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CRYSTALLINITY AND ULTRASTRUCTURE OF AMMONIATED WOOD[1]

PART 1. X-RAY CRYSTALLINITY

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ABSTRACT

Crystallite width and degree of crystallinity were determined on loblolly pine wood before and after treatment with gaseous anhydrous ammonia at room temperature. Crystallinity increased in both normal and compression wood, but no detectable change in crystallite width resulted from ammoniation. The increase in crystallinity was probably apparent and due to a cell-wall consolidation—a shrinkage of microvoid space and/or amorphous material between crystallites. However, other factors that might contribute to an actual increase in crystallinity are discussed.

INTRODUCTION

The molding or bending of solid wood to form has been shown in recent years to be most satisfactorily accomplished (at least on samples of limited size) through plasticization of the stock with anhydrous ammonia (NH_3). After the wood has been subjected to either a liquid or vapor-phase treatment, a variety of shapes is attainable, the permanence of which is a substantial improvement over that attained with steam (Davidson and Baumgardt 1970; Schuerch 1964; Davidson 1968). This is apparently due to a physical rearrangement of wood structure at the molecular level.

Numerous investigations have been directed at describing both chemical and physical properties of ammoniated wood, and these studies will undoubtedly prove invaluable for predicting the behavior of such material in process application. More interestingly, however, data from these investigations have led to the careful consideration and appraisal of the plasticization mechanism itself and its relation to wood and fiber structure. It is a fair judgment to say that only after such knowledge has been gained can the nature of the wood ammoniation process and perhaps its extension to treatment of other product forms, such as pulp, paper, chips, or lumber, be fully understood or rationally considered.

Wood-ammonia interaction

It is relatively well established that liquid or gaseous ammonia interacts with essentially all major wood constituents—cellulose, hemicelluloses, and lignin—and a brief review of this information is now presented to provide an overall picture of the ammoniation process.

Cellulose. Normal wood substance is composed of approximately 42 ± 2% of cel-

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lulose polymer, the latter a molecular chain incorporating about 10,000 (average) anhydroglucose units (Timell 1965). A certain fraction (or segments) of these molecular chains pack together to form ordered regions (crystallites), giving wood its semicrystalline nature, but the exact morphology or spatial relationship between the ordered and unordered cellulose is still unclear (Fengel 1970; Heyn 1969; Mühlethaler 1967). In any event, ammonia has the capacity to swell both the ordered or crystalline cellulose as well as the unordered polymer. This is probably its most valuable asset, together with its ability to soften wood lignin, contributing to its use as a plasticizing agent.

Water is also capable of plasticizing wood or cellulose but to a lesser extent and only through swelling of the material in the unordered or paracrystalline regions. Ammonia has a much stronger tendency for hydrogen bonding than does water (Stamm 1964), so strong that it is able to separate even intra-crystallite cellulose and form O-H-N bridges between the closely packed chains. This weakens the chain cross-links of adjacent polar groups and effectively acts as a molecular lubricant (Schuerch 1964). If a piece of wood so plasticized is then stretched, compressed, or bent, polymer chain segments probably undergo considerable movement with respect to one another. Removal of the ammonia permits reformation of molecular bonds between the cellulose chains at the same initial sites or at different sites if the molecules have undergone translation. X-ray diffraction studies have shown that the cellulose crystal structure is maintained after ammoniation but is in the ammonia cellulose or cellulose III lattice. This crystal form is revertible to original cellulose I (at least partially) by exposure to water vapor, but even saturation of the treated wood with water and redrying cannot greatly reduce physical changes in the wood caused by ammoniation and stressing (Davidson and Baumgardt 1970).

Cellulose III can also be formed by treatment of cellulose I with anhydrous ethylamine, and it appears that a greater proportion of research has been concerned with this treatment than with one utilizing ammonia. In any case, it has been suggested that cellulose III is a "disordered" form of cellulose II (Howsmon and Sisson 1954), and in terms of crystallinity, less so than type I (Segal, Loeb, and Creely 1954; Segal, Nelson, and Conrad 1953; Venkateswaran and Rieman 1965; Venkateswaran and Van den Akker 1965). It is also suggested that cellulose III may possess a crystallite of smaller average width (Schuerch 1964).

Most of the aforementioned experiments related to cellulose III have been performed on isolated or cotton cellulose, not on wood, and have employed a variety of X-ray diagram interpretations. There has been some conjecture alluding to a more X-ray amorphous wood following ammoniation but no concrete evidence. Since X-ray crystallinity of wood is a function of the amount of crystalline material per unit volume of wood substance, it seems that other wood constituents need be considered here and especially the ultrastructural changes in the cell wall that might ensue as a result of ammonia treatment. Substances such as hemicellulose and lignin do not contribute directly to the cellulose X-ray diagram; however, any amorphous scatter arising from these materials is incorporated into the total X-ray picture and therefore used in the calculation of sample crystallinity.

Hemicelluloses. During ammoniation, hemicelluloses exhibit solute characteristics similar to those of low molecular weight celluloses (Schuerch 1964). Reactions with ammonia can yield amines from some reducing sugars, amides from acetylated polysaccharides, and produce ammonium salts from free carboxylic acid groups or ester groups (Wang, Bolker, and Purves 1964). Reorientation of partially solubilized hemicellulose within the cell wall may be possible, but diffusion out of the wall into any liquid ammonia should be slight (Schuerch 1964).

Lignin. Recent experiments with isolated kraft lignin show that it exhibits limited swelling, discoloration, and tackiness in ammonia (Schuerch 1964). Molecules are probably separated enough to cause softening but not enough for complete solvation of the lignin. At room temperature, about 1% of maple wood lignin has been extracted with liquid ammonia. Nine percent of the Klason lignin from spruce meal has been solubilized at 100 C and 24–30% from beech and maple at the same temperature (Yan and Purves 1956a, b).

Thus, it is seen that ammonia has a sizeable effect on all wood constituents, not just the cellulose. Crystallinity of ammoniated cellulose has already been investigated to some extent, but since the crystalline state of ammoniated wood seems to be unclarified at the present time, this investigation was directed toward providing some concrete evidence in this area.

EXPERIMENTAL

Material

Because of structural simplicity in comparison to a hardwood, a softwood species, loblolly pine (*Pinus taeda* L.), was selected as experimental material. Most researchers thus far working with ammoniated wood have employed diffuse porous hardwoods, and the present data could be said not to apply specifically to previous research. However, since the present study was concerned primarily with intra cell-wall organization, those wood parameters dependent upon such structure should still be considered interrelated by type if not degree of effect.

For a more realistic and meaningful study, both normal and reaction wood were considered. A cross-sectional disk 4 inches in thickness was cut from an upright pine and from one that was leaning about 20°. These disks were from the 5-ft and 2-ft levels, respectively. Normal earlywood and latewood samples were restricted to one quarter of their disk and to the 23rd annual ring. Compression wood came from latewood of the 22nd ring, all samples from a relatively small area of the reaction wood zone. All material used for X-ray diffraction or electron microscopy were exhaustively extracted with 2 : 1 benzene-ethanol, ethanol, and water.

The ammoniation was a vapor-phase treatment carried out at 25 C and 145 psi (Davidson and Baumgardt 1970). Samples were suspended during treatment so as to avoid soaking in any condensed ammonia. The wood was oven-dry before treatment, which lasted for 72 hr. Specimens were then air-dried of excess ammonia and again oven-dried (8 hr at 102 ± 3 C).

X-ray diffraction

For X-ray work, it was decided to use longitudinal microtome sections of an appropriate thickness that would yield an acceptable fiber diagram in a reasonable exposure time. Five radial (*R*) and tangential (*T*) sections of earlywood (*EW*), latewood (*LW*), and compression wood (*CW*) were cut as closely matched as possible from within their respective zones. Dry section thicknesses of 500 μm for *EW* and 300 μm for *LW* (and *CW*) produced an acceptable X-ray pattern within 25–60 min. All sections were dried and subsequently handled between glass slides clipped with a clothespin. They were X-rayed dry, treated, redried, and re-X-rayed or stored over P_2O_5.

Sections were reduced to about 4 × 7 mm and mounted by means of easily removable transparent tape (around the edges) to the face of a 25-mil (0.635 mm) collimator for the X-ray beam. Kodak Medical No Screen X-ray film was placed in a flat-plate camera 5 cm from the specimen, both camera and film being encased in a Warhus vacuum-camera apparatus. Copper radiation ($\lambda = 1.542$ A) was isolated by filtering through a 0.00075-inch nickel foil before striking the sample. Tube controls were set at 35 kv and 20 ma.

Fiber diagrams were scanned equatorially with a recording microdensitometer. Crystallite width and degree of crystallinity were calculated from the recorded diffractograms. The angular spread of the (002)

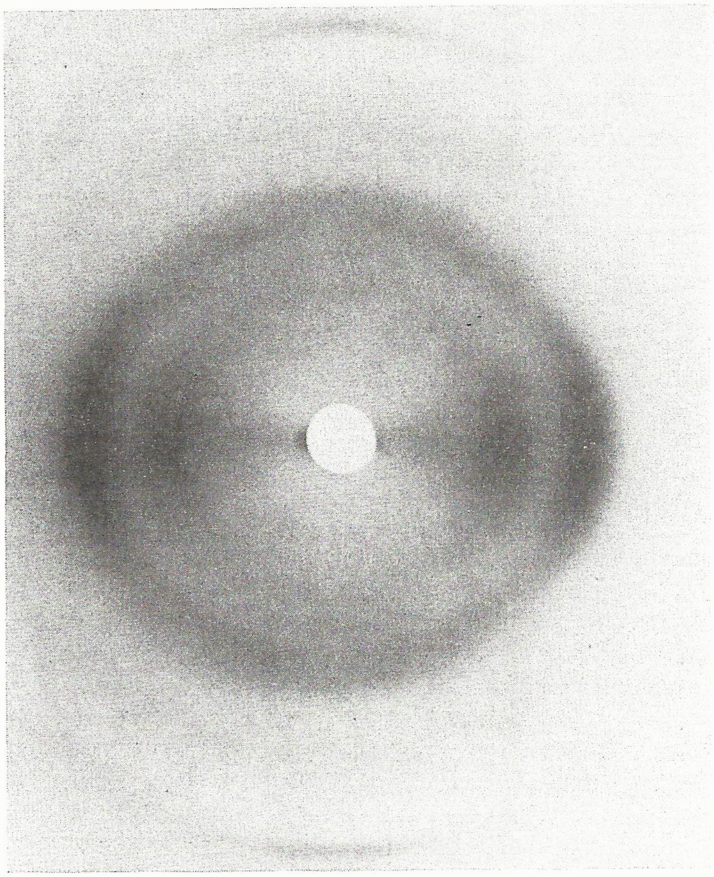

FIG. 1. X-ray fiber diagram of untreated loblolly pine latewood, tangential section. Cellulose I pattern.

peak, *B*, at one-half maximum intensity was substituted into the Scherrer formula, $t = 0.9\ \lambda/B \cos \theta$, for crystallite width in Angstroms (see Parham 1970). Degree of crystallinity was determined by the planimetric technique outlined by Jayme and Knolle (1964), Ellefsen, Kringstad, and Tonnesen (1964), Ellefsen, Lund, and Tonnesen (1957). This method of interpreting the diffractogram has been shown to provide a better assessment of crystallinity than that based only on peak heights (Jayme and Knolle 1964).

It is well known that the X-ray technique of estimating crystallinity is only a relative one and not absolute unless carefully calibrated with standard samples (Hermans and Weidinger 1948). However, it is a nondestructive method by which the exact same sample and sample area can be measured before and after a particular treatment. And, since the present study was concerned mainly with any changes in crystallinity produced by ammoniation, absoluteness of the findings was considered secondary.

RESULTS AND DISCUSSION

X-ray fiber diagrams

Typical fiber diagrams of untreated and ammonia-treated loblolly pine wood are seen in Figs. 1 and 2, respectively. All untreated diagrams showed the usual and somewhat diffuse X-ray pattern characteristic of wood. This type of pattern is indicative of a relatively low degree of crys-

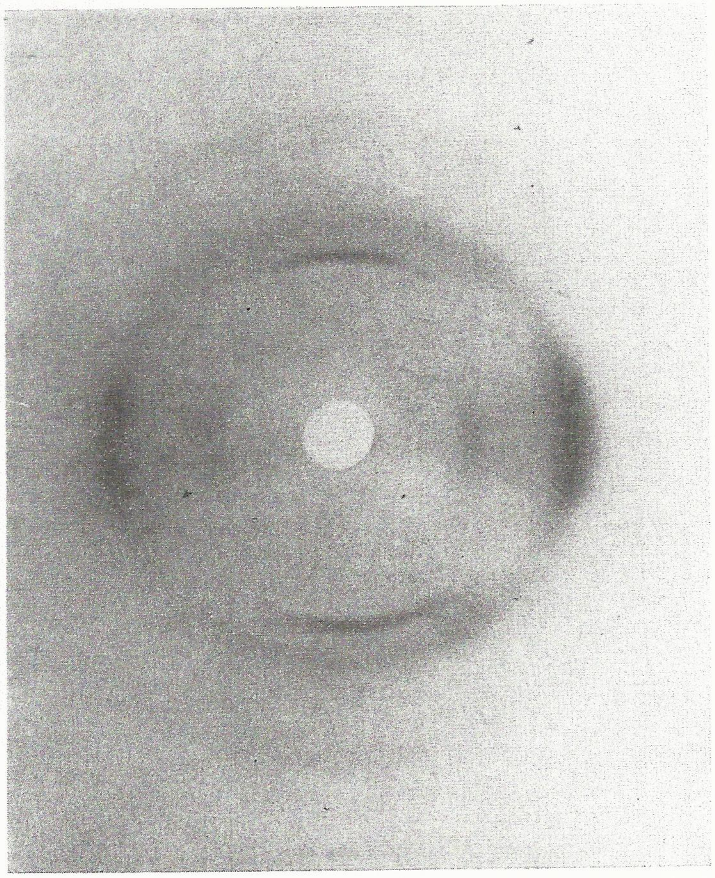

FIG. 2. X-ray fiber diagram of ammoniated loblolly pine latewood, same tangential section as in Fig. 1. Cellulose III pattern.

tallinity in contrast to sharper patterns produced by cotton, ramie, or bleached wood pulp (Howsmon and Sisson 1954; Parks 1959).

No interplanar spacings were calculated to determine if the ammoniated wood contained fully developed cellulose III. Nevertheless, the X-ray patterns (representing 72 hr of treatment) seemed to imply a complete lattice changeover.

It was noted that fiber diagrams of all ammoniated wood required considerably less exposure time and were of sharper contrast than those of untreated samples (Parham 1970). Qualitatively, this effect may be interpreted as an increase in the degree of internal order of the sample (Parks 1959).

Crystallite width

Numerous investigations have been undertaken in recent years in efforts to establish dimensions for the smallest morphological unit of cellulose structure in the wood cell wall. Resulting X-ray and electron microscopic evidence suggest this unit to be approximately 30–35 A in diameter, composed of about 40 cellulose chains, and of uncertain length (Fengel 1970; Heyn 1955, 1969; McGovern 1968; Mühlethaler 1967). The width of this "elementary" or "proto" fibril has been suggested to be quite variable between species (Sullivan 1968) and possibly between earlywood and latewood (McGovern 1968). Recent models for the elementary fibril (Fengel 1970; Mühlethaler

TABLE 1. *Crystallite width of untreated and ammonia-treated wood of loblolly pine*

Sample	Untreated width (A)	NH$_3$-treated width (A)
EW-T	27.56[1] ± 0.56[2]	28.29 ± 1.74
R	27.53 ± 0.86	27.22 ± 1.84
LW-T	28.01 ± 0.83	28.81 ± 0.83
R	28.24 ± 0.64	27.63 ± 0.92
CW-T	27.33 ± 1.02	25.51 ± 1.03
R	27.19 ± 0.52	27.35 ± 2.27
T	27.63 ± 0.82	27.54 ± 1.90
R	27.66 ± 0.78	27.40 ± 1.66
All samples	27.64 ± 0.79	27.47 ± 1.75

[1] Average of 5 matched samples.
[2] Standard deviation.

TABLE 2. *X-ray crystallinity of untreated and ammonia-treated wood of loblolly pine*

Sample	Untreated crystallinity (%)	NH$_3$-treated crystallinity (%)
EW-T	37.49[1] ± 1.94[2]	38.02 ± 3.12
R	37.76 ± 2.36	38.78 ± 0.14
LW-T	43.41 ± 1.67	48.23 ± 2.25
R	40.22 ± 0.82	45.48 ± 1.07
CW-T	26.79 ± 1.07	40.61 ± 0.72
R	30.63 ± 1.80	40.09 ± 3.53
EW	37.63 ± 2.04	38.40 ± 2.13
LW	41.81 ± 2.09	46.85 ± 2.21
CW	28.71 ± 2.45	40.09 ± 2.46

[1] Average of 5 matched samples.
[2] Standard deviation.

1967) picture it as semicrystalline, the crystalline regions extending across the entire width of the fibril, and it would appear that this is the "crystallite" width commonly extracted from X-ray diffraction data. Such an analogy is adopted in the present report.

Crystallite widths of 30 wood samples, including different tissue types and fiber faces, implied that (1) the untreated width is a more or less constant dimension (at least in the loblolly pine material examined), and (2) that ammoniation exerts no significant effect on crystallite width.

Untreated material averaged 27.64 A in crystallite width with a total sample variation of 3.10 A (Table 1). The very consistent measurements from *EW*, *LW*, and *CW* suggest that there is no actual crystallite width difference in *EW* and *LW* of the same ring, and that even reaction wood from a different tree can be composed of similar units. This situation also appears to be the case for radial and tangential crystallites. Statistical comparisons of untreated *R* and *T* sample means, as well as other pooled combinations, showed a difference only in the *LW-CW-R* specimens (Parham 1970). This difference represented the extreme sample range but again was only 3.10 A.

A paired-observation analysis (with sample size ≧ 10) showed no significant change in crystallite width as a result of ammoniation. Other treatments of wood or cellulose, such as mechanical beating (Alexander, Marton, and McGovern 1968), ball-milling the fibers (Caulfield and Steffes 1969), or alkaline hydrolysis (Meller 1961) have induced changes in the average crystallite width. Apparently just the absorption and desorption of ammonia is not sufficient to cause an increase or decrease in the degree of aggregation of cellulose chains in the lateral direction.

Degree of crystallinity

Untreated wood. Wood crystallinity of mature loblolly pine examined in the present study decreased in the order *LW* > *EW* > *CW* (Table 2). A previous study on another conifer, Douglas-fir, revealed the same relationship utilizing compressed pellets of macerated tracheids (Lee 1961). The latter crystallinity values were considerably greater than those determined in the present investigation, but one must realize that in macerated tissue the amorphous middle lamella is omitted from an X-ray diagram. It is also conceivable that maceration (acetic acid-hydrogen peroxide) may leach out noncrystalline material from the cell wall.

Normal wood and compression wood crystallinity averaged 39.72% and 28.71%, respectively, compared to Lee's values (1961) of 54.3% and 46.0%. Now consider that the alpha-cellulose content of mature loblolly pine ranges from about 47% to 56% (Gladstone 1970; McMillin 1968; Van Buijtenen, Zobel, and Joranson 1961). If the alpha-cellulose were as much as 70% crystalline (which would be high, since cotton is about $72 \pm 2\%$ [Hermans and Weidinger 1948]), then there would be a maximum of 0.70×56.0 or 39.2% of crystalline cellulose per unit volume of wood. This would be considering all lignin and hemicellulose to be amorphous. Mark (1967) found X-ray crystallinity of eastern red cedar to average 41.39%. Thus, the mean value of 39.72% calculated for loblolly pine seems quite reasonable.

Gladstone (1970) determined that *LW* of loblolly pine contains more alpha-cellulose than *EW*. This is probably reflected in the higher *LW* crystallinity here and in Douglas-fir (Lee 1961).

Compression wood of loblolly pine appears to be substantially lower in crystallinity than normal wood. Lee (1961) found the same situation in Douglas-fir. The higher lignin content, lower cellulose, and higher hemicellulose content than normal wood are probably the responsible factors.

There was some difference between radial and tangential sample crystallinity. It is proposed that different proportions of amorphous middle lamella substance and semicrystalline wall material penetrated by the X-ray beam are responsible for this directional variation.

Ammoniated wood. As a consequence of ammonia treatment and contradictory to previous findings for strictly cellulose, all wood samples, *CW* > *LW* > *EW*, exhibited an increase in crystallinity. Therefore, anatomical and/or ultrastructural changes in the wood material were suspected that might explain an apparent if not actual increase in crystallinity.

Mechanisms for crystallinity change

A review of the molecular and microscopic structure of wood reveals only a limited number of ways by which wood may be rendered more crystalline. These include chemical and physical alterations, but the end product should possess a greater proportion of crystalline substance per unit volume of starting material.

It was first conjectured that the exaggerated shrinkage occurring during ammonia desorption (Parham 1970) was causing such an increase in wood density that there was consequently more crystalline substance (crystalline cellulose) in the X-ray path. This proposal is obviously inadequate when one considers that such shrinkage would bring proportionate amounts of both crystalline and noncrystalline wood substance into the path of a collimated X-ray beam. Thus, further explanations were sought through consideration of changes that might be confined to the cell wall itself, namely:

(1) increase in crystallite width by lateral aggregation of cellulose chains,
(2) increase in crystallite length,
(3) spontaneous conversion of amorphous cellulose to a crystalline form, but at sites removed from a preexisting crystallite, and
(4) drawing closer together of entire crystallites laterally as a result of shrinkage of any space and/or amorphous substance between them.

Possibility (1) was ruled out because of the previous experimental phase that detected no obvious change in crystallite width. Possibility (2) was unstudied in this investigation. Crystallite length is extractable from meridional reflections on the X-ray diagram, but those on the wood diagrams resulting from wide-angle diffraction were very weak. Such a phenomenon, increase in crystallite length, has been proposed to occur, however, as decrystallized cellulose is allowed to recrystallize upon exposure to water vapor (Caulfield and Steffes 1969). Ammonia cellulose passes through a completely X-ray-amorphous state as it is saturated with ammonia (Schuerch 1964). Therefore, perhaps a similar process is able to take place during wood ammoniation. Only further investigation will determine if this is the case or not, but at least the possibility should not be ignored.

The third mechanism would most likely involve the hemicelluloses, which are generally cited as amorphous since their removal apparently sharpens an X-ray diagram and increases the average crystallite width (Nelson 1961). Spontaneous conversion of these substances to a crystalline form might seem only remotely possible. However, some type of crystallization has been observed to occur as these materials are purified (Horio and Imamura 1964; Lindberg and Meier 1957; Yundt 1951). The fibrillar appearance of these same hemicelluloses (Fengel 1970) also casts some doubt as to their amorphous nature under *in situ* conditions. Thus, the exact effect of ammonia on hemicellulose crystallinity is difficult to describe, but as inferred previously, any change in their crystalline state could indirectly affect the X-ray picture of wood cellulose.

The last proposed mechanism for an increase in cell-wall crystallinity is a purely physical situation. It implies the shrinkage of amorphous material and/or microvoids between crystallites.

Substantiation of micropores in the wood cell wall has been the object of critical research of late, attention being given to determining exactly what is being measured by various techniques. Relevant to the present study, a regular pattern of cell-wall voids has been observed microscopically in loblolly pine pulp (Jurbergs 1969). A figure of 4% void volume has been suggested for loblolly pine wood (Wangaard 1969). Heyn (1969) showed 20–30-A interstices between elementary fibrils of delignified wood. He postulated that the spaces may result from packing conformation of the crystallites, but the exact nature of the spaces—whether voids or filler substance—is uncertain. In any event, when the wood cell wall is thoroughly plasticized with ammonia, it does not seem unrealistic to propose that rearrangement or shrinkage of these voids or interfibrillar material may take place as ammonia is allowed to evaporate. The present research was carried out at room temperature as opposed to –30 C used in most other ammoniation experiments. Perhaps this could have had some effect on the mobility and crystallization potential within the cell wall.

The foregoing discussion implies a cell-wall consolidation and hence, a higher cell-wall density following ammonia treatment. Clarification of this aspect of the wood-ammonia complex would be enlightening, but as of this time, controversies concerning the measurement of this parameter (see Kellogg and Wangaard 1969) have deterred experimentation using this factor to characterize ammoniated wood.

CONCLUSIONS

Treatment of loblolly pine wood with gaseous anhydrous ammonia at room temperature causes an increase in the crystallinity of both normal and compression wood but no detectable change in crystallite width. The increase in crystallinity may be entirely apparent because of a cell-wall consolidation, but other factors related to an actual increase should be considered. Electron microscopic evidence seems to support the contention for a wall consolidation. These results will be presented in Part 2 of this paper.

Further research is needed on the ammoniation of cellulose and wood at room temperature. Particularly, data are needed on the crystallinity of strictly cellulose treated at this temperature, and the cell-wall density of ammoniated wood would also be very useful.

Note added after completion of manuscript: A recent book published in Russian by the Latvian Academy of Science (1967, *Modification of Wood*) reports on their research in the area of wood plasticization. Most experiments were performed on birchwood, and ammoniated stock responded physically in much the same pattern as has been observed in this country for birch and other hardwoods. Aqueous solutions of ammonia degraded all wood components to some extent, as indicated by an increase in the substances soluble in water and benzene-ethanol. Hemicelluloses were degraded the most, but lignin was shown to play a major role in determining the plasticization capacity of wood. Data relevant to the present study showed that wood treated with aqueous ammonia (20% and less) followed by direct drying exhibited an increase in X-ray crystallinity, the increase being noticeable after solutions as low as 1% ammonia. The magnitudes of initial and final crystallinity were also in relative agreement with those determined by the author. The Latvians proposed that the increase in wood crystallinity resulted from an improvement in the orientation of amorphous or disordered cellulose. This prediction is inconsistent with previous literature describing cellulose III, but the same phenomenon was not ruled out in the present study. Seemingly consistent with the author's interpretation, it has recently been shown (Thompson, N., and O. Kaustinen. 1970. TAPPI, **53**(8):1502–1506) that individual fibers after treatment with aqueous ammonia are stiffer with a decrease in specific volume. Still, only further research on the cell-wall density and crystallinity of ammoniated wood and cellulose fibers will ascertain whether the observed increase in wood crystallinity is actual or only apparent.

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