Some internal changes in ammonia treated woody materials

Book review

ZÜRICH 1969 / 2

Editor: A. Frey-Wyssling, ETH Zürich
This is the swan song of your Secretary-Treasurer as an editor of this Bulletin.

During my office of 12 years activity the publication of the "Multilingual glossary of terms used in wood anatomy" with 7 versions has become possible in 1964. This was an old postulate of our Association and I thank all the colleagues who co-operated for this goal. The Bulletin could also be developed to a semi-annual publication thanks to the endeavours of Dr. Rosehart. However, due to our weak financial position, it was not yet possible to convert it into a printed periodical.

As to the development of wood science in our field it has extended in the direction of woody monocotyledons. It has also taken profit on a broad scale of ultrastructure research, which has yielded considerable results along three different avenues; they may be briefly summarized as follows:

a) Cell wall ontogeny: The technological view that the lignified cell wall is a static cellulosic structure incrusted by lignin, hemicellulose and pectin must be replaced by the knowledge that not only the wood sample as a whole, but also every individual wall has to be considered as a dynamically grown structure. The electron microscope has disclosed that originally a wall of amorphous carbohydrates is formed by golgi activity. Only later cellulose polymerizes and crystallizes as elementary fibrils within this matrix, in a way which is still unsatisfactorily understood. Then, in a third step phenylpropionic glucosides are excreted into this system where the phenols are enzymatically set free and polymerize randomly into lignin.

b) Interpretation of the ultrastructure of the lignified wall: Hitherto the ultrastructure of the lignified cell wall has been compared with reinforced concrete in which system the fibrillar cellulose would account for its tensile and the incrusting material for its compressive strength. However, the matrix mentioned proved to be a hydrogel which displays some plastic properties even in its dehydrated state. Therefore, in the model of the ultrastructure the elastic concrete must be replaced by the slightly plastic matrix. This new concept of the reinforced matrix allows of explaining such important technological features as shrinkage or creep and the deplorable fact that there is no ideally elastic wood.
c) **Morphogenesis of the wall textures:** There has always been a tendency to explaining the arrangement of the cellulosic elementary fibrils i.e. the texture of the wall in expanding cells, in bordered pits, or in the cells of compression and tension wood by exogenous stresses; but the electron microscope shows how these textures are realised by the differentiating meristematic cell long before any stress is active. So it has been proven that morphogenesis generates textures which will serve their purpose in the future, before the stresses under discussion occur. The former mechanic explanations were based on a confusion of cause and effect.

The considerations under a), b), and c) indicate that wood anatomy in addition to its classical field of wood histology, has expanded its activities in the direction of **ultrastructural wood cytology.**

A. Frey-Wyssling
Secretary-Treasurer

Unfortunately, a contribution from Prof. Dr. W. Bisseg on bamboo anatomy, promised for fall 1969, could not be completed until now due to trouble caused by the students' politics at the University of Hamburg. The manuscript will be sent to the new Secretary-Treasurer, Prof. Dr. W. A. Goldé, Syracuse, N.Y., who eventually will include it in a future number of the Bulletin.

---

**Some internal changes in ammonia treated woody materials**

by Mikaly Bariska

Institut für Mikrotechnologische Holzforschung, ETH Zürich

Since A.J. Stamm (1955) and C. Schüerch (1964) proved that ammonia is a good wood plasticizing agent and that the ammonia technique could be applied for practical wood bending purposes, interest in this topic has been developing. Several publications on this subject have appeared (C. Schüerch, et al., 1966, R.R. Pennock 1966, B.W. Davidson 1968, F.J. Pollis 1969) trying to explain the mechanism and consequences of ammonia plasticisation of wood. The present article attempts to give some further information about microscopic observations and about physico-chemical changes in various species, Bassia cellulose, aspen hemicellulose and lignin, respectively.

Water and ammonia have many physical properties in common. This gives rise to assume that the mechanism of wood plasticization by both of these materials follows similar laws. Yet, it may be only partly true. The well known softening properties of steam appear only above those temperatures at which the molecular structure of wood is obviously loosened, whereas ammonia possesses similar thermodynamical activity and thus has a similar plasticizing effect already at room temperatures. That ammonia has a more far-reaching influence on wood than water has been shown by A.J. Barry, F.G. Davidson and A.J. King (1956). They found that the crystalline pattern of native cellulose changed when soaked in ammonia. Schüerch, et al. stated later (1966) that ammonia was a weak solvent of all the main chemical components of wood, that is, of celluloses, hemicelluloses and lignin. Keeping in mind that the distribution of these chemical components within the cell wall is not homogenous, the selective adsorption of ammonia over the cell wall can be tested on the basis of microchemical reactions.

Ammonia treated thin sections of sugar maple (**Acer saccharum** Marsh.) were stained with a specific ammonia indicating agent - methyl purpur - then studied under the light microscope. Proportionality between colour intensity and ammonia concentration in the tissue can be assumed. Figures 1 and 2 present such stained transversal wood sections prior to and
after ammonium impregnation. The specimen were subjected to gaseous anhydrous ammonia. As clearly visible in the pictures the middle lamellae and walls of the parenchymatic cells showed a darker coloration, e.g. sites of the cell wall which are strongly lignified. The cell walls of fibers remained, however, lighter. It appears that ammonia penetrates the fibrous cell walls containing essentially cellulose to a lesser extent. Sumer wood also showed darker color than spruce wood. Cell walls and middle lamellae of treated material seem to be superwollen in water. The sum of cross sectional cell wall area increased some 20% after exposure to ammonia. Highly swollen middle lamella can be seen at the corners of some cells.

Further observation indicated that other species like ash (Fraxinus americana L.) and Yellow birch (Betula alleghaniensis Britton) react to ammonia saturation in a similar manner. Thus, it can be concluded that the chemical composition of various species would partly account for differences in plasticization.

By means of water vapour sorption measurements, changes in molecular level and in submicroscopic structure of specimen upon treatment can be detected. Generally, it is assumed that differences in sorption properties at low vapour pressures (up to ca. 0.2 p/p₀) indicate alteration in the internal active surface. Deviations in sorption capacity above 0.6 p/p₀ are due to altered capillary condensation within the affected pore structure.

![Figure 1: Methyl-purpur stained micro-
section of sugar maple prior to ammonium treatment.](image)

![Figure 2: Methyl-purpur stained micro-
section of sugar maple after ammonium treatment.](image)

![Figure 3: Moisture uptake of maple cell-
ulose at various rel.humidities before and after ammonium impregnation.](image)

![Figure 4: Moisture uptake of maple hemi-
cellulose at various rel.humidities before and after ammonium impregnation.](image)

![Figure 5: Moisture uptake of lignin at
various rel.humidities before and after ammonium impregnation.](image)

![Figure 6: Moisture uptake of Yellow
birch and of the chemical components
summarized at various rel. humidities
before and after ammonium impregnation.](image)
The water vapour adsorption behaviour of Ramie cellulose, aspen hemicellulose and lignin mixture was studied before and after ammonia impregnation. The results are plotted in figures 3, 4, and 5. As the curves in figure 3 exhibit, Ramie cellulose displays upon treatment what seems to be a somewhat opened molecular structure. Its water capacity has been enhanced in the low vapour pressure range. This loosening reduces the micropore volume in the fibers since a smaller amount of water condensed in the capillaries. Hemicelluloses behaved to the contrary after exposure to ammonia. At low vapour pressure water adsorption was slightly hindered as shown in figure 4. Ammonia probably causes some sorption sites of hemicellulose to mutually block. Since hemi- celluloses dissolve fairly well in water, the mutually saturated sorption sites must have broken down at a higher rel. humidity. In the vapour pressure range of capillary condensation, ammonia treated hemicelluloses took up more water than the control specimen, thus indicating a more loosened submicroscopic structure. From figure 5 it is evident that the most pronounced changes took place in lignin. From the beginning, ammonia soaked specimen presented increased water sorption capacity that grew with higher vapour pressures. These measurements can not be compared with the measurements for green wood without reservation. It is very likely that the chemical separating and purifying procedures effect the natural sorption behaviour of Ramie cellulose, aspen hemicellulose and lignin. Despite this fact, it is supposed only a gradual change in their physico-chemical features. If the sorption capacities of these materials are added up in a ratio, cellulose : hemicellulose : lignin = 47 : 37 : 16 = 100, which is a rough approximation of the contribution of these three components to the wood sorption capacity (S.H.CHristensen, K.E.Kelsey, 1958), such a comparison is possible with reservation. Figure 6 shows the water uptake of yellow birch and of the mentioned materials at various rel. humidities. Similarity between the isotherms of the two types of specimen is obvious. The effect of ammonia treatment seems to follow the same pattern as well. The influence of ammonia on the chemical components appears to show up in the moisture sorption properties of whole wood. The following conclusions can be made thereof:

Ammonia saturation causes a substantial change in the hemicelluloses. They tend to gain in solubility, which may effect their distribution within the cell wall. On the other hand, impregnation makes cellulose more inaccessible to water. Since its active surface remains nearly the same but the volume of capillary holes decreases, a slight collapse of the porous structure in cellulose must occur.

The fact that repeated ammonia treatment makes the cellular structure of woody tissue collapse remarkably supports the idea of diminishing pore volume in cellulose due to ammonia penetration. Figures 7 and 8 give a picture of the extent of cell collapse in ash treated about 15 times with ammonia.

Such deformation of tissue occurs only in highly plasticized wood. The spontaneous tendency towards distortion leads to the presumption that the stiffness of wood, for which lignin is mainly responsible, is reduced temporarily. The findings underline the important role of lignin and cellulose. But, to all appearances, their interplay is shifted in the process of plasticization. Lignin seems to be affected first. For instance, it already interacts strongly with low concentrations of ammonia, which was demonstrated with microchemical reactions (M.Bariška, 1969). Cellulose, however, underwent significant changes at rather higher ammonia concentrations. N.W.Davidson (1968) found that the crystalline pattern of nature cellulose was not altered below a threshold pressure value of ammonia vapour of 0.4 p/p.ø.

Presumably, lignin is softened first during wood plasticization with gaseous anhydrous ammonia, then gradually cellulose.
INTERNATIONAL ASSOCIATION OF WOOD ANATOMISTS

Domestic Affairs

Supplement to the Bulletin 1969/2

1. Membership

a) New members: We have pleasure in announcing the nomination of three new members:

Dr. W. C. DICKINSON
Dept. of Botany
University of North Carolina
Chapel Hill, N.C. / USA

Dr. J. B. STAHL
ETH-Inst.f.Konkovertechnologische
Holzforschung
Universitätstr. 2
8006 Zürich/Switzerland

b) Changes of address:

In the last Domestic Sheet (1969/1) a mistake occurred in the changes of address: Instead of "Dr. E. W. J. Phillips, Glebe Cottage, Horsenden, Aylesbury" it should read:

Mr. B. J. Rendle
Glebe Cottage
Horsenden
Aylesbury (Bucks.) G.B.

Dr. E. W. J. Phillips' address is: Pentewan, Shootacre Lane,
Princes Risborough (Bucks.) G.B.

Mrs. Mary Wilkie Brinkerhoff
5922 Nalbar Lane
Madison, Wisc. 53711 / USA

"World Timbers" Volume 3: Europe and Africa
Compiled and edited by B. J. RENDLE; Ernest Benn, London, 1969
pp 191; price £1.05 s (15/6 d)

In this work, the first of three planned volumes, 79 timber species or species groups are described and backed by colour plates. The illustrations and technical informations are a revised part of the series 'World Wood Specimens'.

World Timbers is the wellknown journal WOOD, later published in book form, which are now out of print.

The aim of the newly arranged issue is as before to explain the main items of distribution, supplies, general description, technical properties and uses.

The content is comparable with the Handbooks of the Forest Products Research Institute, Princes Risborough. The colour plates are in general of high quality and only the medium textured species are of lesser representation.

World Timbers can recommended primarily to architects, timber traders and the wood manufacturing industries as a valuable and reliable information source.

H. Gottwald, Reinbek

BOOK REVIEW

"World Timbers" Volume 3: Europe and Africa
Compiled and edited by B. J. RENDLE; Ernest Benn, London, 1969
pp 191; price £1.05 s (15/6 d)

The following two members have expressed their wish to resign from our association:

Dr. D. A. Fraser
Head of Tree Physiology Section
Dept. of Forestry, Petawawa
Forest Experiment Station
Chalk River (Ontario) Canada

Mr. R. H. B. Boulton
Rentokil Ltd. Ltd.

Dr. G. R. Metcalfe, Keeper
Jodrell Laboratory
Royal Botanic Gardens
Kew, Richmond on Thames, G.B.
2. Financial

a) Statement of receipt and expenditure

<table>
<thead>
<tr>
<th>Receipt SFr.</th>
<th>1968</th>
<th>1969</th>
<th>Expenditure SFr.</th>
<th>1968</th>
<th>1969</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contributions</td>
<td>2113.68</td>
<td>2135.53</td>
<td>Printing Bull.</td>
<td>912.--</td>
<td>1906.--</td>
</tr>
<tr>
<td>Sale Bull./Glossary</td>
<td>1326.50</td>
<td>319.50</td>
<td>Office/Stat.</td>
<td>143.15</td>
<td>989.20*</td>
</tr>
<tr>
<td>Subscriptions</td>
<td>369.48</td>
<td>293.47</td>
<td>Postage</td>
<td>283.10</td>
<td>402.55</td>
</tr>
<tr>
<td>Bank Interest</td>
<td>87.45</td>
<td>96.--</td>
<td>Profit</td>
<td>2558.86</td>
<td>-</td>
</tr>
<tr>
<td>Reverse</td>
<td>-</td>
<td>453.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3897.11</td>
<td>3297.75</td>
</tr>
</tbody>
</table>

*Transfer of office papers to USA

b) Balance

| Balance brought forward in SFr. | 7'535.33 |
| Reverse 1969 | 453.25 |
| Balance 1969 | 7'082.08 ** |

** Swiss Bank Corporation Deposit Book No.4151 SFr. 1'642.40
Swiss Bank Corporation Current Account SFr. 4'825.--
Post Cheque Account SFr. 317.71
Balance in Hand SFr. 296.97
3. XI. International Botanical Congress, Seattle 1969, Campus of University of Washington

Scientific meeting, August 26, 1969, 2.00 p.m.
Health Sciences Auditorium

Programme:

Vascularization in the stem of arborescent monocotyledons
by M.H. Zimmermann and P.B. Tomlinson (Cabot Foundation, Harvard Forest, Petersham, Mass. USA)

Anatomy of insular woods
by S. Carlquist (Claremont Graduate School and Rancho Santa Ana Botanic Garden, Claremont, Calif. USA)

Recent studies in anatomical terminology
C.R. Metcalfe and D. Cutler (Royal Botanic Gardens, Kew, Richmond, Surrey, G.B.)

Business meeting, August 27, 1969, 4.30 p.m.
Bagley Building

Attendance:
4 Council members (Frey-Wyssling, Côté, Stern, Wardrop)
18 Members
3 Observers (aspirant members)
25

Welcome:
The chairman welcomes the members after five years intermission (last session 1964 in Edinburgh) and thanks Dr. Stern for the organization of our scientific session "Wood Anatomy" on August 26, 2.00 p.m.

Agenda:
1. Report of the retiring Secretary Treasurer
2. Council and Membership
3. Finances
4. Election of new Secretary Treasurer
5. Remarks
6. Miscellaneous
1. Report

see Editorial of Bulletin 1969/2

2. Council

The council for 1969-1974 has been re-elected by the members through circulating letters. According to four demissions four new members have been chosen: Prof. Dr. H. H. Bossard (Switzerland) to replace Prof. Dr. A. Frey-Wyssling (Switzerland), Dr. J. D. Brazier (G.B.) to replace Dr. E. J. Phillips (G.B.), Prof. Dr. W. A. Côté (USA) to replace Prof. J. Collardet (France) and Dr. E. Perem (Canada) to replace Dr. J. D. Hale (Canada).

Membership:
- Europe: 61
- Asia: 19
- Africa: 2
- Americas: 65
- Australia: 10

Total: 157

3. Finances

The financial report for 1968 is found in the domestic sheet as a supplement to Bulletin 1969/1. Since those statements are made in Swiss francs, a summary statement in US$ is produced on the blackboard. The yearly income of roughly $800.- is mostly used for the Bulletin (reproduction and expedition). Office and stationary consumed about $30.-. A profit of around $200.- will result. A balance of over $1000.- will be transferred to the new Secretary-Treasurer at the end of this year. The annual contribution of SFr. 15.- = $3.50 can be maintained.

4. Election

According to Article VI.c. of our constitution the council has appointed Prof. Dr. W. A. Côté, State College of Forestry, Syracuse, N.Y. as the new Secretary-Treasurer for the period of 1969-1974. This appointment is approved by acclamation.

The chair passes from the retiring Secretary-Treasurer Prof. Frey-Wyssling to Prof. Côté.

5. Program of Secretary-Treasurer Côté

Formerly the members of IAWA received "Tropical Woods" and a domestic sheet called "News letters". The Bulletin had to take over the function of Tropical Woods, when this periodical disappeared. Its basis with a circulation of less than 200 is too small for publishing important original work. Therefore, authors have been asked to
present extensive summaries of their research work in the Bulletin, of which one or two appeared in each issue. Members are invited to formulate their opinion how the scope of the Bulletin can be improved (many shorter résumés and/or abstracts of current literature, extension of the Bulletin with a raise of the annual contribution etc.). A questionnaire will be sent to all members.

The base of the association should be broadened by including new activities into the list of article III of our constitution, not so much in the technological, but first of all in the cytological and ultrastructural direction. According to the proposition of Dr. Metcalfe, the characteristics of the primary tissues can be just as, or even more important for the identification of a tree than those of the secondary xylem. The former decision of the council to restrict our activity to the wood anatomy alone must be reconsidered.

6. Miscellaneous

Dr. Stern draws the attention to the fact that several important wood sample collections all over the world and especially that of Yale are in danger to be lost (some are badly neglected, others on sale). The assembly votes that the council should take action towards the salvation of this precious reference material. A motion concerning this action is formulated.

In addition Dr. Stern states that the documents of Dr. Record concerning the foundation of the IAWA still are in Yale, where they will certainly disappear some day. The assembly wishes that these historical documents ought to be brought over to the new seat of the IAWA in Syracuse.

Drs. Meier and Stern propose that the retiring Secretary-Treasurer and Dr. Metcalfe should be elected as honorary members. The assembly decides so by acclamation.

End of the meeting 6.00 p.m.