl cellulose, alkyl resin and rosin for the stabilization of wood
Since 1935	D. Rosen works on the development of the wax immersion method in the United States
About 1950	Frequent use of cellulose acetate. Poly(vinyl acetate) is used as an adhesive
1956	Consolidation of the high altar of the Gurk cathedral in Austria with 1500l shellac solution in alcohol
1956	Plenderleith introduces phenol-formaldehyde resins, poly(vinyl acetate), unsaturated polyester resins and polyacrylates for the consolidation of art objects
1958	Kenaga (USA) and Frejdin et al. (USSR): production of the first wood-polymer combinations by impregnating wood with monomers and polymerizing these by irradiation
Since about 1958	Use of epoxy resins to stabilize severely deteriorated wood
1970	Stabilization of a polychromed sculpture with poly(vinyl acetal) by Pluska
1972	First investigations of the impregnation of art objects with styrene/polyester and polymerization in situ by irradiation at the French nuclear research center in Grenoble
1978	Klapwijk describes the Dutch 'Beta-process' for the strengthening of beam ends with epoxy resins
1984	Schiessl: publication on the state of strengthening treatments in wood conservation.
	Schniewind and Kronkright investigate the effectiveness of several consolidants for deteriorated wood
	Unger et al. impregnate parts of the carriage of an old piece of large bore, heavy artillery with methyl methacrylate followed by a thermocatalytic polymerization in situ.
1989	Cuany et al. test various consolidants for their suitability to stabilize wood damaged by insects and decay fungi

Table 5. Chronology of stabilization methods for waterlogged archaeological wood

1858/1860	C.F. Herbst in Denmark treats waterlogged wood with alum $[\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$
Since 1890	G. Rosenberg: attempts to improve the alum method for the conservation of waterlogged wood
1903/1904	W. Powell applies for a patent for the stabilization of wood with sugar in both the United States and Germany
1921	A large steel container is built for the treatment of waterlogged wood finds from Hjortspring, Norway. A mixture of alum and glycerol is used
1924	F. Rathgen lists a number of methods for the conservation of waterlogged wood in his book
1937	A. J. Stamm points out that a variety of sugars would be suitable for wood conservation
1948	R. Cebertowicz treats the wood unearthed at Biskupin, Poland, by petrification with silica
1949/1956	B. Brorson Christensen: development of new methods of waterlogged wood conservation, such as freeze-drying in the presence of tert-butanol
Since 1950	W. Kramer of Switzerland develops the alcohol-ether-resin method, which comes into extensive use beginning in 1952
1950/1955	B. Centerwall and R. Morén: impregnation of waterlogged wood with poly(ethylene glycol) (PEG)
About 1956	A 3 m-long boat is freeze-dried in Groningen, Holland
1957/1958	H. Mueller-Beck and A. Haas: first use of melamine-formaldehyde resin (Arigal C) for wet-wood conservation
1961/1962	Barkman and collaborators: beginning of the conservation of the <i>Wasa</i> in Stockholm, using PEG
1967	R.A. Munnikendam treats waterlogged oak with methyl methacrylate (MMA) and gamma radiation
1970	Freeze-drying of swamp wood using PEG 400 by W.R. Ambrose
1970/1972	Italian researchers treat archaeological wet wood with sugar
1972	Stabilization of wet wood with styrene and polyester resins and gamma radiation in the project Nucléart at the nuclear research center in Grenoble
	Ů.V. Vichrov and collaborators obtain a USSR patent for conservation of archaeological finds with phenol alcohol (phenol-formaldehyde precondensate), the "Method of Minsk"
1975/1976	K. Borgin tries out the Thessaloniki process, where barium borate and barium silicate are precipitated inside the wood
1982	Start of the conservation of the <i>Mary Rose</i> . The hull is sprayed with PEG, and smaller parts are soaked in PEG and freeze-dried
Since 1985	Increasing interest in using sugar and sugar alcohols for wet wood
1986	Two-step PEG treatment for waterlogged wood of varying degrees of deterioration recommended by P. Hoffmann

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Conservation of Wood Artifacts

This handbook is the most comprehensive, up-to-date source of information on the history of wood conservation, on the structure and properties of wood, on organisms causing deterioration, on methods of diagnosis of wood condition, on materials and methods of wood preservation, on consolidation of deteriorated wood, and on wood adhesives. Although it provides many techniques of wood conservation in detail, it goes far beyond the scope of a "recipe book" by giving an overview of the use of particular materials and methods as they apply to dry as well as wet or waterlogged wood. Access to the enormous wealth of information is facilitated by separate indexes for trade names, pests, and conservation materials. The latter, together with their methods of application, were gathered from the literature and organized chronologically. For liquid preservatives, fumigants, and consolidants, these listings are preceded by important data on each of the materials.

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