MOLECULAR RHEOLOGY OF CONIFEROUS WOOD TISSUES

by

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ABSTRACT

The time dependent molecular motions of wood components at straining parallel to fibre direction were observed by infrared polarization technique.

A two-stage molecular motion involving three wood components, cellulose, hemicellulose and lignin is suggested as the course of wood molecular relaxation. The first stage begins at equilibrium, when the specimen is not stressed, and extends immediately to a minimum dichroic ratio ($\frac{A_{\perp}}{A_{\parallel}}$) of carbohydrate components represented by 1160 cm^{-1} and 1730 cm^{-1} bands, and the maximum dichroism of lignin (1500 cm^{-1}). The second stage starts at the end of the first stage and extends to equilibrium recovery.

Regardless of the form of external excitation (creep or stress relaxation), and the time of excitation (ramp- or step-loading), the basic pattern of the two-stage molecular motion was followed, while damping of the molecules accompanied the whole rheological process.

Thus, the wood macromolecular structure maintains an "internal state" of equilibrium on receiving external excitation. This equilibrium state is achieved by moving the carbohydrate and lignin components in opposite directions.

The described pattern of molecular motion for a component in wood is a compensatory result from the interference

of other components. Removing one or more components from wood changes the motion patterns of the remaining components.

The conformation of cellulose in the specimen without the presence of lignin and hemicellulose is comparable to that of other synthetic linear polymers.

Energy transfer system of wood was postulated as being due to the directional movement of molecular components which results in association and high steric interference between carbohydrates and lignin, similar to cross-linked chains of lignin and carbohydrates.

This energy transfer system of wood is further facilitated by the existence of a systematic structure of wood microfibrils which permits a zone of gradual transition from high crystallinity to a diffuse state. The lignin network of the system may do more than transfer energy, it may act also as an "energy sink" and thereby function to maintain the memory of the excitation.

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INTRODUCTION

It may be theorized that physical mechanical characteristics of polymeric materials are the combined molecular response to external excitation. Classical elasticity and viscosity theories, which interpret mechanical behaviours as idealized solids and perfect fluids, do not adequately explain these events. Molecules are kept from flowing indefinitely through formation of three-dimensional networks either by chemical bonding or by growth of crystalline regions (133). Thereby, molecular packing represents an equilibrium condition approaching stability. When external excitation is applied, the system undergoes deformation or flow. Motion of molecules depends on their composition and history, as well as magnitude and nature of the external force.

Rheology is the science dealing with deformation and flow of matter, especially as characterized by interdependence of stress, strain and time. Several means may be used for observing molecular rheology, such as birefringence, nuclear magnetic resonance, dielectric constant and more recently, infrared dichroism.

Birefringence has been the most widely used method. Its application to illustrate dynamic molecular relaxation has been successfully performed with some simple polymers (155, 169, 171, 190). One recent example is the birefringence study of polyvinyl chloride relaxation by Utsuo and Stein (190). Their results show the development of negative birefringence as polymer films were subjected to tensile strain. During

relaxation the negative birefringence gradually reduced, while the sustained stress decreased at a similar rate. Both birefringence and dielectric constant techniques suffer from a fact of grossness, in that they represent composite sample properties and thereby do not reflect behaviours of identifiable molecules or chemical groups (179), while nuclear magnetic resonance is limited to the observation of proton, F^{19} , C^{13} and a few other nuclei, and is difficult to apply to solids. In contrast, dichroism obtained by polarized infrared methods may be made specific for given functional groups. Thereby, dichroism represents transitional moment directions with respect to the molecular chain axis and is useful for approximations with many absorption bands (33,149,205).

The first observation on dichroism of polymers with polarized infrared radiation was made by Bath and Ellis in 1940 (7, 34). Because of equipment limitations, however, the use of infrared dichroism for dynamic study of polymer relaxation was only reported after 1965 (48, 49, 92, 135), five years after development of the wire grid polarizer (11, 33).

In this recent period, Gotoh et al. (48, 49) reported that stretching of vulcanized natural rubber subjected to tensile strain gave rise to instantaneous dichroism of some infrared bands. They further noted correspondence between change of dichroism for amorphous bands and stress relaxation. The crystalline band (844 cm^{-1}), on the other hand, completed orientation almost immediately after elongation. Stress relaxation was thus attributed to molecular reorientation in

amorphous regions. A dichroism-stress behaviour has been reported also during relaxation of phenyl methyl silicone polymer (92). Further, Onogi and Asada (135) also demonstrated with polyethylene that infrared absorption bands at 720 cm^{-1} (amorphous) and 730 cm^{-1} (crystalline) attain an equilibrium state about one second after tensile stressing of specimens. There are a few studies on polymers which describe changes of infrared dichroism at different rates of elongation. Polymers examined in this way have been polyethylene (83, 85, 149, 170), polypropylene (155), polyethylene terephthalate (84) and polyvinyl chloride (172). In no instance have wood or wood products been studied in these ways.

Wood is an extremely complex material. Its main components are macromolecular systems known as cellulose, hemicellulose and lignin. These may occur as separated or continuous arrangements in the wood matrix, and may be permeated partly with extraneous materials. The comprehensive study of wood molecular dynamics requires detection techniques not available with birefringence, nuclear magnetic resonance or dielectric constant methods. Ideally, the approach should enable selective study of functional group activities with the native or treated wood matrix. The polarized infrared technique could provide such an approach.

Three hypotheses were set for examination in the present study.

First, that wood molecular activity accompanies physical-mechanical excitation, that this may be observed by suitable

technique, and when observed will be found to be time dependent.

Second, that each major wood component has an individual time dependent pattern of molecular motion, and that some major component must differ directionally from the others in order to provide the unique property of damping in wood.

Third, that energy transfer in wood requires the participation of all major components, and that the mechanism is seriously modified by adjustment of the system.

LITERATURE REVIEW

I. Coniferous Wood Morphological Structure

Two spatial systems of tissue organization exist in the wood of coniferous stems. The axial system consists mostly of longitudinal tracheids, which comprise up to 90 per cent of the wood volume and over 95 per cent of the wood weight (113,136,141). The radial system lies perpendicular to the stem axis and includes mostly ray parenchyma cells. Depending on species, other minor cell types may occur in varying amounts.

Wood morphological units are held as a matrix by lignin. The lignin rich inter-cellular layer is called the middle lamella (M). The cell wall itself was observed early (78) as having a layered structure. These layers are known as the primary wall (P) which is thin and adjoins the middle lamella (M), and the thick secondary wall which is further subdivided as an outer (S_1), central (S_2) and sometimes inner (S_3) layer. As example, cell wall layer thickness of Japanese red pine (*Pinus densiflora* Sieb. et Zucc.) earlywood tracheids are reported (53) as 0.6μ (P), 0.31μ (S_1), 1.93μ (S_2) and 0.17μ (S_3). Differences in thickness and proportioning of layers appear in the associated latewood.

Microfibril orientation within cell walls varies with the cell layers and has been extensively studied as regards mechanical and physical importance (53,145,194). Microfibrils in the primary wall are thought to be randomly arranged and much permeated with lignin (27,53). The primary wall, however, has been reported as a two layered structure (126,194).

Microfibrils of the S₁ layer are oriented at high angles to the tracheid axis, providing flat helical patterns (53). Dunning (27) found that there were at least three lamellae in the S₁ layer. These lamellae appeared as a left or right hand helix with microfibrils at angles of 65 to 75 degrees to the fibre axis.

The dominant S₂ layer shows a steep helical structure, oriented at angles of 20 to 30 degrees to earlywood tracheid axes and 5 to 10 degrees with latewood tracheid axes in Japanese cedar [Cryptomeria japonica (Linnæus fil.) Don.] and Hondo spruce (Picea jezoensis Maxim.) (53). According to estimates of Harada (53) and Jayme and Fengel (68, 69) this layer occupies about 78% of the whole wall thickness. In longleaf pine (Pinus palustris M.) latewood, the microfibril alignment appeared to be very uniform (27). The perfection of S₂ parallelism is greater for latewood than earlywood (53).

The S₃ layer has a flat helical pattern similar to the S₁ layer (53) and alternating lamellae with different orientations occur in the layer.

From the above, it is apparent that microfibril organization in the cell wall varies considerably between the different cell wall layers, as well as between different cells in the same growth increment. The high parallelism of the S₂ layer, which occupies three-quarters or more of the total cell wall area, and the gradual transition from the S₂ microfibril pattern to that of S₁ and S₃ layers through lamellar system gives the impression that wood is organized with purpose at the ultracellular level. These biological provisions could relate in some important ways to wood rheological behavior.

II. Chemical Organization of Coniferous Wood

1. Tracheid Wall and Growth Zone Chemical Composition

Coniferous wood is composed of carbohydrates, lignin and lesser amounts of various extraneous substances. Ritter (151), first reported that 75% of the coniferous wood lignin is located in the middle lamella. This concept was extended by Bailey (5), who found by analysis following micro-dissection that the middle lamella of Douglas fir [Pseudotsuga menziesii (Mirb) Franco] is comprised of 70% lignin and 14% pentosans. This lignin concentration was later confirmed by ultraviolet absorption studies of Lange (90), who concluded also that there was increasing lignification in the outer layers of the secondary wall and in the primary wall toward a maxima in the middle lamella. Recently, Berlyn and Mark (10) reviewed earlier data and calculated lignin distribution in the cell wall by considering that the compound middle lamella comprises approximately 10 to 12 per cent of the volume in coniferous wood. Thereby, lignin content of the secondary wall appears to be about 86.4 per cent of the total lignin in comparison with 13.6 per cent in the compound middle lamella. This postulation is verified by Scott et al. (160) in a recent experiment.

Electron microscopic observations of Sachs et al. (153) have demonstrated uniform distribution of lignin in the S₂ layer of white spruce [Picea glauca (Moench) Voss], while the S₃ layer also showed high lignin density. This was confirmed later by Côté et al. (21,22), who further showed that lignin forms a continuous network in the cell wall.

The pattern of lignin distribution in coniferous woods can be altered by conditions of tree growth. A good example

is compression wood, which has higher lignin content than the associated regular wood (21). Compression wood tracheids are found also to have an adjusted organization of wall layers, in that an isotropic layer with high lignin concentration occurs immediately inside the S_1 layer (22).

The distribution of polysaccharides in coniferous wood cell wall layers was studied by Meier (117, 118) and Meier and Wilkie (119). Their results with Scots pine [Pinus sylvestris (L.)] and European spruce [Picea abies (L.) K.] are summarized in Table 1. They concluded that maximum amounts of cellulose and glucomannan occur in the S_2 layer, while the S_3 layer has the highest values of glucuronoarabinoxylan.

The radial distribution of hemicelluloses in cell walls was demonstrated also by Luce (102), who employed a chemical peeling technique. Residual xylan and mannan of unbleached and bleached pulps were found to be highly concentrated at the fibre surface in the primary wall and middle lamella regions and to decrease toward the lumen.

A radial distribution for cellulose degree of polymerization (DP) in cell walls was proposed by Jayme and Von Koppen (70), where the primary wall DP has lowest and the S_3 layer maximum values. This pattern of DP distribution is supported by experimental data of Luce (102).

The uneven distribution of tracheid wall chemical constituents has been advanced as explanation of chemical differences between earlywood and latewood, mostly as a result of the thicker latewood S_2 layer (118, 183). The relative percentages of carbohydrate constituents isolated from Scots

pine earlywood and latewood by Meier (118) are shown in Table 2. In contrast to Meier's values, Ifju (65) showed that Douglas fir earlywood contained more araban and xylan than latewood, while the latewood had more galactan than earlywood.

The lignin-carbohydrate ratio in wood has been a subject of study. Three to five per cent higher lignin content of earlywood in contrast to the associated latewood has been reported by many researchers (20,50,89,94,95,198,201). In addition, Wu and Wilson (201) and Chow (20) using ultraviolet and infrared spectrophotometric methods independently showed that minimum lignin content occurs regularly in the last-formed latewood while maximum lignin content is not found usually in the first formed earlywood, but more often somewhat later in the growth season. This pattern of lignin variation led to the postulation (201) that the initial earlywood tissue arising from "overwintered" xylary mother cells has some "memory" factor as chemical predisposition towards the preceding season's growth.

In more recent work on lignin-carbohydrate balance within growth increments, Squire (168) postulated that proportioning of wood alpha-cellulose and lignin is manipulated by a mutually exclusive principle.

2. Cellulose Lattice Structure

The cellulose crystal unit cell is cellobiose which is formed from two glucose residues linked by the 1,4-0- β -D-glycosidic bond. Length of the (poly) glucose or cellulose macromolecule is given by degree of polymerization (DP) measurements. Cellulose DP estimates vary with the

source of materials, methods of isolation and means used for measuring and calculating data. The DP of wood celluloses has been reported by Goring and Timell (47) to be 7500 for jack pine (Pinus banksiana Lamb.), and 8000 for Engelmann spruce [Picea engelmannii (Parry) Engelm.]. A difference between earlywood and latewood cellulose DP of Douglas fir was reported by Ifju (65) as 5250 and 5660, respectively. If length of the cellobiose unit is accepted as $10.3 \text{ \AA}$ (167), the wood cellulose chain length appears to range up to $80,000 \text{ \AA}$, thereby transcending numerous areas of supermolecular order.

The long cellulose chains are thought to be arranged according to some supermolecular order, the exact nature of which has been the subject of much argument, and remains a current issue. Fine lattice structures are proposed as amorphous, paracrystalline, perfect crystal, crystal defect model, fringed micelle, fringed fibril and a lamellar model (57). In addition, a protofibril concept has been introduced recently (104,175). Three of the most used explanations have been the fringed-micelle, fringed-fibril and lamellar models.

A. Fringed-Micelle Model

This is an early model proposed by Herrmann et al. in 1930 (59) to account for observations of polymer molecules and their behaviour. The long molecule is considered as threading through several adjacent crystalline and noncrystalline (fringe) regions (14). Accordingly, amorphous and crystalline regions coexist, interact and resist separation (14). For wood cellulose, Frey-Wyssling (41) further proposed a gradual transition between the crystalline and amorphous

states. The crystalline regions are arranged at regular intervals but scattered along the axis at random. This concept of cellulose fine structure is supported by Marchessault (108) and Mark (113) with some modifications. Marchessault (108) suggested that crystallized cellulose regions are segregated as fibrils, while oriented hemicelluloses occupy the interfibrillar space. Mark (113), with his concept of stress analysis, proposed that the short crystalline cellulose region is end-coupled with hemicellulose during the synthesis of microfibers, while the non-crystalline cellulose is deposited between crystalline regions at a later stage.

B. Fringed-Fibril Model

This model was introduced by Hearle (55, 56, 57) because the fringed-micelle concept does not explain satisfactorily the apparently infinite length of microfibrils observed with electronmicroscopy (56, 166) and the process of polymolecular growth by spherulitic arrangement. This concept permits successive growth of crystallites giving a continuous dendritic network.

In this model, the fibrils are assumed to be long, imperfect, possibly branched crystals made up of comparatively short segments of cellulose chains packed together. Any one long-chain molecule passes alternately through a number of crystalline fibrils and through the non-crystalline regions between them. This theory applied to cotton cellulose structure received the support of Tripp et al. (186). However, the model has been criticized by Michie et al. (122) in application to rayon, and by Mark (113) and Cowdrey and Preston (23) in

application to wood tracheids. Disagreements are based on inability of the model to explain observed fibre mechanical properties.

According to Hearle (56, 57), the fringed-micelle structure is part of a larger fringed-fibril structure having very short fibrillar length.

C. Lamellar Model

The individual cellulose chains of this model, as suggested by Keller (77), are considered to fold back on themselves with regularity providing a form that is much thinner in the direction of the chain than the length of the chain itself. Structures of this type are proven for various materials including cellulose derivatives, as by Manley (104), who used electron diffraction techniques. Manley's finding was recently supported by Sullivan (175) for celluloses from six pines and two pored woods. This model, however, has been criticized by Mark (113) because it does not satisfy the observed physical and mechanical behaviours of wood cell walls, which are characterized by low extensibility, very high strength, and lack of glass transition behaviour which is also typical of synthetic polymers.

It is believed that none of the above three models completely explain the physical and mechanical behaviour of wood, which is not fully understood at this stage. Lack of better understanding relates to variations in native cell wall structure, complications introduced by the presence of lignin and hemicelluloses and difficulties in isolation of pure systems.

3. The Unit Cell Structure and Hydrogen Bonding of Cellulose

A. Unit Cell Structure

The crystalline nature of cellulose was first demonstrated by Nishikawa and Ono in 1913 (129). Their discovery opened a new field for studying cellulose structure. In 1921, Polanyi (167)*published the first unit cell dimensions and postulated that a unit cell of the observed dimensions could accommodate four glucose residues. Sponseler (167)*revised Polanyi's concept, adding that two glucose units comprised the unit cell (b-axis of the cell). Results of various studies on unit cell dimensions are recorded in Table 3.

The literature on unit cell dimensions for celluloses treated by acid, amine and salt has been summarized by Rydholm (152).

Values of unit cell dimensions as listed in these sources vary greatly. In addition, great variation in microfibril width is reported, i.e., ranging between 30 to 300 Å (123). Angular arrangement of the bridging 1,4- β -D-linkage also varies according to different authors as shown in Table 4.

B. Hydrogen Bonding

The nature of forces which hold the unit cell structure in spatial form has been reviewed up to 1940 by Mark (112). While the concept of hydrogen bonding is introduced, detailed understanding of bonding mechanisms is lacking.

Further examination of cellulose hydrogen bonding has been facilitated by progress with infrared spectrometry, whereby Marrinan and Mann (106, 114, 115) described in a series of papers the possible nature of hydrogen bondings within the cellulose unit cell as deduced from infrared

* Original not seen. Cited from literature (167).

spectra in the 3300 cm^{-1} wave number ($3\text{ }\mu$ wavelength) region. All cellulose hydroxyl groups were found to engage in hydrogen bonding (114), although the unit cell structures for celluloses I, II and III were different (106, 115). All three crystalline modifications showed that some hydroxyl groups make a relatively small angle with the chain direction, whereas others show angles greater than 55 degrees (106). Since only hydroxyl groups which form intramolecular hydrogen bonds cause small angles with the chain direction (73), the possible intramolecular bonds which link successive glucose units in cellulose chains were inferred as $O-3\dots\rightarrow O-5$ and $O-2\dots\rightarrow O-6$ (where dashed lines refer to adjacent residues of the same chain and the number noted represents the position of oxygen in the pyranose unit) (73). A further study by Jones (74) on cellotetraose single crystals, which are similar to cellulose II, showed the likelihood of faults and distortions in the cellulose crystal. This observation on disorder in the cellulose crystalline structure was confirmed by Poppleton and Mathieson (143).

The infrared spectra of native cellulose in the 3300 cm^{-1} wave number region was also examined by Liang and Marchessault (98). From difference in polarization of OH stretching bands, a slightly modified system of hydrogen bonding was proposed for the crystal structure of cellulose I. It seems that conformation of the cellobiose unit permits intramolecular hydrogen bonding between the C-3 hydroxyl and the ring oxygen of a contiguous glucose unit. Intermolecular hydrogen bonds in the 101 plane were proposed between the C-6 hydroxyls of

antiparallel chains and the bridge oxygens of adjacent parallel chains. The C₆ hydroxyls of the parallel chains were thought to be hydrogen-bonded to the bridge oxygens of adjacent antiparallel chains in the 10 $\bar{1}$ plane. Hydrogen bonds in the 101 plane were explained as shorter than those in the 10 $\bar{1}$ plane. Similar results were observed by the same authors with mercerized cellulose (110). The intramolecular hydrogen bonding between O-3 of one residue and the ring oxygen of the adjacent residue is suggested by Jacobson et al. (66) as the basic factor controlling relative orientation of the cellobiose unit.

4. Orientation of Hemicelluloses

A. Arabino-4-O-methylglucurono-xylan

Xylan was the first hemicellulose fraction reported as oriented within wood tissues (96, 108, 111). In the native state, this polysaccharide is believed to surround cellulose microfibrils as a somewhat amorphous matrix (108, 194, 196).

The xylan of coniferous woods was first reported by Dutton and Smith (29, 30) as a backbone of D-xylose units, jointed by 1,4-0- β -D-linkage, to which units of 4-O-methyl-D-glucuronic acid are attached at C-2, and occasional L-arabinofuranose residues occur at the xylan C-3. Separated coniferous xylans have a DP of about 120 units, and contain one acid side chain per five or six xylose residues, while one arabinose occurs per seven to eight xylose units (182). The existence of O-acetyl groups in native 4-O-methyl glucuronoarabino-xylans have been shown to be attached to xylose residues, but their distribution has not been established as yet (15).

The X-ray diagram of an oriented xylan sample has been shown to be entirely different from that of cellulose (108). The backbone conformation was postulated as corresponding to a threefold screw symmetry with an advance of $5 \text{ \AA}$ per residue ("fibre repeat" being $15 \text{ \AA}$) and rotation of 120° . The infrared spectrum of separated xylan has revealed a higher frequency of OH bands associated with intramolecular bonding, than found with cellulose II, indicating a longer O-3...O-5 distance. It was concluded that a conformation including a threefold screw symmetry occurs in the xylan molecule.

In further work, Settineri and Marchessault (164) reported that the left-handed helix of the separated xylan was a more probable conformation for 1,4-anhydro- β -D-xylose. Calculated parameters for xylan chains with O-3...O-5 distance at $3.0 \text{ \AA}$ are recorded in Table 5 (108).

Direct drying of xylan hydrate films, when xylan contained 4-O-methylglucuronic acid, was found to provide patterns of low crystallinity (204). No layer line structure was observed in the X-ray diagram (108), possibly due to a more compact lattice which would not accommodate the uronic acid without deformation. Unit cell dimensions for the xylan hydrate as compared with cellulose II by Marchessault (108) are shown in Table 6. Based on these unit cell dimensions a co-crystallization has been postulated (108) between xylan and cellulose which forms a low order lattice. This is consistent with the view of Astbury et al. (1), but has been questioned by Caulfield (19).

Deacetylation and mild hydrolysis studies on native xylan, show an overall sharpening of X-ray diagrams and the

formation of a new typical xylan reflection. Marchessault et al. (108, 109) argued that xylan is crystallized inside the fibre cell walls following orientation of the main axis, i.e. preferentially parallel to that of the cellulose. This postulation is consistent with the concept of Cowdry and Preston (23).

It should be noted, however, that the highly branched structure of coniferous xylans could prevent crystal formation in the cell wall (93, 127).

In coniferous wood, the ray cells have been reported to contain more xylan than tracheids (141). Since by volume these ray cells account for only 5 to 10% of the total wood volume and the structure of ray cell xylans has not been reported, the effect of this xylan on wood properties may be only of secondary importance.

B. O-Acetyl-galactoglucomannans

The O-acetyl-galactoglucomannans are the predominant hemicellulose of coniferous woods. This hemicellulose was first reported by Hamilton et al. in 1956 (51,52). The molecular backbone consists of β -D-glucopyranose and β -D-mannopyranose residues, (1-4) linked, and probably distributed at random. Some units have an α -D-galactopyranose residue directly attached to C-6, while the O-acetyl groups are distributed at C-2 and C-3 of the mannose units with about the same number of groups in each of these positions (100,101). The DP of separated glucomannans has been measured at 60 to 140 hexose residues (118, 181, 182, 183).

After deacetylation, the separated galactoglucomannan can be crystallized (101, 204). X-Ray diagrams have shown that glucomannans may be closely associated with cellulose microfibrils, as between the cellulose chains (127).

Removal of the mannan-rich hemicellulose fraction

sharpens the 002 diffraction peak, which indicates greater packing perfection for the cellulose crystalline microfibril structure. The linear molecular chains of glucomannan are believed to be deposited in parallel with the cellulose microfibril surface (23, 147).

5. Orientation of Lignin

Lignin, which is comprised mainly of phenylpropane units (17), has been considered as the encrusting substance of the woody plant cell matrix. The detailed structure of poly-molecular lignin in situ is complex and partly obscure at the present time.

Lignin is generally believed to be a three-dimensional macromolecule. It is first recognized after completion of the cellulose skeleton (193, 195). During wood maturation lignin is first observed at cell primary wall corners, and subsequently it appears to extend to the intercellular layer and among various layers of the secondary wall in association with hemicellulose. Lignification limits further surface enlargement of the cells by immobilizing those components of the matrix which permit surface growth to take place (194). Consequently, the cell wall becomes rigid, strong and somewhat fixed.

Because of the highly branched nature of polymolecular lignin, it has not been anticipated as having a crystalline structure in wood. Orientation of lignin in the cell wall, however, has been the subject of some argument. Frey (39) in 1928 found that the incrustation of cell wall lignin did not change the birefringence of cell walls and concluded that lignin occurs in an amorphous state, with incorporation in

the cell wall representing a swelling phenomenon.

The discovery of ultraviolet (UV) dichroism ($\frac{A_{\parallel}}{A_{\perp}}=1.2$ or $\frac{A_{\perp}}{A_{\parallel}}=0.83$) at 280 mμ for lignified wood cell walls by Lange (90) suggested that lignin was oriented inside the cell wall, since native wood carbohydrates do not absorb UV light at this wavelength. The dichroism found was explained as "intrinsic", meaning a true effect of lignin orientation. This discovery prompted Frey-Wyssling (40) to further investigation of the problem with ultraviolet and fluorescent dichroism. Frey-Wyssling stated that Lange's view of lignin orientation seemed plausible, since a lattice of graphite-like layers was shown in isolated cuproxam lignin by Jodl (71) and the monomeric molecules of polymeric lignin are in part coniferyl alcohol. These units show a system of conjugated double bonds which cause absorption of UV light. The amount of absorbed light differs in parallel and perpendicular polarization according to alignment with the aromatic ring of the molecule. Thus, a sufficient number of equally oriented molecules should yield a dichroic effect visible in the polarizing microscope. This coincides with the observation of Pearl on experimental results of Kringstad and Ellefsen (88), who studied lignin-carbohydrate bonding by comparison of polysaccharide molecular weight distribution following stepwise delignification of holocelluloses. Pearl (138) explained that lignin in the holocellulose occurs in the form of short, non-crosslinked branches in the polysaccharide chain which could be easily accommodated and oriented inside the carbohydrate lattice.

Although the results of Frey-Wyssling show also a

slight "intrinsic" dichroism, he declared the UV dichroism observed within lignified cell walls to be "form" anisotropy due to a rodlet composite body, which mirrors the ordered cellulosic supermolecular structure. Careful examination of infrared polarization spectra on thin wood sections recorded by Liang et al. (96) clearly shows dichroism for the 1500 cm^{-1} lignin band of western red cedar (Thuja plicata Donn), although the original authors deny polarization effects for lignin. This is an important point, since polarization is prerequisite to dichroism.

The physical association between lignin and cellulose has been extensively investigated. Preston and associates (1, 144) examined the effect of delignification on X-ray patterns for plant tissues and found that the treatments produced little change. This led to the conclusion that lignin did not penetrate the cellulose micelle structure (1, 144, 196). On the other hand, Wardrop (191, 193) and Wardrop and Preston (196) showed that wood delignification changed the line breadth corresponding to the 002 planes in X-ray diagrams of mountain ash (Eucalyptus regnans E). The calculated apparent crystal size for wood cellulose and holocellulose indicated an increase of 18.8% in crystallinity, which was consistent with values obtained for hydrolyzed cellulose crystals. In further experiments, Wardrop (192, 193) reported that hydrolysis during delignification and subsequent hydrolysis of holocellulose products produced aggregated clumps of microfibrils visible in electron microscopy. This was attributed to crystallization of the less ordered paracrystalline structure surrounding the microfibrils, which had been prevented from crystallization in the original specimens.

by lignin infiltration. Thereby, the change in microfibril order was suggested as analogous to changes between micelles within the microfibrils that cause sharpening of diffraction lines. Wardrop (193) argued that some of the cell wall lignin must be associated with the paracrystalline phase of cellulose.

The effects on X-ray diffraction patterns of chlorite delignification and alkaline extraction of hemicelluloses with slash pine (Pinus caribaea M.) was studied by Nelson (127). The results showed that the 101 plus $10\bar{1}$ peak intensities remained relatively constant, while the 002 peak intensity increased greatly. The 002 peak change, however, may or may not have represented an increase in crystallite width. The changes were explained as: (i) lateral union of crystallites which had been maintained as separate structures by lignin in the whole wood; (ii) reduction of liquid type lignin scattering, allowing crystallite portions to diffract a greater share of energy during analyses; or (iii) relief of minor strains or distortions in the cellulose framework imposed by cell wall growth, the presence of lignin or drying. For these reasons, lignin was postulated as extracrystalline.

Later, Sachs et al. (153) showed orientation of lignin around the S_1 cell wall layer of loblolly pine (Pinus taeda L.) and white spruce by electron microscopy. This finding agrees with the earlier observation of Jayme and Fengel (69). Sachs et al. (153) further reported the presence of high density lignin in the compound middle lamella, where a layered lignin structure appears to exist.

Since there has been little research dealing directly with lignin orientation, it is extremely difficult to define the exact controversial concepts of this topic.

III. Rheological Behaviour of Wood

Literature on wood rheology, published before 1962, was reviewed by Kingston (79), Pentoney (139), and Pentoney and Davidson (140). Literature published between 1957 and early 1968 was reviewed recently by Schniewind (158). Only some points relevant to the present study are discussed here.

Creep and stress relaxation tests are two approaches used in study of wood rheological behaviour. The creep test is characterized by a constant load with changes in strain or deformation measured over time. In the stress relaxation test, on the other hand, the strain is kept constant and the change of stress arising with lapsed time is observed (31, 165). Creep compliance and stress relaxation appear to be related for materials which approximate linear viscoelasticity (2). This has been described as, "the same animal, but its skin is stained a different colour" (4). Thereby, it is possible that one response function can be calculated from the other, at convergence of the known function (2).

Stress relaxation of wood was first studied twenty years ago by Kitazawa (80), who examined gross wood compression perpendicular to the grain. Relaxation time was observed over the time range of one to one thousand minutes. His empirical equation for stress decay was :

$$\frac{\delta(f)}{\delta_1} = 1 - m \log t \quad [1]$$

$$\frac{\delta(f)}{\delta_1} = \text{fractional stress relaxation, based on stress at one minute.}$$

t = time

m = constant; a relaxation coefficient.

From these results with a variety of species a linear viscoelastic behaviour was indicated.

Linear viscoelasticity for stress relaxation in compression and tension perpendicular to the grain was found also by Young (203) in bending, and in tension parallel to the grain by Johnson (72). It should be noted that investigators have disregarded the wood relaxation response within the first minute. Their results often show a non-linear behaviour at high strain. As Bach (2) pointed out, "The viscoelastic mechanical behaviour of hard maple is shown to be clearly non-linear. However, as a first approximation, the response of wood (to longitudinal tensile stress) may be considered elastic for ambient conditions of low moisture content and room temperature, and as linear viscoelastic for low stress". Therefore, the linear viscoelastic behaviour of wood is in doubt according to systems that have been used. Ignoring wood response within the first minute of test, which has been found to be important for synthesized polymers (135, 169), could be a serious mistake of wood rheologists which limits interpretation of their results.

Recent studies in Japan on wood rheological behaviour provide some interesting information. Norimoto et al. (131, 132)

examined the stress relaxation of Japanese cypress (Chamaecyparis obtusa Endl.) in bending and torsion creep. The authors found a peak which appeared in the relaxation spectrum or retarded spectrum of every specimen at 10^3 to 10^4 seconds (17 to 160 min). The peak moved to shorter time as relative humidity was increased. Consequently, the time-temperature or time-humidity superposition principle did not apply to wood.* This is consistent with results of Goldsmith and Grossman (46) and the Schniewind (158) interpretation of results from Davidson (25) which indicate that wood rheological behaviour is not simply governed by the Boltzman principle (184). Instead, it is proposed (91) as similar to the stretching of rayon, silk and Nylon 66, where crystalline reorientation occurs during loading.

The transitory nature of wood crystallites during load application has been observed by a few researchers (124, 177). Murphey (124) found that there was an increase of wood crystallinity as measured by X-ray diffraction immediately after loading. A change in dielectric constant during stress relaxation was also observed by Suzuki (177). The dielectric constant decreased at time of loading, returned to the original value after about 10 minutes, and then stabilized at slightly lower values between 10 to 100 minutes.

An increase in crystalline orientation of holocellulose fibres during creep loading tests was observed by Hill (61). A correlation between Young's modulus and the cellulose helical angle obtained by 002 plane measurements on Sitka spruce (Picea sitchensis (Bong.) Carr) wood was shown by Cowdrey

* It is also probable that applied stress causes changes in wood equilibrium moisture content.

and Preston (23).

An attempt to illustrate wood creep behaviour through molecular structure studies was made by Yamada et al. (202). Wood sections containing nujol were stretched at 20 and 60% of their ultimate stress levels and their infrared transmittance and polarization spectra were recorded. Results reported by the authors showed the appearance of a very weak 1495 cm^{-1} wave number band* and occasionally another band at 1115 cm^{-1} . Their polarization results provided little additional information. In most cases the spectra were poorly resolved and the noise to signal ratio was too large for reading meaningful results.

The rheological behaviour of delignified wood was investigated recently by Eriksson (35, 36) and Fushitani (42, 43, 44). Eriksson (35, 36) studied the effect of sodium chlorite delignification on creep parallel to grain with Scots pine. He found that no noteworthy changes occurred by removing up to 10.5% of the sample. Lignin was thought to contribute to wood mechanical properties indirectly. The lignin in cell walls, due to the hydrophobic nature, was proposed as preventing the fibres from absorbing large quantities of water. The fibres would have otherwise suffered a radical strength reduction.

Fushitani (42, 43, 44) in a series of experiments studied stress relaxation in bending tests on delignified

* We have observed a split band in the $1500 \pm 10\text{ cm}^{-1}$ region on tangential wood sections of coniferous woods without stretching.

Hinoki and found that: (i) The amount of stress relaxation with air-dried specimens increased little with decreased lignin content, while a significant increase in amount of relaxation was observed with water-saturated specimens; (ii) the time-temperature superposition relationship did not apply to either delignified or acetylated wood even when tested under water-saturated conditions; and (iii) the relaxation spectrum of untreated wood showed a broad peak between $10^{4.5}$ to 10^6 sec while that for delignified wood was relatively flat across the same time and the spectrum peak for acetylated specimens shifted to longer times. The influence of moisture content associated with decreased lignin content was thought to contribute only minor effects. The high lignin content of initial specimens was considered as hindering hydrogen bonding of holocellulose.

Sarkanen et al.(157) proposed a role for lignin in regulating wood rheological behaviour, as due to lignin ester groups, whereby: "The ester groups may exert a kind of plasticizing effect upon the lignin by reducing the opportunity for internal hydrogen bonding. Furthermore, the conjugated ester groups, if connected with the α -carbon in lignin as presumed, reduced the number of sites that otherwise may participate in lignin-lignin bonds or lignin-polysaccharide bonds. Consequently, ester groups may act as regulators of the rheological properties of the wood tissue as a whole. The fact that lignin ester groups are prominent in juvenile pinewood, which is quite flexible, but almost absent in the rigid compression wood, supports

such a supposition".

IV. Infrared Spectrophotometric Study of Wood

Wood is an aggregate of cellulose, hemicellulose, lignin and various extraneous components. The extraneous complex is not discussed here.

Lignin spectral structures have been extensively studied since first examined in 1948 by Jones (75). It is believed that infrared studies on cellulose structures began prior to this period. The infrared spectrum of whole wood was first recorded by Kratzl and Tschamler (87) in 1952, with the aid of paraffin oil (nujol). Since nujol absorbs in the 2940 and 1470 cm^{-1} regions, their spectra did not cover the whole range of wood absorption. At about the same time, Brauns (16) recorded the infrared spectra of colloidal homogenized coniferous wood between 3570 and 900 cm^{-1} . Later, Tschamler et al. (187) obtained wood infrared spectra using radial microscopic sections about five microns thick. Their results enabled differentiation between coniferous woods and pored woods. Difficulties in preparing the very thin wood sections required for instrumentation of the time seems to have delayed use of the method.

Recently, Harrington et al. (54) recorded the spectra of mountain ash and Monterey pine (Pinus radiata D. Don) sapwoods and assigned the various absorption bands to wood constituents. It was found that better spectra were obtained from wood sections than from pelletized milled woods.

A number of sections pressed as a sandwich in a potassium chloride pellet gave a sharper spectrum than a single section, similarly prepared. The superiority of non-imbedded wood section spectra is reported by Chow (20). Taniguchi et al. (180) also found better band resolution especially in the 1000 to 1200 cm^{-1} region. Their objective, however, was to relate bands at 1110, 1060 and 1040 cm^{-1} to wood cellulose crystallinity.

The infrared spectra of tangential wood sections obtained from various positions within growth increments of four western and eastern Canadian coniferous woods were examined by Chow (20). The spectral structures of extractive-free wood for the different species were similar, but the relative intensities between various bands within one spectrum differed between species, and from the initiation of earlywood to the last-formed latewood within single annual increments.

One important method of infrared spectrometry is the use of polarization for assignment of absorption bands based on known molecular orientation of the polymers. Ellis and Bath (34) studied ramie fibres by the technique as early as 1940. They observed absorption bands characteristic of hydroxyl groups in the 6060 to 5000 cm^{-1} wave number (1.5 and 2.0 μ) region, with results suggesting that hydrogen bridges of variable distances and variable bond angles occur between hydroxyl groups of adjacent cellulose chains.

The first wood cellulose spectrum recorded across the region from 3600 cm^{-1} to 750 cm^{-1} using polarized infrared radiation was reported in 1950 by Darmon and Rudall (24). A number of strongly polarized bands were observed in the 1250 cm^{-1} to 950 cm^{-1} region. These frequencies were expected to originate mainly from C-O (single bond) linkages such as C-O-C and C-OH groups of the pyranose ring, and the glucosidic C-O-C linkage. The glucosidic bridge frequency should give high parallel dichroism to the region. Further study by Tsuboi (188) provided some means for interpreting bands on the basis of spatial molecular orientation of cellulose. Strong parallel dichroism of the 1160 cm^{-1} band was noted among the spectra recorded.

The studies of Liang and Marchessault (97,98) on bleached ramie and bacterial celluloses gave great detail on the nature of cellulose polarization. Besides illustrating hydrogen bonding phenomenon at 3300 cm^{-1} wave number (3μ region), the dichroism of bands from 1700 to 690 cm^{-1} were thoroughly studied. The strong and highly parallel polarized band at 1160 cm^{-1} was assigned to the antisymmetric bridge $C_1\text{-O-C}_4$ stretching mode. The weak parallel band near 895 cm^{-1} , which had been assigned earlier by Barker et al. (6) to the $C_1\text{-H}$ bending mode of the β -linkage, was reassigned to antisymmetric out-of-phase ring stretching. This assignment was later adapted to wood spectra (96,107).

In wood spectra, the 1730 cm^{-1} band and its perpendicular polarization have been assigned to hemicellulose carboxyl or acetyl groups. This assignment by Marchessault was supported by Sumiya et al. (176), who found also that the infrared band intensities at 1160 and 895 cm^{-1} decreased with wood decay by fungi which were capable of hydrolyzing the cellulose $1,4\text{-O-}\beta\text{-D}$ -linkage. The infrared band of other wood components is also assigned by Maekawa and Kitao (103). Association of the 1160 cm^{-1} band with the wood structure will be further described.

The various band assignments recorded for coniferous wood spectra are listed in Table 7. Mostly the absorption band above 3000 cm^{-1} is reported to result from O-H valence vibrations (9). Water vapour is thought to account for 3652 cm^{-1} symmetric stretching, 1595 cm^{-1} bending and 3756 cm^{-1} antisymmetric stretching bands, whereas water in liquid form absorbs at 3450 , 1640 and 3615 cm^{-1} (163). Water absorption influences infrared spectral quality by changing hydrogen bonding, thereby causing a shift to lower frequency and increasing width and intensity of the absorption bands (62). The energy of hydrogen bonding is reported to be $3.7 - 4.5$ Kcal per mole for liquid water (62), while magnitude of the absorption band shift due to formation of hydrogen bonds is about 35 cm^{-1} per Kcal (9).

Polymeric associations, such as normally found in hydroxylic compounds, give rise to absorption bands in the $3400\text{-}3200\text{ cm}^{-1}$ range (9,148). The effect of solvents on

stretching vibrations of free and intra-molecularly bonded lignin hydroxyl groups may give absorption bands as high as 3550 cm^{-1} (120), as recorded in Table 7 .

In cellulose, all hydroxyl groups have been reported to engage in hydrogen bonding (114). Marchessault and Liang (110) attributed the 3440 to 3480 cm^{-1} band to intra-molecular hydrogen bonding and the other lower wave numbers to 3000 cm^{-1} to inter-molecular hydrogen bonding of cellulose. This complexity is shown in Table 7, where band locations for O-H absorption appear to vary greatly with the materials used. Differentiation of compounds based on these particular absorption frequencies is difficult or perhaps impossible.

Absorption bands in the 3000 cm^{-1} region are assigned to C-H stretching vibrations. In contrast, alkane groups exhibit C-H stretching at frequencies lower than 3000 cm^{-1} (9, 148). In a complex organic polymer state such as wood, absorption by C-H stretching may contain contributions from lignin, cellulose and hemicellulose, with all absorbing at almost the same frequency (9, 28, 107, 111, 156).

No absorbing species has been found for native wood spectra between 2800 cm^{-1} to 1900 cm^{-1} . Deuterium exchange of cellulosic -OH groups, however, reduces absorption frequencies by approximately $1/\sqrt{2}$ (105, 125), which provides a new band at $2300 - 2600\text{ cm}^{-1}$ with wood spectra (20). Compounds containing carbonyl and carboxyl groups give rise to strong absorptions at $1900 - 1550\text{ cm}^{-1}$,

which is ascribed to stretching of the C-O bond. In addition, groups β to the benzene ring absorb in the typical 1730cm^{-1} region of carboxyl groups (13, 32, 58, 87, 107). In wood, the perpendicular dichroism at this frequency has been assigned to the absorption of hemicellulose carbonyl or acetyl groups (96, 103, 107, 111). For separated lignin, the 1715 and 1735cm^{-1} bands have been assigned to aromatic ester and acetate groups, respectively (157). The bands from $1700\text{--}1550\text{cm}^{-1}$ are due mainly to absorptions of other carbonyl groups (32, 86, 107, 187). In this region, atmospheric moisture also absorbs at $1650\text{ to }1630\text{cm}^{-1}$ (9, 20, 107, 163), which further complicates matters. Lignin double bonds absorb at 1640cm^{-1} (187), and typical aromatic skeletal vibrations are shown between $1600\text{--}1400\text{cm}^{-1}$ (28, 75, 87, 156). For both wood and isolated lignin spectra the absorptions at 1600 and 1500cm^{-1} appear to be relatively independent functions.

Absorption bands below 1500cm^{-1} are considered to be in the complicated "fingerprint" region. For example, lignin absorption bands found at 1493cm^{-1} appear to represent double bonds (187), while methylene and methoxyl C-H deformations seem to absorb at $1470\text{--}1420\text{cm}^{-1}$. These, too, may be mixed with contributions from similar carbohydrate groups (9, 28, 58, 87, 120, 121, 206).

Assignment of wood absorption bands between 1400 to 450cm^{-1} wave numbers is complicated by the multiplicity of wood component absorptions which appear at similar wave numbers. Obviously, the many problems of band assignment necessitate further study.

MATERIALS AND METHODS

I. Wood Specimens

Wood tissues from four Canadian coniferous species were used in the experiments. Sitka spruce [Picea sitchensis (Bong.) Carr.], Douglas fir [Pseudotsuga menziesii (Mirb.) Franco] and grand fir [Abies grandis (Dougl.) Lindl.] mature stems were from Vancouver, B.C., while the balsam fir [Abies balsamea (L.) Mill.] sample originated from St. Michels des Saints, P.Q. and was supplied by the Pulp and Paper Research Institute of Canada.

Immediately after felling, stem sections were taken at breast height, wrapped in polyethylene sheet and transported to the laboratory where they were stored in the cold under conditions maintaining original tree moisture.

In addition to taxonomic variation, stems were selected to meet other experimental needs, such as suitable growth characteristics for providing acceptable microsections. Sapwood zones were used for reasons of minimizing spectrophotometric interference from extractives (20), and because of greater assurance in preparing quality microsections (26, 76). To further explore wood zone differences, a Douglas fir sapwood sector containing compression wood was examined. Since dehydrating extractive treatments were not used, results are thought to represent native wood properties.

Serial tangential microsections (0.5 x 2- in. surface area) were obtained in the usual manner from water saturated, but otherwise untreated, wood blocks. Alternate 20±5 micron

and 100 $\pm$ 10 micron microsection blanks were prepared, which provided 15 to 18 sections of both thicknesses for each growth increment examined. Thin sections were used for experiments to be described, while the thicker sections were examined in other work. Compression wood was especially difficult to manufacture to acceptable thicknesses. In all cases, care was taken to insure exact alignment between grain direction and the knife cutting edge.

The sampling plan within two growth increments each of Douglas fir and balsam fir, the woods most studied, is shown in Table 8.

II. Chemical Treatments

Although many tests were done with untreated wood specimens, it seemed useful also to alter some features of wood composition. Thereby, requirements for maintaining original energy transfer patterns were briefly examined, and the validity of certain infrared band assignments was verified.

Delignification to various levels was done according to the chlorite method as modified by Wise et al. (199, 200) and Uprichard (189). Wood microsection blanks contained in 50 ml flasks were immersed in 10 ml of buffer solution (48 g sodium hydroxide, 144 g acetic acid, 1920 ml water), then 1 ml of 27% (w/v) aq chlorite solution was added. The loosely stopped flasks were heated in a water bath at 76 $\pm$ 1°C with gentle mixing at 1/2 hr intervals, at which times additional 1 ml amounts of chlorite solution were added. At each of six treatment times up to 4 hr one flask was removed, cooled in an ice bath for 5 min and 15 ml of cold, distilled water

was added. The samples were then washed with ten-10 ml portions of aq 1% acetic acid and finally two-5 ml portions of acetone. Samples were air-dried and made ready for testing.

A companion set of wood sections processed 4 hr by the method described was further treated with 1, 5 or 17.5% sodium hydroxide solution. The fragile nature of thin wood sections necessitated special handling. Individual sections were laid flat on glass microslides with ends beneath cover glasses, but with mid-sections exposed. The assembly was immersed in the base for 45 min at 25°C. Samples were washed while on the glass with 100 ml of distilled water, 10 ml of aq 10% acetic acid, 200 ml of distilled water and finally 50 ml of acetone. Filter paper was placed over the sections, microslides were laid over the surface and air-drying was continued for at least three days before the treated samples were recovered and tested.

Wood microsections provide too little material for determining lignin by conventional means. A technique (20) employing ratios of specific infrared absorbance bands, such as 1500/2880 or 1420/2880 cm^{-1} or other wave numbers, was used with untreated samples. Comparative absorbance at 1500 cm^{-1} wave number of matched samples was used for assessing percentage residual lignin of delignified samples.

III. Micro-mechanical Techniques

Microtensile tests (65) were done to determine wood tissue ultimate strengths. Specimens were prepared from 20 $\pm$ 5 micron tangential microsection blanks. Grain direction was defined and longitudinal 2.5 x 220 mm rectangular strips

were cut by a specially machined die fixed to a 1/2-ton arbor press. In order to avoid failure at grips, test specimen ends, but not the mid-section, were saturated with polyvinylacetate and reinforcing papers were applied to the tangential faces. Testing was done on a recording, table model Instron housed in a standard conditioned room ($72 \pm 1^{\circ}\text{F}$ dry bulb and $65 \pm 1^{\circ}\text{F}$ wet bulb). Specimens were gripped at exactly 0.5-in. jaw spacing, while 30 and 50 foot-pound torques were applied to tighten grips with earlywood and latewood specimens. Load was applied with constant rate of strain at 0.45-in /min, chart speed was 1-in /min and sensitivity of chart reading was 2 g. Two replications constituted a determination. Ultimate tensile strain was read directly from recorder charts, and portional strain and associated stress values for tests to be described were determined from these data. This assumes a relationship between stress-strain behaviour in this customary test and that occurring at more rapid rate of loading.

Some comparative stress relaxation tests were done with the system described and at rate of strain of 0.45-in /min. This required approximately 2 sec for loading to 50% of ultimate strain. The machine was stopped at this position (t_0) and the load required to maintain constant deformation was recorded automatically over a period of 40 min. Fractional stress relaxation is expressed as

$$\frac{\xi(t)}{\xi(0)} \quad [2]$$

where $\xi(t)$ is stress at any time, t ; and $\xi(0)$ is initial stress at initial time, t_0 . This differs from the conventional expression

$$\frac{\delta(t)}{\delta(1)}$$

as introduced for mathematical convenience by Kitazawa (80), where $\delta(1)$ refers to stress at expiration of one minute following completion of loading.

The nature of infrared recording spectrophotometers is such that space is not available for accommodating specimens held in conventional test engines. New systems were needed to apply controlled loads for wood tissue relaxation studies. Early trials were done with an apparatus providing ramp-function excitation, while the main experiments as reported here included simulated step-function excitation as derived from a second apparatus. For completeness, both instruments are described and some comparative results are given. It was not the purpose of the present study, however, to examine effects of loading history. In addition, a relatively simple third system was devised for doing creep studies with wood microspecimens exposed to the infrared field.

The prototype apparatus for examining effects under constant deformation is shown in detail as Fig.1-A and mounted in test position in Fig.1-B. The principle involves controlled thermal expansion of metal holders (A_1) which transmit preselected spatial adjustments through a guided (A_2) rod (A_3) to separated surfaces (A_4) on which the specimen (A_5) is affixed. The flanking holders (A_1) are hollow copper tubes held as a structure by welded iron end plates. Tube inside diameter is 1/2 in. and length is 1 ft. The bottom tube ends are sealed and quartz radiant heater rods (A_0) are inserted. The tube surfaces are insulated with asbestos and further wrapped with

cotton to limit radiant heat effects. An aluminium rod (A_3) is fastened to the top plate and kept in alignment by guides (A_2). Hard maple blocks (A_4) are fixed to the assembly with spacing of 1/2-in. at $25 \pm 1^\circ\text{C}$, which is the initial span length for specimens (A_5). Linear expansion over the span was calculated according to setting of a powerstat used to control heating of the rods (A_0). Amount and rate of strain were examined by mounting a Budd metal film strain gauge on a specimen put under test. The method was shown to provide uniform, ramp-function excitation requiring 10 to 12 min to reach 1% strain by raising the system from 25 to 45°C .

A second apparatus was designed for observing relaxation effects following short-time loading, which approaches step-function excitation (Fig. 1C and 1D). In principle, stressed springs (C_0) released by a clutch (C_1) activate a sliding plate (C_2) for rapid transmission of controlled (C_3) extension to a mounted specimen (C_4). The dove-tail, sliding plate (C_2) is linked to the upper part of the supporting body by two strong springs (C_0). A micrometer (C_3) with accuracy of ± 0.0001 in. is attached to the supporting body and used to preset the desired deformation. The sliding plate performs before a window with motion controlled by two mechanisms; the micrometer clutch and the release clutch (C_1). In operation, both clutches are released before mounting the specimen. Distance between the sliding upper plate (C_2) and fixed lower plate is adjusted to 0.5 ± 0.0005 in. by turning the micrometer and

forcing its piston forward. Both clutches are then engaged and the sample is mounted across the test span. The micrometer clutch is released, the piston is retracted according to setting on the micrometer and the micrometer clutch is re-engaged. The test is executed by triggering the release clutch, the sliding plate moves to the position limited by the piston and the release clutch is then re-engaged to hold the specimen in the spatial adjustment attained. Experiments employing a linear variable differential transformer have shown that approximately 10^{-3} sec is required to attain 1% strain with the method.

The third apparatus was designed for rapid application of constant loads, and thereby observation of creep effects. The mechanism is simply a bored plate fitted to the instrument holder, with spacers fixed above and below the aperture. In operation, the specimen is mounted between the upper spacer and a free-hanging thin, triangular copper sheet with small hole at the apex. The assembly is placed in position and a known weight is added with instant release.

With all test systems, specimen fibre direction was found by tearing the edge and this was carefully aligned with the loading direction. Thereby, longitudinal wood tissue features served as reference for infrared polarization measurements. This coincidence of biological alignment with direction of loading is a powerful point of the experiment, as contrasted to randomly ordered molecular (plastic) and particle (paper) structures where

the polarization reference only relates to loading direction. Quick-setting Budd GA-1 strain-guage cement was found to be a suitable adhesive for fixing specimens to sample holders.

Three strain levels, 30, 50, and 80% of ultimate strain, were examined in preliminary molecular stress relaxation experiments with balsam fir wood tissues. These strains were chosen to represent elastic, intermediate and plastic regions as shown by typical stress-strain curves developed in static testing. The 50% strain level was selected for the main experiment, since dichroism, while similar, was not always as well distinguished at the lower strain level and specimens did not always survive for required times at the higher strain level. Bach (3) described this effect of static fatigue under constant tensile strain for thicker wood tissues, and predicted survival with loading at 90% of estimated ultimate strain.

Molecular creep tests were done only on balsam fir tissues with stress loads calculated to provide 50% of strain to failure.

Effects of temperature and moisture were not examined as variables of the present experiment. Measurements on wood tissues exposed to the infrared field showed that temperature was $40 \pm 0.5^{\circ}\text{C}$ and moisture content $6 \pm 1\%$ (moisture-free basis) when dichroism was determined.

IV. Optical Techniques

A critical feature of the present study is accurate measurement of changes in dichroism. The property characterizes of materials, including solid organic macromolecular conformations,

which preferentially absorb energy according to coincidence with structure orientation. Observations may be made when random field energy vectors are resolved in a plane, as by polarization, and superimposed on the material structure. At a particular frequency the probability for maximum energy transfer occurs when the directed energy plane is aligned with the fixed vibrating moment direction of the structure. Conversely, minimum energy transfer occurs when the two directions are perpendicular. Although the property should appear at numerous points of the electromagnetic spectrum, its study has been almost entirely restricted to the infrared region.

Infrared measurements were made with a Perkin-Elmer 521 grating spectrophotometer equipped with linear absorbance attachment and Honeywell Electronik 19 external-strip chart recorder. Atmospheric moisture effects were removed by continuous purging with dry air. A Perkin-Elmer Wire Grid Polarizer was used to resolve the sample beam. Polarization errors are thought to be negligible, since 35% of the incident radiation is transmitted at 99% efficiency across the range studied. To compensate for loss of sample beam intensity, an attenuator was used to reduce intensity of the reference beam.

Possible errors due to sample birefringence (99, 149, 205) were eliminated by passing the sample beam through the specimen before polarization. Machine polarization and decline of base line were corrected by positioning both polarization

and specimen axes at 45° to the spectrophotometer slit (Fig.1) for obtaining the parallel component. The perpendicular measurement was obtained by setting the polarizer dial at 90° to the specimen axis. By coincidence, the polarizer arrangement in our technique is also that published recently by Read and Stein (149), who examined polyvinyl chloride films.

The apparatus with specimen mounted is positioned in the instrument as shown in Fig.1. In operation, the mechanical loading mechanism is activated and spectrophotometric scanning is started. By automatic setting, regions of interest are recorded at $120 \text{ cm}^{-1}/\text{min}$ while the speed suppression switch is operating. The drum is set to return automatically to the starting point, polarization angle is changed and a second trace is recorded. Thereby, data for calculating a single dichroic ratio may be obtained at one to three minute intervals. This time required for obtaining measurements is a limitation of the technique, especially for studying effects immediately following mechanical excitation.

The dichroic ratio $(D)^*$ is expressed (205) as

$$D = A_{\perp}/A_{\parallel} \quad [3]$$

where $A_{\perp}$ is absorbance perpendicular and $A_{\parallel}$ absorbance parallel to the loading direction which, by specimen arrangement, coincides with the fibre axis. Thus, dichroic ratio and orientation angle (θ) for molecular transition moments relate to the fibre axis as

$$D = A_{\perp}/A_{\parallel} = 0.5 \tan^2 \theta \quad [4]$$

* $D=1$, no orientation. $D < 1$, parallel orientation. $D > 1$, perpendicular orientation.

Equation [4] provides means for comparing between spectral molecular motion activities (θ) and mechanical stress relaxation ($\delta(t)/\delta(0)$, [2]) observed under the same experimental conditions.

A second technique, X-ray diffraction, was employed in the study for assessing treatment effects on the native wood structure. A Phillips Eindhoven X-Ray diffractometer was used, which generates a $\text{CuK}\alpha$ beam at $1.54 \text{ \AA}$ wave length. The diffracted ray is filtered, passed through a slit to a goniometer and intensity is recorded automatically. Measurements were made on matched, air-dry specimens mounted on glass plates fitted into the sample post. Diffraction patterns were recorded for 2θ angles between 5 and 35° , with scanning speed at $1^\circ/\text{min}$.

Estimates of crystalline fraction were obtained by analyzing X-ray diagrams according to the method of Jayme and Knolle (67). Briefly, the area subtended by a triangle formed between the interpeak minima and base line is considered background intensity arising from disordered diffraction (d). Subtracting this amount from total area under the curve provides an intensity measurement for ordered diffraction (o). Specimen crystallinity, termed total crystallinity per cent (C,%), is obtained by the simple calculation

$$C, \% = o/(o+d) \times 100 \quad [5]$$

Means are available also for estimating contributions from the various planes.

Electron microscopy was used to examine lignin distribution patterns in wood tissues following various periods

of delignification. Cross sections of 800 Å thickness were prepared from test specimen fragments embedded in 80:20 methyl and butyl methacrylate and stained with 1% aq potassium permanganate. A Hitachi-Hu-11-electron microscope was used at magnification of 6000 x.

RESULTS

Dichroism in the infrared region was used to derive information on wood molecular structure, such as initial biological conformation and reorientation adjustments during accommodation of external mechanical excitation. This introduces "molecular rheology" to wood science. Presently, band assignments are accepted as established by other means, whereby interpretations are only as valid as certainty of assignment. A second use of dichroism is for reexamining assignments already given particular absorption frequencies. This use is examined briefly, since wood "molecular rheology" may contain new means for more rigorous proofs of structure.

Coniferous wood tissues yield more than twenty distinct absorption bands between 3530 and 450 cm^{-1} wave number (2.8 to 21.0 μ wave length) as summarized in Table 7. About one-half, especially frequencies assigned to certain carbohydrate vibrations, are described as polarized (96, 97), either parallel or perpendicular to the major biological axis. The present study does not attempt to follow all these opportunities, but does aim at including specific functional groups for representing each of the three major

wood components; cellulose, lignin and some hemicellulose fractions.

Absorption at 1730 cm^{-1} wave number ($5.8\text{ }\mu$) was used to characterize a hemicellulose activity. The frequency is associated with C=O stretching vibrations of acetyl and/or carboxylic acid groups (32, 87, 98), but may contain minor contributions from lignin β -keto structures (13, 32, 58) or other groups (32) as demonstrated for lignin isolates. The assignment for wood tissues of the present study refers to C=O of -COOH and -COOCH₃ groups in 4-O-methylglucuronoacetyl xylan. If the xylan axis parallels wood ultrastructure and the parent functional body is oriented perpendicular to the xylan chain, polarization perpendicular to the biological axis would be predicted for the 1730 cm^{-1} mode. This has been shown previously with wood tissues (96), and is reaffirmed by studies of wood xylan films(111).

Lignin activity was observed at 1500 cm^{-1} wave number ($6.6\text{ }\mu$). This characteristic C=C stretching vibration is unequivocally assigned to lignin aromatic skeletons, including those of the coniferous wood matrix (107, 156). Other lignin absorption bands do not appear as attractive, due to interference by water and polyphenolic extractives or lack of specificity. Either initial or induced polarization is prerequisite to dichroism, and polarization of the 1500 cm^{-1} lignin mode is denied (54,107). As will be shown, lignin orientation effects do occur.

A second carbohydrate activity was studied by observations at 1160 cm^{-1} wave number ($8.6\text{ }\mu$). This strong absorption

frequency appears to be closely associated with polysaccharide main chain structure. Exact assignments are controversial, while regional masking from complex interrelated vibration modes has raised questions on validity for any specific assignment (60). According to various interpretations the frequency represents C-O-C bridge asymmetric stretching vibrations (107), or bending for the C-OH group (206). Since interpretations parallel main carbohydrate chains which follow the biological axis, it is not surprising that the band shows strong parallel polarization (107). For reasons to be described, we prefer the bridge stretching assignment which has been given for coniferous wood tissue polysaccharides (96, 107).

The infrared polarization spectra of regular wood and compression wood of Douglas fir are shown in Fig. 2.

The range in orientation of the chemical components of four native woods, earlywood and latewood only and Douglas fir compression wood is indicated in Table 9. From the data, the relationship between orientation angles calculated from 1500 and 1160 cm^{-1} dichroic ratios is linear as shown in Fig. 3 and significant at the 1% level as

$$Y_{\theta} = 47.95 + 0.15 X_{\theta} \quad [6]$$

$$r = 0.75^{**} \quad N = 38 \quad SE_E = 1.43$$

where Y_{θ} is the orientation angle at 1500 cm^{-1} (degree)

X_{θ} is the orientation angle at 1160 cm^{-1} (degree).

The relationship between orientation angles at 1500 and 1730 cm^{-1} is also linear and highly significant at the 1% level as

$$Y_{\theta} = 100.25 - 0.79 X_{\theta} \quad [7]$$

$$r = 0.73^{**} \quad N = 37 \quad SE_E = 1.48$$

where Y_{θ} is the orientation angle at 1500 cm^{-1} (degree)

X_{θ} is the orientation angle at 1730 cm^{-1} (degree).

For treated specimens, the lignin contents are expressed as per cent of original lignin in non-treated specimens and are shown in most of the later figures and tables describing the relationship between delignification and molecular activities. These lignin contents seem reasonable and compare favourably with values reported on wood tissues by Stone and Clayton (174). Electron photomicrographs for control and delignified specimens of balsam fir latewood as shown in Fig. 4 indicate that the delignification was rather mild. After 60 min treatment, the lignin was not significantly removed from cell walls. Even after 240 min, lignin still remained in the wood tissue, with ordered organization still retained. The electron photomicrographs show that the lignin was removed uniformly from the cell wall and middle lamella. Tensile failure patterns for wood crosssections following 240 min treatment show rupture across the fibers, not in the middle lamella region.

Delignification appears to change dichroism of 1160 and 1730 cm^{-1} bands. The relationship between these dichroic ratios and the lignin content of specimens is shown for earlywood and latewood of Douglas fir and balsam fir in Fig. 5.

The X-ray diffraction patterns for Douglas fir earlywood and latewood are shown in Fig. 6. The diffraction patterns for both earlywood and latewood of balsam fir, which are not presented, were similar to those of Douglas fir latewood.

Delignification of Douglas fir specimens changed the X-ray diffraction pattern based on the relative intensity of 002 and $(101 + 10\bar{1})$ peaks as shown in Fig. 6, while the same treatment did not significantly change the diffraction pattern of balsam fir. The per cent crystallinity in respect to the lignin content of Douglas fir and balsam fir wood tissues is shown in Fig. 7.

When the per cent total crystallinity of the Douglas fir and balsam fir specimens is plotted against the initial orientation angle derived from the dichroic ratio at 1160 cm^{-1} , a highly significant linear relationship is obtained as shown in Fig. 8 and expressed as follows

$$Y = 87.6 - 0.91 X_0 \quad [8]$$

$$r = -0.90^{**} \quad N = 23 \quad SE_E = 3.59$$

where Y is the per cent total crystallinity

X_0 is the orientation angle at 1160 cm^{-1} (degree)

Results of molecular motions of 1160 cm^{-1} , 1730 cm^{-1} and 1500 cm^{-1} components of Douglas fir across an annual increment during stress relaxation are shown in Tables 10, 11, 12 and Fig. 9, 10, 11, respectively. The results for balsam fir, although not presented in figures, are shown in Tables 13, 14 and 15 for 1160 cm^{-1} , 1730 cm^{-1} and 1500 cm^{-1} components, respectively.

The comparison of the results on the molecular motions for wood components during creep and stress relaxation of balsam fir is shown in Fig.12. Effects of excitation-time on molecular relaxation of the 1730 cm^{-1} component is shown in Fig.13.

The experimental results on the effect of removing lignin and hemicellulose on the molecular relaxation of Douglas fir earlywood are shown in Tables 16, 17 and Fig. 14, 15 for the 1160 cm^{-1} and 1730 cm^{-1} components, respectively. Tables 18, 19 and Fig. 16, 17 show the molecular relaxation of 1160 cm^{-1} and 1730 cm^{-1} components of Douglas fir latewood.

The results for the molecular relaxation of 1160 cm^{-1} and 1730 cm^{-1} components for treated balsam fir earlywood are shown in Tables 20 and 21, respectively. The results for latewood of the same species are shown in Tables 22 and 23, respectively, for 1160 cm^{-1} and 1730 cm^{-1} components.

The trends for the stress relaxation of the delignified wood specimens, regardless of earlywood or latewood, are similar. The difference between the tree species is also small.

The results on physical-mechanical stress relaxation of Douglas fir earlywood and latewood are shown in Tables 24, 25 and Figs. 18, 19 respectively, while those for balsam fir earlywood and latewood are shown in Tables 26 and 27.

DISCUSSION

Despite its complexity, wood is a naturally ordered polymer complex. The main chains of cellulose and hemicellulose in the cell walls preferentially align parallel to the fibril direction. Therefore, wood carbohydrates can be treated as polymers of nearly perfect, but varying axial orientation (205). This bio-orientation, plus the high degree of carbohydrate linear polymerization, makes wood an ideal substance for examining molecular reorientation effects. In addition, some wood chemical components can be removed in stepwise fashion without seriously impairing the basic cell wall organization. This provides means for examining individual molecular motions of certain wood chemical constituents. These advantages do not exist with other polymers examined earlier (48, 83, 84, 85, 92, 133, 135, 149, 170, 171, 172).

Because the nature and techniques of this work are new to wood science research, some results which relate directly to wood fine structure but indirectly to the topic, require explanation. Therefore, this discussion begins with exploration of the fine structure and orientation of wood components, and then examines the time dependent molecular behaviour observed in stress relaxation. Finally, this molecular behaviour is related to the energy transfer mechanism in wood.

I. Orientation, Crystallinity and Systematic Structure of Wood

One of the major chemical components of wood, lignin is generally believed to be a three-dimensional polymer (199) without apparent crystallinity or orientation. Experimental results given in Table 9 demonstrate lignin dichroism at

1500 cm^{-1} . Lignin dichroic ratios range from 0.7 to 1.3 for the various untreated, unstressed wood tissues of four coniferous woods including specimens from different seasons of growth. Thus, the lignin portion of the native wood matrix is proven to be oriented to some degree. This finding agrees with that of Lange (90), who observed ultraviolet dichroism of lignin for European spruce, but disagrees with later interpretations of Frey-Wyssling (40), Harrington et al. (54) and Marchessault (107) who claim that lignin is not oriented within wood.

The controversial finding on lignin orientation in wood can be partly explained by dissimilarity of the experimental materials used. Tangential sections, as used in this experiment, allow sequential investigation across growth zones. This approach maximizes the opportunities for finding differences, since most properties of wood vary more radially than tangentially. As shown in Table 9, the average 1500 cm^{-1} dichroism of annual increments investigated were 0.91, 0.98, 1.09 and 0.93 for Sitka spruce, Douglas fir, balsam fir and grand fir woods, respectively. The grand average for these four values is 0.98, which is consistent with proving an amorphous structure by infrared dichroism (205). These average values obtained on earlywood and latewood tangential section should be similar to those obtained by exposure of radial sections. Therefore, statements on lignin non-orientation by Marchessault (107) and Harrington (54), who used radial sections as experimental materials, are understandable.

As shown also in Table 9, the average lignin dichroism

differs for earlywood, latewood and compression wood. This suggests that lignin orientation in wood depends greatly on tree species, portion of growth zone examined and perhaps other effects of growth.

Besides the aforementioned phenomena, lignin orientation in woody plants was found to be linearly associated with the carbohydrate structure at the 1% level of significance (see Formulae 6 and 7, and Fig.3). This is the only evidence available to date that relates lignin and carbohydrate orientation systems in wood.

The X-ray diffraction patterns shown in Fig.6 present other new information. Although the diffraction pattern for compression wood is not given in the same figure, the $(101+10\bar{1})$ intensity in native Douglas fir wood tissue specimens decreased in the following order, compression wood, earlywood and latewood. This order indicates that the wood X-ray diffraction pattern is related to lignin content. The quantity of lignin in wood specimens has been shown (21, 22) to follow the same order as intensity of diffraction $(101+10\bar{1})$ found in this investigation.

The $(101+10\bar{1})$ peak in the X-ray diffraction pattern was assigned to the diffraction of crystalline cellulose as found in the tangential plane, while the 002 peak relates to crystalline diffraction corresponding to the plane paralleling the fibre axis (123, 150, 159). Hence the crystalline structure of wood must be different in the three tissues mentioned. The stronger the peak in the $(101+10\bar{1})$ plane, the greater the amount of crystalline cellulose in the tangential direction. This agrees with results of Kocon (82), who reported that the crys-

talline cellulose of spruce and larch compression wood is preferentially oriented tangential to the fibre axis. Furthermore, crystalline cellulose from narrow annual rings has been found to be oriented more parallel to the fibre axis than that from wide annual rings of the same pinewood log (81). These results are also supported by Okano (134), who mathematically characterized the orientation of crystalline cellulose in four Japanese coniferous species by 002 plane diffraction. Crystalline substances in the cell wall were found to be distributed non-uniformly around the fibre axis.

Based on the above observation, it seems reasonable to conclude that wood X-ray diffraction shows the same dependence on tree species, growth zone portion (earlywood or latewood) and tree response, as found for wood infrared dichroism.

When lignin is removed stepwise from wood tissues, the X-ray diffraction patterns for Douglas fir, as presented in Fig.6, show a significant decrease of $(101+10\bar{1})$ peak intensity in comparison to the corresponding 002 peak. Decrease of the $(101+10\bar{1})$ peak is consistent with diffraction patterns of sodium chlorite delignified woods as shown earlier by Maekawa and Kitao (103) and Pew and Weyna (142). Accordingly, the $(101+10\bar{1})$ plane crystalline cellulose must be partially penetrated by lignin. This supports results on infrared dichroism of untreated wood tissue specimens, which suggest that orientation of lignin and cellulose is linearly related as shown in Fig.3, while delignification changed the 1160 cm^{-1} and 1730 cm^{-1} orientation (Fig.5). Therefore packing distances between lignin and carbohydrates in the paracrystalline to crystalline regions

must be very short. These findings provide the association necessary for establishing the much postulated lignin-carbohydrate bonding. The biological suggestion is an overlapping period for formation of cellulose and lignin, or as suggested by Marx-Figini (116) crystallization and biosynthesis of cellulose need not take place simultaneously. Thus even if lignin is formed after cellulose, the coexistence of lignin and cellulose in crystalline regions is highly possible. This reasoning is also indirectly supported by the most recent finding of Scott et al. (160) that the secondary wall of spruce earlywood tracheids contains over 70% of the wood lignin.

Based on the above evidence, it is reasonable to postulate two crystalline structures with different orientations in wood tissue. One is the basic model which aligns axially and diffracts in the 002 plane. The other is the crystalline cellulose which is oriented tangentially in the fibre axis and diffracts in the $(101+10\bar{1})$ plane. Thus, the crystalline structure of wood can be considered as having an 002 crystalline core which is surrounded by paracrystalline layers which yield the $(101+10\bar{1})$ plane, possibly rich in lignin. This consideration is consistent with wood ultrastructure as demonstrated by electron microscopy (68, 70).

Mann's (105) explanation of the difference between infrared and X-ray crystallinities obtained from the same cellulosic materials supports the existence of a paracrystalline phase. X-ray crystallinity is higher than infrared crystallinity because the former also measures the blurred crystal versions

which are amorphous to the infrared, i.e., more easily accessible during deuterium oxide exchange. Thus the quantity of hydroxyl groups revealed by infrared crystallinity are hydrogen bonded in the regular crystalline manner which could be a reflection of the 002 intensity in the X-ray diffraction curve. On the other hand, accessible hydroxyl groups included in X-ray crystallinity are reflected in the $(101+10\bar{1})$ peak intensity.

Keeping Mann's interpretation in mind, and considering that the magnitude of the $(101+10\bar{1})$ peak from wood tissues varies from species to species and tissue to tissue (Fig. 6 and 7), the conclusions of Nelson (127) and Preston and Allosopp (144) are not surprising, as only little change in the X-ray diffraction diagram was observed on wood delignification. Similar results were found on delignification of balsam fir wood in this experiment (Fig. 7).

The increase of 002 peak intensity of delignified specimens is also observed in this experiment (Fig. 6 and 7). Probably this is caused by a crystallization of the paracrystalline cellulose surrounding the micelle (64, 191, 193, 195). However, the interpretation of Nelson (127) as mentioned earlier should be kept in mind. In addition, hindrance of the $(101+10\bar{1})$ paracrystalline layer to diffraction from the 002 core in wood should not be passed over. The presence of this hindrance is indicated by the fact that the X-ray wavelength used is only $1.54 \text{ \AA}$, which is much shorter than that expected for $(101+10\bar{1})$ paracrystalline cellulose. Thus a specimen which has a thick paracrystalline zone $(101+10\bar{1})$ in plane, such as Douglas fir

earlywood, will greatly mask diffraction from the 002 core. Delignification removes this hindrance and by so doing exposes more 002 core for reflection.

The evidence mentioned above proves the penetration of lignin into at least surface layers of the commonly accepted crystalline structure, thereby forming the so called paracrystalline zone. The lignin which exists inside this zone must be mainly oriented in the same direction as the cellulose and hemicellulose. Association between lignin and carbohydrate provides a systematic structure for wood substance in transverse direction to the microfibrils. This suggests a new structure for wood microfibrils.

The wood microfibril centre could be a crystalline core capsulated by paracrystalline layers which are amorphous with partly ordered to completely random organization. The crystalline core could be a pure cellulose structure of crystalline perfection (56, 104) or a fringed-micelle system (41), while the paracrystalline layers may contain imperfections as less ordered crystalline cellulose in admixture with oriented hemicellulose and lignin. The ordered amorphous zone consists mainly of oriented cellulose, hemicellulose and lignin while the completely amorphous region is dominated by non-oriented lignin. This systematic structure would permit a zone of gradual transition from high crystallinity to a diffuse state. This also provides a zone for physical association or bonding between carbohydrate-carbohydrate, carbohydrate-lignin and lignin-lignin.

Such an interfacial system could be important to energy transfer in wood.

II. Wood Molecular Relaxation

1. Patterns of Wood Molecular Relaxation

It is understood that although single infrared functions are not entirely descriptive of wood chemical components, as a matter of convenience hemicellulose, lignin and cellulose will hereafter be referred to as components absorbing at 1730, 1500 and 1160 cm^{-1} wave numbers, respectively. Since these chemical components are likely arranged systematically in wood, their time dependent molecular motions are apt to be inter-dependent.

The experimental results of this work show different patterns of molecular relaxation for wood lignin and carbohydrate fractions.

In the course of stress relaxation, the carbohydrate components represented by 1160 cm^{-1} and 1730 cm^{-1} bands show initially a marked reduction of dichroic ratio to the parallel position, followed by recovery to the equilibrium level after about 20 min relaxation time according to experimental conditions used in the present study.

The two-stage motion observed with carbohydrates is suggested as the course of molecular relaxation. The first stage begins at equilibrium, before the specimen is stressed, and extends immediately to a minimum dichroic ratio. The second stage starts at the end of the first stage and extends to recovery of equilibrium. The continuing presence of numerous small irregular peaks in the relaxation curve is considered to be

a damping effect which will be discussed later.

On the other hand, the lignin dichroic ratio calculated at 1500 cm^{-1} (Fig. 11), moves immediately to the perpendicular position upon the application of an external force. The maximum dichroic ratio of lignin, in most cases, coincides with termination of the first stage described above, i.e., the time at which the other two components attain minimum dichroism. In the second stage, the lignin component returns to the equilibrium position within about 20 min. This motion pattern is strong evidence refuting previous concepts that lignin is a rigid, component structure incapable of deformation (79). It is further suggested that at least some wood lignin must have ability for reorientation complementary to that of carbohydrates, or its conformation as shown in Fig. 11 would be unlikely to occur. Above all, the results suggest that lignin plays an important role in modifying wood stress relaxation. This suggests that removing lignin should alter relaxation patterns.

Although it is not the prime purpose of this experiment, the molecular motion pattern measured as dichroism at 1160 cm^{-1} does provide further evidence confirming correctness of the band assignment to the cellulose 1,4-0- β -D-linkage as reported by Marchessault (107).

2. Varying Molecular Relaxation Across Annual Increments

Intra-incremental differentiation of 1160 and 1730 cm^{-1} relaxation is difficult, since patterns are very similar (Fig. 9 and 10). Examination of the data show, however, the main difference to be in the time required to regain equilibrium. The 1160 cm^{-1} component reaches equilibrium earlier than the

companion 1730 cm^{-1} . This observation indicates that the motion patterns for 1730 and 1160 cm^{-1} components are different. Consequently, hemicellulose could prevent cellulose from fast recovery of equilibrium. This possibility will be examined further in a later section.

The variation of molecular motion patterns across annual increments suggests some biological implication. Similarity in conformational spectra of the 1160 cm^{-1} and 1730 cm^{-1} components (Tables 10, 11, 13 and 14, Fig. 9 and 10) for specimens of the first formed earlywood and the preceeding last formed latewood suggests that these wood tissues originated from same cambial cells as postulated by Wilson and associates (198,201). Also similarity in the conformational spectra of 1160 cm^{-1} and 1730 cm^{-1} components in the apparent transition wood (about 50% to 60% position) is noteworthy. The rapid rate of decrease in dichroism for the first stage and short equilibration period suggest that the two species studied have molecular similarities in transition zones.

In the case of the 1500 cm^{-1} component (Tables 12 and 15, Fig.11), the first stage rate of dichroic ratio increase to the perpendicular position is slower for earlywood specimens than for latewood specimens.

These results lend strong support to the postulation that differences within wood zones lie at a molecular level.

3. The Wood Molecular Relaxation Mechanism

Based on results discussed thus far, a tentative mechanism may be described for molecular relaxation of wood specimens.

The mechanism involves two stages of molecular motions

including all three major wood components. In the first stage, the two carbohydrate components as represented by 1160 and 1730 cm^{-1} band activities, independent of their state of crystallization, promptly yield in the direction of stress as shown by attainment of dichroic minima, while the lignin component (1500 cm^{-1}) rotates to a position perpendicular to the direction of stress as evidenced by maximum dichroic ratio. At start of the second stage, the lignin component begins yielding in the stress direction and regains equilibrium. The two carbohydrate components, on the other hand, move against the stress direction with decreasing damping amplitudes and eventually reestablish equilibrium.

On receiving external excitation the wood macromolecular structure maintains an "internal state of equilibrium". This equilibrium state is achieved by short and long term molecular events through movements of the carbohydrate and lignin components in opposite directions. Over prolonged time, all molecular structure has reattained a stable state.

This mechanism of molecular relaxation questions the postulation of Nissan (130), that the rheological behaviour of cellulosic materials is solely due to activity of hydrogen bonds which are proposed as storing all energy in the system. Experimental results of this thesis show that stretching of the 1,4-0- β -D-linkage (covalent bond) is also involved, if the usual assignment of the 1160 cm^{-1} band is accepted. Other evidence arises from the apparent activation energy of wood and delignified wood in stress relaxation, which is found to be 35 to 56 and 17 to 53 Kcal/mole, respectively (42). This is far higher than

hydrogen bonding energies (137). It appears that Nissan's postulation is an oversimplification of complex phenomena.

Furthermore, since the stretching of 1,4- β -D-linkage is involved, the 10.3 Å spacing of cellobiose units must be considered to arise only under one condition of stress, strain and time of excitation.

When the above mechanism derived from stress relaxation studies is compared with creep phenomenon, it is interesting to note that molecular motions of the creep specimen are essentially the same as those of stress relaxation. This molecular mechanism for creep behaviour is consistent with the electron microscopic observation made by Senft (162), who found that long-term effects of a creep-inducing stress applied along the grain are not registered by any changes in microfibrillar angle. These experimental results suggest that the basic molecular mechanism of wood rheological behaviour is similar (Fig. 12) for external forces applied as constant strain or constant stress.

In addition, experiments on the effect of loading time on the molecular relaxation of wood gave interesting results. As shown in Fig.13, the dichroic ratio decreased to a parallel position after loading by a ramp function system. This terminated either at the end of loading (earlywood) or several minutes after the end of loading (latewood), then the dichroic ratio increased to nearly the original value. Identical molecular motion curves were found for step-loading experiments with both earlywood and latewood. This evidence suggests that wood is an excellent material for dissipating energy from external excitation. Regardless of the excitation time, the process of dissipation

is not disturbed, but loading history may be confused with relaxation.

III. Relationship Between Wood Molecular Relaxation and Stress Relaxation

In the previous discussion, the compensating molecular motions of different wood components are suggested as means for maintaining internal equilibrium. These motions are expected to result in loss of energy by internal work, which should be observed as phenomenological relaxation.

Physical stress relaxation is one phenomenological observation of relaxation. A means for studying molecular relaxation is to test and compare results with wood tissue specimens modified in varying ways. Thereby, delignification provides a gradual modification of the three-component wood system to a two component body which can be examined for molecular motion. Further removal of hemicellulose from the two-component body allows examination of an approximate one-component system, the cellulose alone. This approach for examining molecular behaviour is believed to be the first attempt of its type with complex polymeric systems.

1. Delignification and Wood Fine Structure

As described under Results, wood specimen dichroism varies with the wood tissue examined. Latewoods, regardless of species, had lower 1160 cm^{-1} dichroic ratios than corresponding earlywoods. This means that the alignment of 1,4-0- β -D-linkage in latewoods is more parallel to the fibre axis than that of earlywoods. As delignification proceeded (Fig.5), the 1160 cm^{-1} latewood dichroism increased linearly. This is

supported by other observations that delignification causes an increase of wood section shrinkage (154) and the bending of microfibrils (68, 70).

The 1160 cm^{-1} dichroic ratio for Douglas fir earlywood decreased slightly on delignification, while that for balsam fir remained relatively constant. The 1160 cm^{-1} dichroism in lignin-free specimens was similar for earlywood and latewood of the same species, but varied between species. This suggests indirectly that the unit cell length of native wood cellulose can vary as discussed in a previous section. The value of $10.3\text{ \AA}$, as generally accepted (167) for the cellulose I b axis, therefore deserves reexamination under varying condition of stress, strain and time.

The 1160 cm^{-1} dichroic ratios for delignified specimens were linearly correlated to total crystallinity as measured for the same specimens (Fig. 8). Because the correlation coefficient (slope) is negative, this experiment supports the previous statement that lignin exists inside at least part of the supposed wood crystalline structure. Delignification appears to have destroyed the crystallinity to some extent, perhaps by disturbing parallel cellulose orientation.

The effect of delignification on 1730 cm^{-1} dichroic ratios is similar for both species examined (Fig. 5). The latewood dichroism was slightly decreased or remained constant, while earlywood showed a marked increase when the lignin content was lowered to less than 60% of that in original tissues. The cause for this increase of dichroism in earlywood, although not known, is presumably due to adjustments caused by delignification,

or to the oxidation of terminal reducing groups to carboxyl groups (128).

The above results show conclusively the close association between lignin and cellulose and restraining effects of lignin on the carbohydrate components. Removing lignin therefore liberates a carbohydrate which is less restrained in molecular motion.

2. Molecular Relaxation

During early stages of delignification, when the specimen residual lignin is more than one-half of the original amount, elements as represented by 1730 cm^{-1} and 1160 cm^{-1} bands show numerous peaks in the relaxation curve (Tables 16, 17, 18, 19, 20, 21, 22 and 23, and Fig. 14, 15, 16 and 17). These peak intensities decrease with lapsed time. This decay pattern may be due to a molecular pendulum motion during the course of equilibrium recovery. The phenomena will be called "damping", herein.

Magnitude of the damping effect is directly related to the amount of lignin present. As shown in Fig. 14 and 15, when the lignin content of specimens was less than one-half the original amount (before the removal of hemicellulose), earlywood relaxation curves were of simpler form. This was similar to the molecular relaxation of transition wood (Fig. 9 and 10). The rate of decrease in dichroic ratio in the first phase was large, while the time required to reach equilibrium in the second phase was shortened. Also, the oscillations within curves were not as significant as during relaxation of specimens having initially high residual lignin contents. Among individual

absorption bands, the 1160 cm^{-1} component reached this simpler form at a higher residual lignin level than the 1730 cm^{-1} component. This suggests more intimacy between lignin and hemicellulose, than between cellulose and the other two components.

On the other hand, the latewood relaxation curves were markedly different from those of earlywood (Fig. 16 and 17). The 1160 cm^{-1} component showed a simpler form of relaxation when part of the lignin was removed. As specimen lignin contents approached one-half the original amount, the relaxation curve became a straight line. This could be due to the fast equilibrium recovery of the 1160 cm^{-1} component which is similar to the descriptions of Gotoh and coworkers (48, 49), Onogi and Asada (135) and Stein (169) on the experimental results of other simple polymers by different means. The latewood relaxation curves of 1730 cm^{-1} components, are similar to their counterparts in earlywood (Fig. 15 and 17).

These results suggest that there is a time difference in relaxation of 1160 cm^{-1} and 1730 cm^{-1} components. The reason for the small difference in the wood specimen could be due to the influence of lignin. Delignification appears to increase differentiation. The 1730 cm^{-1} component may retard rapid recovery of 1160 cm^{-1} component when external excitation is received. In such a system, the main stress flow passes along the long cellulose chains, while lignin and hemicellulose dissipate the force either directionally or by out of phase motions, and thus retard the cellulose recovery.

3. Stress Relaxation

Stress is a form of energy which indicates the resistance

of material to yield (184).

Delignification, as shown in Tables 24, 25, 26 and 27, and Figs. 18 and 19, induces change of shape in stress relaxation curves. The stress relaxation curves for specimens which have lignin content more than one-half the original amount are almost identical to the molecular relaxation curves of 1160 cm^{-1} and 1730 cm^{-1} components either in shape or timing of damping. This is the first evidence showing conclusively that the wood rheological behaviour is a composite expression of the molecular motions of the wood components.

The stress relaxation curves of the present study using thin wood sections are consistent with curves observed by Norimoto et al (131, 132) on macrospecimens examined in torsion bending tests, and by Takemura et al. (178) in bending tests. A rising peak was found in their relaxation spectra (continuous plot of slope for stress relaxation curve against time) between 10^3 to 10^4 seconds of relaxation time with almost every specimen tested, even under different humidity conditions. As the relative humidity increased, this peak shifted to shorter times. Similarly, a peak has been observed in the stress relaxation spectra of wood swollen with aliphatic alcohols of various chain lengths and tested in the alcohol solutions (45). The results indicated that the shorter the chain length (i.e., the greater the swelling), the shorter the time for appearance of the peak.

When the lignin content of specimens in the present experiment was less than one-half the original amount, the damping of relaxation curves became simpler and peaks moved to shorter

times. The tendency of the relaxation curve to damp less is similar to that of molecular relaxation.

As shown in Fig. 18 and 19, the physical-mechanical curves of wood tissues can be separated into two stages according to molecular relaxation. The first stage extends from the zero time decrement to a curve deflection point*. The second stage begins from this point and appears to extend to infinite time.

In the first stage, the magnitude and rate of stress decrement increases rapidly as the lignin content of specimens is decreased. In other words, the relaxation time to reach the end of this first stage is shortened. When the first and second stages are compared, the amount of stress decrement in the first stages is much greater than that of the second stage.

In the second stage, it is interesting to note that the profile of stress decrement at 40 min relaxation time (Fig. 18 and 19) coincides with per cent $(101+10\bar{1})$ crystallinity, as defined earlier, for both woods examined (Fig.7). This suggests that the stress decrement of wood could relate to part of the $(101+10\bar{1})$ crystalline structure which is penetrated by lignin. This phenomenon is similar to effects of swelling solutions on wood stress relaxation (45), where only the paracrystalline region

* A curve deflection point is either

- (1) the point where the stress, instead of continuing to decrease, begins to increase thus causing the stress curve to change its original direction; and
- (2) the point where the rate of stress decrement becomes very small.

is supposedly swollen. This line of explanation, however, is not consistent with that of Fushitani (42). It does, agree, however, with the viewpoint of Eriksson, (35, 36) who considered that the function of lignin in the relaxation modulus is to reduce carbohydrate mobility. This observation also agrees with the hypothesis of Mark (113) that hydrogen bonds lying in the $(101+10\bar{1})$ crystal plane of cellulose are related to the wood shear modulus.

The relative increase of hemicellulose in delignified specimens should be also taken into consideration. As described previously, the 1500 cm^{-1} and 1730 cm^{-1} components of lignin and hemicellulose, respectively, are capable of retarding the cellulose relaxation component as measured by 1160 cm^{-1} activity. Hence, the disproportion of components providing the 1500 cm^{-1} and 1730 cm^{-1} activity due to delignification is equivalent to the removal of one while adding the other. Therefore, the stress decrements in delignified specimens may depend on the difference between the effect of 1160 and 1730 cm^{-1} components.

The relationship between structural components and stress relaxation can be explained also according to the systematic structure of wood substance. Delignification and hemicellulose removal are approaches used to destroy the wood "memory system". The higher the order of bio-structure retained, the stronger the wood "memory system" will be. During later stages of delignification, the lignin portion of the paracrystalline structure, which is related to energy storage and transfer, will be removed. Therefore, removal of lignin from amorphous zones provides materials showing differences in stress decrement, but the effect becomes more pronounced in

later stages of delignification. Probably, the lignin associated with crystalline cellulose is removed and thus the system is greatly impaired. When hemicelluloses are removed, the systematic structure of wood is no longer present and the stress decreases greatly.

Similarly, the low resistance of wood to force perpendicular to the grain direction is explainable on the decrease in functionality of the wood "memory system" due to lessened opportunity to transfer energy.

IV. Proposed Mechanism for the Molecular Motion in Wood

Under Stress

The consistency of infrared dichroism and stress relaxation demonstrated above agrees with the theory of Treloar (185), in that the difference between any two principal refractive indices is proportional to the difference between the corresponding principal stresses. This is also supported by the postulation of Stein and Tobolsky (173) and Tobolsky (184), the stress-birefringence relationship as follows;

This diagram is consistent with recent Russian literature as surveyed by Birshtein and Ptitsyn (12), in that not only entropy, but also the energy of chains, change during polymer deformation.

Accordingly, the time-dependent behaviour of wood polymers can be resolved into one or more processes by considering optical stress coefficients* (12, 173, 184). Motions of lignin in the wood matrix appear to follow viscous flow or diffusion behaviour, while those of the carbohydrates (1730 cm^{-1} and 1160 cm^{-1}) seem to undergo processes representative of crystallization and orientation of crystalline structures. This is supported by results of Murphey(124) and Suzuki (177). Lignin in wood, therefore, may be considered as a Newtonian body (dashpot in a typical mechanical model). The relationship of cellulose and/or hemicellulose to a spring as described by the Maxwell body (31, 37, 165) is not proper, since linear viscoelastic behaviour of polymers is not applicable under conditions where the polymer crystalline character is changing during a viscoelastic experiment (184).

Recognition of the two-stage mechanism for molecular motion of wood constituents fits the argument. According to this mechanism, motions of individual components retain wood stability at the macromolecular level when external excitation is received. In the first stage of motion or immediate response, the development of parallel dichroism for the carbohydrates indicates the possibility of crystallization while at the same time lignin attempts to diffuse into the carbohydrate lattice. This behaviour of polymers results in high steric interference through association, which acts in a manner similar to cross-linked chains of lignin and carbohydrates,

* The optical coefficient is the ratio between stress and dichroism. Each polymer has its own coefficient which depends only on local structure of the polymer chain.

even if there is no lignin-carbohydrate bonding present. Consequently, as the wood receives tensile excitation, the preferred flow of force which is in the cellulose (or total carbohydrate) chain direction will be transmitted to the lignin network through association or steric interference. Therefore, although the excitation will induce a heterogeneous distribution of stresses in the wood during the initial stage (first stage), the immediate reaction of lignin to the applied force reduces the burden on the carbohydrate. The force is then transmitted through the lignin matrix from the paracrystalline to the amorphous regions of the whole wood. During force transmittance, each succeeding set of lignin-lignin, or hemicellulose-lignin association, responds less rapidly because of the larger amount of lignin available for absorption of energy and friction associated with each group, and the response of the more distant chains is delayed. With this interpretation, the prolonged recovery time required for the dichroism of the carbohydrates, in the presence of lignin, to reach equilibrium with the damping action in the second stage of relaxation is reasonably explained. The crystalline reorientation process is therefore expected to occur only in the first stage.

The lignin network of the system may do more than transfer energy; with its large percentage of benzene nuclei it may act also as an "energy sink" and thereby function to maintain the memory of the excitation. Biophysical modifications which could relate to this are high lignin content and abnormal lignin distribution in latewood cell walls of compression wood(21).

higher lignin content of earlywood than latewood (20, 198, 201)
and finally existence of a mutually exclusive relationship
between alpha-cellulose and lignin in coniferous woods (168).

CONCLUSIONS

I. The time dependent molecular activities of wood components at straining can be observed by infrared polarization techniques.

II. A two-stage molecular motion involving three wood components is suggested as the course of molecular relaxation.

The first stage begins at equilibrium, when the specimen is not stressed, and extends immediately to a minimum dichroic ratio of carbohydrate components represented by 1160 cm^{-1} and 1730 cm^{-1} bands, and the maximum dichroism of lignin (1500 cm^{-1}). The second stage starts at the end of the first stage and extends to equilibrium recovery. Thus, on receiving external excitation the wood macromolecular structure can maintain an "internal state" of equilibrium. This equilibrium state is achieved by moving the carbohydrate and lignin components in opposite directions.

Regardless of the form of excitation (stress relaxation or creep), and the time of excitation, the basic pattern of two-stage motion will not be disturbed, while damping of the molecules accompanies the whole rheological process.

III. The molecular motion of wood components is environment dependent. The observed pattern of the motion for each component in the wood macromolecular system is a compensatory result from the interference of other components. The stepwise removal of lignin from wood specimens altered the motional pattern of carbohydrates. The motion of cellulose, without the interference of lignin and hemicellulose, is comparable

to that of the other high polymers (135, 169).

IV. Rheological behaviour of wood, as represented by the stress relaxation process, is shown to be a composite expression of the molecular motions of wood components as evidenced by the consistency of the fluctuation of curves for stress relaxation and molecular motions of carbohydrate components.

V. Energy transfer system of wood was thus explained on the consideration that the motion of each chemical component is for achieving stability of the wood macromolecular system when external excitation is received.

The difference in directional movement in carbohydrate and lignin molecules results in a high steric interference and association which acts in a manner similar to cross-linked chains of lignin and carbohydrates, even if there is no lignin-carbohydrate bonding present. Consequently, as the wood receives tensile excitation, the preferred flow of force which is in the carbohydrate chain direction will be transmitted to the lignin network by the association or steric interference. Therefore, although the excitation will induce a heterogeneous distribution of stresses in the wood during the initial stage, the immediate reaction of lignin to applied force reduces the burden on the carbohydrate. The force is then transmitted through the lignin matrix to the whole wood.

During force transmittance, each succeeding set of lignin, or hemicellulose associated with lignin, responds less rapidly

because of the frictions associated with each group and the large percentage of benzene nuclei in lignin for absorption of energy, the response of the more distant chains is delayed. Thus, damping motion accompanies the molecular relaxation process for chemical components to reach equilibrium.

VI. For fulfillment of the rheological properties described, a systematic structure of wood microfibrils, based on the evidences found by X-ray and infrared spectrophotometers, is proposed.

The wood microfibril center could be crystalline core capsulated by paracrystalline layers which are amorphous with partly ordered to completely random organization. The crystalline core could be a pure cellulose structure of crystalline perfection or a fringed-micelle system, while the paracrystalline layers may contain imperfections as less ordered crystalline cellulose in admixture with oriented hemicellulose and lignin. The ordered/amorphous zone consists mainly of oriented cellulose, hemicellulose and lignin while the completely amorphous region is dominated by non-oriented lignin. This systematic structure would permit a zone of gradual transition from high crystallinity to a diffuse state. This also provides a zone for physical association or bonding between carbohydrate-carbohydrate, carbohydrate-lignin and lignin-lignin.

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TABLE 1 . THE CHEMICAL COMPOSITION OF CELL WALL LAYERS ACCORDING TO MEIER (117, 118)

Layer of cell wall	M+P %	S ₁ %	S ₂ outer %	S ₂ inner + S ₃ %
<u>Pinus sylvestris</u> (L.)				
Galactan	20.1	5.2	1.6	3.2
Cellulose	35.5	61.5	66.5	47.5
Glucomannan	7.7	16.9	24.6	27.2
Arabinan	29.4	0.6	0.0	2.4
Glucuronoarabinoxylan	7.3	15.7	7.4	19.4
<u>Picea Abies</u> (L.) Karst				
Galactan	16.4	8.0	0.0	0.0
Cellulose	33.4	55.2	64.3	63.6
Glucomannan	7.9	18.1	24.4	23.7
Arabinan	29.3	1.1	0.8	0.0
Glucuronoarabinoxylan	13.0	17.6	10.7	12.7

TABLE 2. THE CHEMICAL COMPOSITION OF GROWTH ZONES (Pinus sylvestris (L.) ACCORDING TO MEIER (118)

Polysaccharide	Earlywood %	Latewood %
Galactan	3.4	3.1
Cellulose	56.7	56.2
Glucomannan	20.3	24.8
Arabinan	1.0	1.8
Glucuronoarabinoxylan	18.6	14.1

TABLE 3. THE UNIT CELL STRUCTURE OF CELLULOSES

Type of cellulose	Monoclinic dimension(Å)			Monoclinic angle(degrees)	Author
	a	b	c		
Cellulose I	7.90	10.20	8.45	-	Polanyi(167)*
	12.20	10.25	10.80	-	Sponsler(167)*
	8.35	10.30	7.90	84.0	Meyer and Mark(167)*
					Meyer and Misch(167)*
	15.80	10.30	12.50	60.0	Sen and Roy(161)
	8.70	10.34	7.85	83.6	Jones(74)
	8.20	10.34	7.84	82.0	Fisher and Mann(38)
	8.39	10.58	7.94	82.0	Honjo and
					Watanabe(63)
	8.20	10.34	7.76	82.0	Honjo and Watanabe
					(63), (38)**
	8.20	10.34	7.89	96.0	Wellard(197)
Cellulose II	8.10	10.30	9.10	-	Andress(167)*
	16.30	10.30	9.00	64.0	Sen and Roy(161)
	7.92	10.34	9.08	62.7	Jones(74)
	8.97	10.34	7.31	99.4	Poppleton and
					Mathieson(143)

* The originals were not seen, cited from reference (167)

** These dimensions were calculated from Honjo and Watanabe's data by Fisher and Mann(38) who considered that their value $b=10.58$ Å was too large, and used instead 10.34 Å for calculation.

TABLE 4. THE BRIDGING ANGLE FOR 1,4-0- β -D-LINKAGE OF CELLULOSIC MATERIALS

<u>Angle(degree)</u>	<u>Author</u>
117.0	Ramachandran <u>et al.</u> (146)
116.7	Brown(18)
116.0	Beevers <u>et al.</u> (8)
111.6 to 118.8	Settineri and Marchessault(164)
108.0	Jacobson <u>et al.</u> (66)
108.0 to 113.0	Jones(73)

TABLE 5 . THE UNIT CELL STRUCTURE OF XYLAN (108)

Fiber repeat Å	Angle, degrees		Distance, Å		
	C ₁ -O-C ₄	Trans.moment*	H-1...H-4	O-5...O-3	O-2...H-4
15.00	118.8	89	2.47	3.0	4.5
14.84	116.5	88	2.43	3.0	4.5
14.50	111.6	86	2.32	3.0	4.5

*Defines orientation of the transition moment for the CH₂ group at C₅ in the ring.

TABLE 6 . THE UNIT CELL DIMENSIONS OF XYLAN HYDRATE AND CELLULOSE II(108)

	Dimensions, Å			Angle (degrees)
	a	b	c	
Xylan hydrate	9.16	14.84	9.16	60
Cellulose II	8.14	10.30	9.14	62

TABLE 7. BAND ASSIGNMENTS IN WOOD INFRARED SPECTRA

<u>Wave length</u> (μ)	<u>Wave number</u> (cm^{-1})	<u>Polarization</u>	<u>Assignment</u>
2.82	3550 3545 3540 3525		O-H stretching(4-methyl guaicaol)(156) O-H stretching(guaiacyl glycerol model)(156) O-H stretching(4-methyl syringol model)(156) O-H stretching(milled wood lignin in CH_2Cl_2)(120)(also methanol lignin in CH_2Cl_2 , pulp Halse lignin, pulp Klason lignin (120)
2.84	3520 3510 3490		O-H stretching(Kraft lignin)(120) O-H stretching(methanol lignin in butan-2-one) (120) O-H stretching(milled wood lignin, pulp Halse lignin in dioxan)(120)
2.87	3485 3480		O-H stretching(methanol lignin, pulp Klason lignin in pyridine)(120) O-H stretching(Kraft lignin)(120)
2.92	3425 3420		O-H stretching(milled wood lignin, Kraft lignin, pulp Halse lignin, pulp Klason lignin in butan-2-one)(120) O-H stretching(milled wood lignin, solid methanol lignin)(120)
2.93	3415 3410 3400		O-H stretching(milled wood lignin in pyridine) (120) O-H stretching(Kraft lignin, pulp Halse lignin, solid Klason lignin and pulp Halse lignin in pyridine)(120)
	3350	$\perp$	O-H stretching(188)* O-H stretching(inter-molecular hydrogen bonds in 101 plane)(98)*
	3305	$\parallel$	O-H stretching(intra-molecular hydrogen bonds) (98)*
	3300	$\perp$	O-H stretching(inter-molecular hydrogen bonds in 101 plane)(98)*
3.33	3000	$\parallel$	O-H stretching(188)*
3.37	2970 2945 2914 to 2870	$\parallel$ $\perp$ $\perp$	C-H stretching(98) C-H stretching(98) (188)* CH_2 antisymmetrical stretching(98)* C-H stretching(98)*
3.52	2850	$\parallel$	CH_2 stretching(98)*
5.78	1730 to 1725	$\perp$	C=O stretching of β -keto groups(13,32,58) C=O stretching of acetyl or carboxylic acid(32,87,98)(98)*
5.99	1670 to 1660		C=O stretching of syringyl aldehyde and vanillin(187), lignin(98)
6.06	1650 to 1635		HOH bending of water and due to lignin carbonyl band(21,32,163) C=C bond(187)
6.21	1610 to 1600		Guaiacyl and syringyl models, aromatic skeletal vibrations(156)

<u>Wave length</u> (μ)	<u>Wave number</u> (cm^{-1})	<u>Polarization</u>	<u>Assignment</u>
6.23	1605		Aromatic skeletal vibrations(156)
6.27	1595	$\sim$	Lignin(107)*, aromatic skeletal vibrations(156)
6.33	1580		Lignin(107)
6.58	1520 to 1500		Aromatic skeletal vibrations(156), guaiacyl and syringyl models(156)
6.62	1510 to 1500	$\sim$	Lignin(54,107)*
6.85	1460	$\perp$	Lignin and CH_2 symmetrical bending in the pyran ring(107)*
6.87	1455 to 1400	$\perp$	O-H bending(107)(188)*
6.90	1450 to 1420		Guaicyl and syringyl models(156)
7.00	1430 to 1425	$\parallel$	CH_2 symmetrical bending mode, hydroxymethyl(107)*, aromatic skeletal vibrations(156)* C-H bending vibration in methoxyl groups(13,28)
7.24	1380	$\parallel$	C-H bending(107)*
7.35	1360	$\parallel$	O-H in-plane bending(13,86) C-H deformation(188)*
7.49	1335	$\perp$	O-H in-plane deformation(188)* ring breathing with C=O stretching, syringyl type(with 1245 cm^{-1} , 1125 cm^{-1})(156)
7.42	1330		Ring breathing with C=O stretching, guaiacyl type (with 1240 cm^{-1} , 1110 cm^{-1})(156)
7.61	1315	$\perp$	CH_2 wagging(107)*, C-H deformation(188)*
7.85	1270 to 1275	$\parallel$	CH_2 wagging(188)* Lignin(107) ring breathing with C=O stretching, guaiacyl type(with 1240 cm^{-1} , 1130 cm^{-1})(156)
7.91	1265		C=O-C symmetric stretching vibration of aryl ether linkage(28), lignin(121)
8.00	1250 to 1150		Phenolic OH(156), syringin(hardwood), coniferin and vanillin(softwood) C=O stretching of aromatic ethers(187)
8.07	1240	$\perp$	C=O of acetyl(107), C=O stretching vibration in glucuronoxylan(mainly acetyl, some carboxyl(96,107), CH_2 wagging or CH and OH deformation(188)*
8.13	1230	$\parallel$	C=O-C asymmetrical stretching vibration of aryl-alkyl ether linkage(28), lignin(121) CH_2 wagging or CH and OH deformation(188)*
8.20	1220 to 1205	$\perp$	O-H bending with ring stretching character(156) Band in cellulose and hemicellulose (unassigned(121), (188)*)

<u>Wave length (μ)</u>	<u>Wave number (cm^{-1})</u>	<u>Polarization</u>	<u>Assignment</u>
8.62	1160		C-O-C antisymmetric bridge stretching vibration in cellulose(60,96,97,103)(107)* C-H in-plane bending in guaiacyl compounds(156)
8.89	1125 to 895		C-O stretching and ring vibrational modes(107)
8.93	1120		C-O-C asymmetrical stretching vibration in dialkyl ether linkage(13)
9.01	1110		O-H association band in cellulose and hemicellulose(minor lignin contribution)(60)(188)* Crystalline band(180)
9.05	1105		C-O-C(aliphatic ether) methyl ether of vanillyl alcohol(156) CH ₂ wagging or CH and OH deformation(188)*
9.52	1050		C-O stretching vibration in cellulose and hemicellulose(60,96,97) C-H in-plane bending of guaiacyl group(156) Crystalline band(180)
9.72	1020		CH ₂ wagging or CH and OH deformation(188)* Crystalline band(180)
11.17	895		Characteristic of β -linkage(6,103,206) anomeric carbon group frequency in cellulose and xylan(107)*
11.43	875		Mode due to glucomannan(107)*
11.97	835		Lignin(121) CH out-of-plane bending vibration(9)
1250	800	$\perp$	Mode due to glucomannan(107)*
13.02	768	$\perp$	Mode due to arabinogalactan(107)*
15.38	700 to 650		OH out-of-plane bending(107)*
18.86	530		C-O-C bending vibration(9)
21.27	470		Deformation of aromatic ring(121)

Remark:

* - polarization assignment

|| - parallel polarization

$\perp$ - perpendicular polarization

$\backslash$ - non-polarizing

TABLE 8. WOOD TISSUE SAMPLING PROCEDURE

BALSAM FIR (Abies balsamea(L.) Mill.)

<u>Increment No.</u>	<u>Earlywood</u>										<u>Latewood</u>							
	<u>Section No.</u>																	
31	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	N	N	N	N	N	N	P	P	P	N	P	N	N	N	N	N		
32	D	D	D	D	D	N	P	P	P	P	P	N	D	D	D	D	D	
	i	i	i	i	i	ci						ci	i	i	i	i	i	
32*	D	D	D	D	D	N	P	P	P	P	P	N	D	D	D	D	D	D
	s	s	s	s	s	it						it	s	s	s	s	s	s

DOUGLAS FIR (Pseudotsuga menziesii (Mirb.) Franco)

<u>Increment No.</u>	<u>Earlywood</u>										<u>Latewood</u>							
	<u>Section No.</u>																	
46	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	N	N	N	N	N	P	P	N	P	N	N	N	N	N	N	N		
47	D	D	D	D	D	D	P	P	P	P	D	D	D	D	D	D	D	
	i	i	i	s	s	s					s	s	s	i	i	i	i	
47*	D	D	D	D	D	D	P	P	P	P	D	D	D	D	D	D		
	i	i	i	i	s	s					s	s	s	i	i	i		

REMARKS

- * The same increment obtained from a matched tangential block.
- N Untreated specimen used to study intra-incremental infrared dichroism during relaxation.
- D Sample delignified and then studied as regards infrared i dichroism during relaxation.
- D Sample delignified and then studied as regards stress relaxation.
- S Untreated specimen used to study infrared dichroism
- ci during creep test
- N Untreated specimen used to study the excitation time effect
- it on infrared dichroism during relaxation.
- P Sample used in preliminary experiments or for other purposes.

TABLE 9. DICHROISM OF WOOD COMPONENTS OBSERVED AT 1160, 1500
and 1730 cm^{-1} WAVE NUMBERS

Species and tissue	1160 cm^{-1}		Dichroic ratio ($\frac{A_{\parallel}}{A_{\perp}}$) 1500 cm^{-1}		1730 cm^{-1}	
	Range	Average	Range	Average	Range	Average
Sitka spruce (<i>Picea sitchensis</i> (Bong.) Carr)		0.24		0.91		1.36
Earlywood	0.18-0.43	0.27	0.79-1.04	0.93	1.05-1.60	1.27
Latewood	0.15-0.33	0.21	0.71-0.88	0.87	1.39-1.58	1.49
Douglas fir (<i>Pseudotsuga</i> <i>menziesii</i> (Mirb.) Franco)		0.50		0.98		1.33
Earlywood	0.59-0.70	0.63	1.03-1.32	1.15	1.15-1.25	1.20
Latewood	0.24-0.44	0.33	0.70-0.87	0.85	1.36-1.53	1.45
Compression wood	1.81-2.52	2.32	1.00-1.37	1.22	0.80-1.00	0.86
Balsam fir (<i>Abies balsamea</i> (L.) Mill)		0.56		1.09		1.33
Earlywood	0.47-0.67	0.57	1.07-1.28	1.14	1.26-1.30	1.28
Latewood	0.47-0.66	0.54	1.00-1.05	1.02	1.28-1.45	1.36
Grand fir (<i>Abies grandis</i> (Dougl.) Lindl.)		0.31		0.93		1.28
Earlywood	0.27-0.55	0.44	1.00-1.09	1.01	1.06-1.20	1.14
Latewood	0.25-0.18	0.22	0.77-1.00	0.86	1.19-1.57	1.36

REMARKS :

Dichroic ratio =1.....no orientation
Dichroic ratio <1.....parallel orientation
Dichroic ratio >1.....perpendicular orientation

TABLE 10. INTRA-INCREMENTAL RELAXATION OF THE
1160 cm^{-1} COMPONENT (CELLULOSE) IN DOUGLAS FIR WOOD

Relax- ation Time, min.	Relative position within increment, %				
	7	28	49	70	91
	Lignin content, % *				
	24.7	25.3	24.6	25.4	24.2
0	0.70	0.59	0.42	0.44	0.24
1	0.68	0.54	0.32	0.40	0.18
3	0.65	0.50	0.31	0.29	0.19
6	0.66	0.48	0.33	0.40	0.30
9	0.65	0.59	0.42	0.50	0.32
12	0.70	0.57	0.36	0.47	0.20
15	0.73	0.56	0.20	0.50	0.19
18	0.76	0.55	0.40	0.35	0.22
21	0.68	0.47	0.40	0.44	0.23
24	0.63	0.47	0.38	0.39	0.25
27	0.60	0.49	0.42	0.32	0.30
30	0.59	0.52	0.36	0.40	0.32
33	0.76	0.52	0.33	0.32	0.20
36	0.68	0.49	0.36	0.32	0.23
39	0.72	0.61	0.36	0.35	0.29
42	0.74	0.72	0.42	0.40	0.22
45	0.74	0.70	0.40	0.46	0.36
48	0.76	0.68	0.35	0.38	0.27
51	0.80	0.63	0.38	0.40	0.27
54	0.78	0.56	0.37	0.46	0.24
57	0.81	0.54	0.40	0.47	0.20
60	0.75	0.58	0.42	0.44	0.28
63	0.74	0.61	0.37	0.43	0.24
66	0.74	0.57	0.36	0.43	0.26
69	0.71	0.57	0.33	0.36	0.30
72	0.72	0.61	0.32	0.38	0.33
75	0.71	0.62	0.32	0.33	0.33
78		0.58	0.32	0.42	0.25

* Determined according to reference (20)

TABLE 11. INTRA-INCREMENTAL RELAXATION OF THE
1730 CM^{-1} COMPONENT (HEMICELLULOSE) IN DOUGLAS FIR
WOOD

Relax- ation time , min.	Relative position within increment , %				
	7	28	49	70	91
	Lignin content , % *				
	24.7	25.3	24.6	25.4	24.2
0	1.25	1.15	1.36	1.33	1.37
1	1.03	1.02	1.18	1.32	1.33
3	1.03	0.94	1.07	1.21	1.36
6	1.06	0.96	1.02	1.26	1.46
9	1.00	0.97	1.21	1.21	1.39
12	1.00	0.92	1.31	1.23	1.24
15	1.15	1.10	1.42	1.48	1.20
18	1.15	1.00	1.36	1.30	1.21
21	1.11	1.11	1.31	1.35	1.24
24	1.00	1.20	1.34	1.26	1.42
27	1.00	1.00	1.28	1.11	1.30
30	0.96	1.19	1.30	1.14	1.40
33	1.02	1.01	1.26	1.29	1.49
36	1.15	1.20	1.36	1.26	1.36
39	0.95	1.15	1.31	1.39	1.30
42	1.06	1.04	1.32	1.26	1.28
45	0.94	1.10	1.34	1.36	1.33
48	1.02	1.22	1.28	1.50	1.40
51	1.00	1.23	1.30	1.28	1.29
54	1.14	1.05	1.30	1.34	1.32
57	1.03	1.01	1.30	1.30	1.48
60	0.97	1.07	1.34	1.18	1.36
63	1.08	1.20		1.37	1.37
66	1.14	1.12		1.27	1.39
69	1.00	1.10		1.24	1.35
72	1.23	1.15		1.27	1.45
75	1.15	1.04		1.34	1.50
78	1.10	1.14		1.28	1.48
81				1.30	1.41

* Determined according to reference (20)

TABLE 12. INTRA-INCREMENTAL RELAXATION OF THE 1500 CM⁻¹
COMPONENT (LIGNIN) IN DOUGLAS FIR WOOD

Relax- ation time , min.	Relative position within increment, %					
	7	21	28	56	80	100
	Lignin content, %*					
	24.7	26.8	25.3	23.7	25.2	24.0
0	1.11	1.31	1.03	0.87	0.70	0.86
1	1.31	1.40	1.08	1.30	0.79	1.45
3	1.25	1.26	1.20	1.20	0.91	1.35
6	1.27	1.36	1.21	1.45	0.97	1.32
9	1.33	1.32	1.12	1.30	0.84	1.50
12	1.48	1.27	1.19	1.32	0.84	1.44
15	1.31	1.24	1.10	1.06	0.81	1.45
18	1.24	1.17	1.13	0.95	0.64	1.43
21	1.31	1.34	1.15	1.00	0.66	1.28
24	1.30	1.20	0.90	1.04	0.68	1.27
27	1.29	1.28	0.84	1.04	0.64	1.18
30	1.34	1.13	0.74	1.00	0.61	1.10
33	1.20	1.10	0.78	0.95	0.68	1.12
36	1.26	1.24	0.80	0.96	0.67	1.11
39	1.31	1.17	0.86	0.62	0.61	1.18
42	1.12	1.24	0.80	0.69	0.70	1.11
45	1.26	1.03	0.67	0.91	0.60	1.20
48	1.21	1.24	0.63	0.53	0.78	1.10
51	1.33	1.17	0.68	0.75	0.66	1.10
54	1.25	1.22	0.64	0.64	0.71	0.94
57	1.14	1.12	0.62	0.93	0.65	0.90
60	1.12	1.08	0.70	0.64	0.65	0.87
63	1.18	1.18	0.64	0.84	0.72	0.89
66	1.22	1.16	0.72	0.86	0.70	0.68
69	1.18	1.18	0.86	0.64	0.64	1.04
71	1.08	0.93	0.76	0.78	0.82	0.77
74	1.08	1.00	0.68	0.75	0.70	0.75
77	1.08			0.77		
80	1.03			0.64		

* Determined according to reference (20)

TABLE 13. INTRA-INCREMENTAL RELAXATION OF THE 1160 CM⁻¹
COMPONENT (CELLULOSE) IN BALSAM FIR WOOD

Relax- ation time, min.	Relative position within increment, %					
	18	38	50	64	74	92
	Lignin content, % *					
	34.0	32.8	32.2	33.0	33.2	33.5
0	0.58	0.47	0.67	0.50	0.47	0.66
1	0.50	0.38	0.33	0.42	0.45	0.64
3	0.46	0.35	0.30	0.40	0.44	0.60
6	0.48	0.33	0.48	0.39	0.45	0.47
9	0.41	0.38	0.60	0.43	0.38	0.50
12	0.43	0.36	0.70	0.39	0.37	0.54
15	0.40	0.35	0.70	0.40	0.39	0.52
18	0.50	0.36	0.53	0.40	0.33	0.57
21	0.50	0.33	0.67	0.39	0.56	0.54
24	0.47	0.32	0.70	0.45	0.50	0.50
27	0.48	0.33	0.60	0.45	0.45	0.50
30	0.50	0.37	0.60	0.44	0.40	0.50
33	0.46	0.44	0.67	0.45	0.38	0.47
36	0.50	0.40	0.62	0.37	0.44	0.54
39	0.48	0.46	0.60	0.41	0.42	0.50
42	0.46	0.48	0.53	0.40	0.41	0.64
45	0.48	0.46	0.55	0.42	0.44	0.54
48	0.45	0.52	0.60	0.42	0.50	0.46
51	0.48	0.50	0.67	0.55	0.50	0.48
54	0.50	0.55	0.63	0.48	0.46	0.57
57	0.45	0.48	0.50	0.48	0.50	0.64
60	0.48	0.50	0.52	0.49	0.54	0.62
63	0.50	0.48	0.56	0.46	0.50	0.59
66	0.52	0.45	0.54	0.40	0.48	0.55
69	0.55	0.48	0.52	0.39	0.50	0.60
72	0.58	0.50	0.58	0.46	0.50	0.55
75	0.54	0.52	0.56	0.48	0.47	0.56
78	0.58	0.50	0.50	0.55	0.44	0.64
81	0.52	0.42	0.62			0.64

* Determined according to reference (20)

TABLE 14. INTRA-INCREMENTAL RELAXATION OF THE 1730 CM⁻¹ COMPONENT (HEMICELLULOSE) IN BALSAM FIR WOOD

Relax- ation time, min.	Relative position within increment, %					
	6	24	50	64	87	100
	Lignin content, % *					
	35.2	34.1	32.2	33.0	33.4	33.3
0	1.27	1.30	1.26	1.28	1.24	1.45
1	1.24	1.25	1.14	1.16	1.12	1.42
3	1.24	1.16	1.10	1.18	1.10	1.38
6	1.14	1.21	0.98	1.14	1.06	1.38
9	1.15	1.18	1.10	1.22	1.16	1.30
12	1.04	1.22	1.06	1.30	1.25	1.35
15	1.12	1.28	1.22	1.18	1.16	1.36
18	1.14	1.19	1.22	0.98	1.18	1.45
21	1.31	1.18	1.26	1.02	1.02	1.42
24	1.18	1.14	1.42	1.00	1.06	1.48
27	1.09	1.22	1.38	1.12	1.04	1.32
30	1.00	1.24	1.36	1.18	1.20	1.36
33	1.08	1.30	1.30	1.18	1.28	1.22
36	1.17	1.26	1.38	1.14	1.22	1.18
39	1.29	1.28	1.28	1.14	1.28	1.30
42	1.11	1.34	1.38	1.20	1.20	1.18
45	1.17	1.28	1.30	1.20	1.25	1.40
48	1.20	1.34	1.32	1.22	1.28	1.30
51	1.18	1.30	1.30	1.18	1.31	1.38
54	1.20	1.40	1.28	1.14	1.31	1.38
57	1.20	1.38	1.37	1.14	1.28	1.48
60	1.16	1.30	1.26	1.19	1.28	1.45
63	1.20	1.35	1.32	1.19	1.32	1.48
66	1.24	1.32	1.36	1.16	1.26	1.40
69	1.16	1.30	1.28	1.16	1.22	1.50
72	1.18	1.34	1.28	1.25	1.34	1.42
75	1.20	1.30	1.36	1.16	1.22	1.40
78	1.20	1.34	1.26	1.20	1.30	1.42
81	1.17	1.30	1.34	1.25	1.26	1.42

* Determined according to reference (20)

TABLE 15. INTRA-INCREMENTAL RELAXATION OF THE 1500 CM⁻¹
COMPONENT (LIGNIN) IN BALSAM FIR WOOD

Relax- ation time, min.	Relative position within increment, %					
	18	38	50	64	87	100
	Lignin content, % *					
	34.0	32.3	32.2	33.0	33.4	33.3
0	1.28	1.07	1.07	1.05	1.00	1.05
1	1.46	1.08	1.23	1.05	1.07	1.05
3	1.40	1.10	1.25	1.08	1.20	1.08
6	1.34	1.08	1.20	1.10	1.17	1.11
9	1.25	1.10	1.26	1.04	1.16	1.13
12	1.18	1.00	1.10	1.10	1.27	1.02
15	1.20	1.02	1.08	1.18	1.20	1.10
18	1.21	1.00	1.00	1.15	1.08	0.94
21	1.07	1.03	1.12	1.15	1.14	0.89
24	1.23	1.03	1.00	1.10	1.10	0.90
27	1.21	1.00	1.10	1.15	1.10	0.90
30	1.14	1.00	1.08	1.10	1.14	0.95
33	1.14	1.02	1.00	1.15	1.08	0.85
36	1.23	1.01	1.03	1.10	1.00	1.00
39	1.20	1.00	1.12	1.00	1.07	1.00
41	1.25	0.98	1.05	1.10	1.00	1.00
44	1.23	1.00	1.00	1.05	1.00	0.94
47	1.18	0.98	1.00	1.05	0.98	0.94
50	1.15	0.96	1.06	1.00	0.94	1.00
53	1.14	1.00	1.06	1.05	1.00	0.94
56	1.21	0.94	1.04	0.96	1.02	1.06
59	1.18	0.95	1.10	1.00	0.95	1.00
61	1.16	0.96	1.00	1.06	0.93	0.95
64	1.08	0.94	1.10	1.04	1.00	0.94
67	1.10	0.98	1.08	1.05	1.05	0.95
70	1.14	0.94	1.08	1.05	1.00	0.94
73	1.15	1.00	1.00	1.05	1.00	1.05
76	1.21	0.94	1.01	1.00	1.06	1.00
79	1.15	0.90	1.00	1.00	1.00	0.95
82	1.23		0.92	0.95	1.00	0.94

*Determined according to reference (20)

TABLE 16. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE, ON RELAXATION OF THE 1160 cm^{-1} COMPONENT (CELLULOSE) IN DOUGLAS FIR EARLYWOOD

Relax- ation time, min.	Delignification time, min.							Lignin content, %**		
	0	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%)*
	100	78	68	52	43	30	23	0	0	0
0	0.70	0.78	0.71	0.59	0.65	0.56	0.62	0.52	0.49	0.53
1	0.68	0.70	0.68	0.38	0.65	0.62	0.61	0.51	0.48	0.50
3	0.65	0.62	0.65	0.44	0.62	0.64	0.58	0.51	0.48	0.55
6	0.66	0.80	0.67	0.56	0.59	0.55	0.60	0.50	0.46	0.47
9	0.65	0.85	0.67	0.58	0.60	0.63	0.63	0.49	0.48	0.53
12	0.70	0.89	0.54	0.63	0.64	0.58	0.60	0.54	0.48	0.64
15	0.73	0.71	0.66	0.58	0.69	0.52	0.53	0.56	0.44	0.54
18	0.76	0.70	0.77	0.60	0.65	0.59	0.60	0.44	0.47	0.49
21	0.68	0.71	0.70	0.58	0.62	0.60	0.58	0.46	0.48	0.49
24	0.63	0.70	0.64	0.63	0.65	0.62	0.57	0.46	0.45	0.54
27	0.60	0.73	0.66	0.69	0.62	0.57	0.65	0.51	0.46	0.56
30	0.59	0.72	0.67	0.62	0.68	0.60	0.56	0.47	0.48	0.55
33	0.76	0.80	0.72	0.58	0.66	0.59	0.62	0.50	0.50	0.52
36	0.68	0.82	0.79	0.57	0.71	0.56	0.59	0.48	0.46	0.56
39	0.72	0.67	0.75	0.72	0.65	0.60	0.55	0.50	0.46	0.53
42	0.74	0.76	0.72	0.56	0.65	0.50	0.54	0.52	0.44	0.52
45	0.74	0.82	0.76	0.55	0.57	0.66	0.62	0.56	0.45	0.47
48	0.76	0.80	0.67	0.55	0.66	0.63	0.62	0.55	0.44	0.48
51	0.80	0.71	0.80	0.55	0.61	0.63	0.59	0.53	0.45	0.54
54	0.78	0.72	0.75	0.55	0.62	0.60	0.57	0.51	0.45	0.54
57	0.81	0.77	0.72	0.54	0.60	0.63	0.54	0.50	0.47	0.61
60	0.75	0.70	0.75	0.57	0.59	0.60	0.59	0.50	0.44	0.60
63	0.74	0.80	0.75	0.50	0.53	0.61	0.62	0.53	0.47	0.51
66	0.74	0.75	0.81	0.65	0.65	0.50	0.60	0.47	0.48	0.55
69	0.71	0.85	0.81	0.60	0.63	0.57	0.61	0.55	0.47	0.58
72	0.72	0.78	0.74	0.54	0.67	0.55	0.59	0.53	0.50	0.55
75	0.71	0.74	0.73	0.58	0.61	0.59	0.60	0.49	0.45	0.55
78		0.76	0.75	0.56	0.53	0.57	0.64	0.50	0.45	0.53
81		0.73	0.80	0.64		0.62		0.49	0.50	0.50

* Caustic treatments at 25°C ** Based on 1500 cm^{-1} band intensity

TABLE 17 . EFFECT OF REMOVING LIGNIN ON RELAXATION OF
THE 1730 cm^{-1} COMPONENT (HEMICELLULOSE) IN DOUGLAS FIR EARLYWOOD

Relax- ation time min.	Delignification time, min.						
	0	30	60	90	120	180	240
	Lignin content, % *						
	100	78	68	56	43	30	23
0	1.25	1.40	1.21	1.36	1.31	1.65	1.68
1	1.03	1.35	1.06	1.35	1.10	1.66	1.61
3	1.03	1.35	1.12	1.17	1.18	1.54	1.28
6	1.06	1.32	1.08	1.09	1.20	1.30	1.33
9	1.00	1.21	1.05	1.19	1.16	1.29	1.48
12	1.00	1.12	1.11	1.09	1.15	1.47	1.63
15	1.15	1.42	1.06	1.05	1.14	1.31	1.44
18	1.15	1.32	1.08	1.20	1.18	1.41	1.38
21	1.11	1.38	1.19	1.21	1.14	1.68	1.59
24	1.00	1.20	1.20	1.30	1.17	1.61	1.46
27	1.00	1.16	1.16	1.44	1.07	1.60	1.48
30	0.96	1.35	1.12	1.40	0.90	1.69	1.59
33	1.02	1.29	0.98	1.21	1.06	1.63	1.52
36	1.15	1.25	1.01	1.21	1.19	1.51	1.44
39	0.95	1.24	1.18	1.20	1.10	1.00	1.45
42	1.06	1.26	1.20	1.09	1.05	1.53	1.54
45	0.94	1.28	1.27	1.12	1.27	1.56	1.48
48	1.02	1.20	1.17	1.20	1.10	1.58	1.58
51	1.00	1.12	1.21	1.22	1.15	1.58	1.43
54	1.14	1.30	1.26	1.16	1.13	1.69	1.52
57	1.03	1.26	1.18	1.28	1.27	1.62	1.51
60	0.97	1.18	1.10	1.26	1.05	1.56	1.48
63	1.08	1.39	1.28	1.20	1.12	1.56	1.52
66	1.14	1.26	1.16	1.10	1.14	1.54	
69	1.00	1.37	1.07	1.07	1.21	1.50	
72	1.23	1.25	1.20	1.14		1.54	
75	1.15	1.21	1.02	1.22		1.48	
78	1.10	1.36	1.08	1.17			
81		1.28	1.16				

* Based on the 1500 cm^{-1} band intensity

TABLE 18. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON RELAXATION OF THE 1160 CM⁻¹ COMPONENT (CELLULOSE) IN DOUGLAS FIR LATEWOOD

Relax- ation time, min.	Delignification time, min.									
	0	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%)*
	Lignin content, % **									
	100	97	86	72	60	46	20	0	0	0
0	0.24	0.18	0.37	0.32	0.33	0.31	0.38	0.38	0.41	0.50
1	0.21	0.17	0.34	0.29	0.34	0.29	0.36	0.37	0.40	0.52
3	0.20	0.18	0.35	0.29	0.35	0.34	0.48	0.39	0.39	0.55
6	0.24	0.19	0.36	0.28	0.34	0.29	0.44	0.37	0.44	0.49
9	0.27	0.19	0.37	0.29	0.34	0.30	0.37	0.39	0.44	0.45
12	0.29	0.18	0.34	0.35	0.32	0.28	0.41	0.34	0.39	0.44
15	0.28	0.18	0.31	0.29	0.33	0.34	0.40	0.38	0.39	0.50
18	0.20	0.15	0.30	0.32	0.31	0.32	0.41	0.36	0.39	0.54
21	0.19	0.16	0.39	0.33	0.33	0.30	0.46	0.36	0.47	0.47
24	0.25	0.19	0.36	0.39	0.34	0.28	0.47	0.34	0.42	0.53
27	0.30	0.25	0.36	0.38	0.35	0.28	0.40	0.36	0.39	0.67
30	0.31	0.25	0.40	0.33	0.36	0.29	0.41	0.40	0.40	0.51
33	0.26	0.20	0.26	0.39	0.35	0.29	0.50	0.35	0.43	0.61
36	0.29	0.25	0.34	0.42	0.34	0.25	0.45	0.39	0.41	0.54
39	0.26	0.19	0.38	0.35	0.32	0.33	0.45	0.38	0.42	0.50
42	0.34	0.20	0.38	0.34	0.36	0.28	0.43	0.35	0.41	0.53
45	0.30	0.21	0.36	0.29	0.32	0.32	0.41	0.41	0.41	0.49
48	0.31	0.19	0.30	0.40	0.33	0.31	0.49	0.33	0.33	0.56
51	0.29	0.25	0.39	0.35	0.32	0.31	0.41	0.35	0.41	0.47
54	0.26	0.21	0.36	0.34	0.32	0.26	0.48	0.41	0.41	0.56
57	0.32	0.18	0.38	0.37	0.31	0.27	0.45	0.35	0.35	0.68
60	0.26	0.24	0.38	0.41	0.37	0.31	0.47	0.39	0.44	0.61
63	0.28	0.22	0.38	0.29	0.35	0.32	0.46	0.40	0.49	0.56
66	0.35	0.19	0.34	0.38	0.40	0.32	0.45	0.34	0.43	0.53
69	0.30	0.21	0.34	0.34	0.35	0.32	0.40	0.36	0.45	0.56
72	0.33	0.21	0.31	0.41	0.35	0.32	0.46	0.36	0.47	0.54
75	0.34	0.21	0.37	0.41	0.34	0.29	0.40	0.35	0.42	0.48
78	0.28				0.35	0.29	0.43	0.36	0.47	0.49
81	0.32				0.30	0.31	0.43	0.35	0.45	0.58

*Caustic treatments at 25°C ** Based on 1500 cm⁻¹ band intensity

TABLE 19. EFFECT OF REMOVING LIGNIN ON RELAXATION OF
THE 1730 cm^{-1} COMPONENT (HEMICELLULOSE) IN DOUGLAS FIR
LATEWOOD

Relax- ation time, min.	Delignification time, min.						
	0	30	60	90	120	180	240
	Lignin content, % *						
	100	97	86	72	60	46	20
0	1.53	1.26	1.38	1.33	1.24	1.40	1.31
1	1.52	1.21	1.10	1.30	1.20	1.20	1.23
3	1.41	1.20	1.03	1.21	1.21	1.16	1.16
6	1.46	1.15	1.24	1.43	1.41	1.30	1.13
9	1.41	1.17	1.39	1.26	1.57	1.24	1.25
12	1.43	1.15	1.28	1.30	1.44	1.05	1.36
15	1.68	1.10	1.13	1.08	1.48	1.20	1.40
18	1.50	1.30	1.17	1.15	1.28	1.14	1.30
21	1.35	1.44	1.26	1.17	1.38	1.20	1.27
24	1.26	1.50	1.21	1.21	1.24	1.20	1.24
27	1.11	1.44	1.38	1.25	1.27	1.20	1.28
30	1.14	1.47	1.28	1.20	1.30	1.20	1.17
33	1.26	1.26	1.43	1.16	1.46	1.20	1.20
36	1.26	1.30	1.33	1.26	1.32	1.26	1.32
40	1.39	1.24	1.23	1.26	1.43	1.25	1.21
43	1.26	1.24	1.24	1.17	1.41	1.15	1.29
46	1.36	1.35	1.26	1.17	1.31	1.25	1.30
49	1.40	1.23	1.20	1.24	1.28	1.20	1.21
52	1.28	1.31	1.20	1.24	1.38	1.19	1.26
55	1.34	1.29	1.22	1.18	1.24	1.14	1.20
58	1.30	1.30	1.17	1.18	1.18	1.09	1.28
61	1.34	1.34	1.07	1.30	1.31	1.22	1.17
64	1.37	1.29	1.19	1.22	1.27	1.20	1.24
67	1.27	1.28	1.13	1.12	1.32	1.16	1.17
70	1.24	1.23	1.22	1.27	1.27	1.23	1.19
73	1.27	1.20	1.21	1.28	1.24	1.24	1.27
76	1.34	1.24	1.13	1.21	1.30	1.13	1.31
79	1.28	1.37	1.20	1.17	1.33	1.27	1.24
81	1.30	1.28				1.17	

* Based on 1500 cm^{-1} band intensity.

TABLE 20. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON RELAXATION OF THE 1160 cm^{-1} COMPONENT (CELLULOSE) IN BALSAM FIR EARLYWOOD

Relax- ation time, min.	Delignification time, min.						240 (5%) 240 (17.5%) *	
	0	30	60	90	120	180	240	
	Lignin content, % **							
	100	78	62	55	52	45	30	14 0
0	0.66	0.70	0.68	0.68	0.68	0.65	0.68	0.70 0.68
1	0.62	0.61	0.58	0.52	0.54	0.58	0.54	0.66 0.66
3	0.48	0.50	0.54	0.48	0.50	0.48	0.50	0.66 0.64
6	0.47	0.45	0.46	0.48	0.52	0.45	0.48	0.68 0.68
9	0.50	0.55	0.48	0.49	0.50	0.35	0.40	0.68 0.68
12	0.54	0.57	0.50	0.48	0.68	0.46	0.39	0.72 0.70
15	0.56	0.70	0.53	0.50	0.62	0.42	0.50	0.68 0.66
18	0.61	0.78	0.52	0.48	0.68	0.60	0.52	0.72 0.68
21	0.57	0.67	0.62	0.52	0.64	0.58	0.47	0.66 0.71
24	0.50	0.60	0.50	0.58	0.71	0.56	0.46	0.70 0.68
27	0.51	0.55	0.43	0.62	0.71	0.45	0.50	0.73 0.70
30	0.57	0.67	0.48	0.60	0.68	0.50	0.52	0.68 0.72
33	0.64	0.65	0.60	0.60	0.68	0.54	0.44	0.72 0.70
36	0.58	0.57	0.63	0.60	0.67	0.46	0.50	0.68 0.74
39	0.57	0.69	0.58	0.56	0.64	0.42	0.54	0.70 0.68
42	0.54	0.68	0.66	0.54	0.57	0.54	0.42	0.69 0.66
45	0.61	0.55	0.57	0.55	0.60	0.55	0.46	0.72 0.70
49	0.60	0.58	0.54	0.52	0.56	0.47	0.44	0.70 0.70
51	0.56	0.54	0.54	0.54	0.71	0.61	0.48	0.72 0.72
54	0.63	0.56	0.56	0.53	0.60	0.56	0.50	0.73 0.70
57	0.61	0.57	0.56	0.53	0.58	0.64	0.46	0.70 0.70
60	0.58	0.67	0.57	0.54	0.69	0.62	0.48	0.70 0.68
63	0.56	0.73	0.49	0.51	0.66	0.66	0.50	0.68 0.66
66	0.60	0.71	0.57	0.56	0.71	0.52	0.52	0.73 0.72
69	0.58	0.65	0.55	0.55	0.68	0.50	0.52	0.70 0.69
72	0.60	0.53	0.53	0.55	0.67	0.64	0.52	0.68 0.68
75	0.56	0.67	0.49	0.53	0.57	0.52	0.50	0.72 0.70
78	0.63	0.54	0.60	0.52	0.58	0.62	0.51	0.68 0.72
81	0.63	0.73	0.58	0.52	0.64	0.57	0.53	0.71 0.70

* Caustic treatments at 25°C **Based on 1500 cm^{-1} band intensity

TABLE 21. EFFECT OF REMOVING LIGNIN ON RELAXATION OF
THE 1730 cm^{-1} COMPONENT (HEMICELLULOSE) IN BALSAM FIR EARLY-
WOOD

Relax- ation time, min.	Delignification time, min.						
	0	30	60	90	120	180	240
	Lignin content, % *						
	100	78	62	55	52	45	30
0	1.18	1.16	1.26	1.28	1.26	1.37	1.34
1	1.06	1.08	1.17	1.13	1.19	1.21	1.24
3	1.04	1.10	1.20	1.07	1.18	1.11	1.09
6	1.08	1.06	1.26	1.14	1.18	1.12	1.06
9	1.10	1.06	1.34	1.27	1.04	1.18	1.03
12	1.12	1.08	1.30	1.20	1.08	1.14	1.16
15	1.18	1.15	1.11	1.09	1.09	1.23	1.28
18	1.15	1.14	1.13	1.03	1.23	1.35	1.20
22	1.10	1.17	1.18	1.25	1.28	1.30	1.14
25	1.05	1.10	1.22	1.30	1.14	1.35	1.15
28	1.04	1.12	1.30	1.33	1.15	1.38	1.20
30	1.18	1.20	1.23	1.26	1.13	1.34	1.10
33	1.18	1.15	1.29	1.20	1.20	1.30	1.26
36	1.18	1.20	1.20	1.35	1.28	1.19	1.20
39	1.22	1.15	1.16	1.27	1.19	1.30	1.26
42	1.18	1.20	1.23	1.15	1.15	1.22	1.18
45	1.15	1.14	1.10	1.20	1.22	1.19	1.28
48	1.14	1.14	1.20	1.26	1.20	1.26	1.30
51	1.18	1.22	1.23	1.26	1.12	1.20	1.22
54	1.16	1.13	1.15	1.17	1.16	1.18	1.19
57	1.30	1.16	1.21	1.21	1.14	1.31	1.20
60	1.18	1.18	1.20	1.17	1.15	1.22	1.22
63	1.23	1.24	1.28	1.15	1.16	1.27	1.19
66	1.24	1.24	1.20	1.14	1.24	1.28	1.16
69	1.20	1.22	1.30	1.21	1.20	1.24	1.26
72	1.24	1.15	1.32	1.12	1.16	1.22	1.17
75	1.20	1.20	1.28	1.24	1.22	1.20	1.24
78	1.24	1.20			1.18	1.25	1.20
81	1.31	1.16			1.22		1.24

* Based on the 1500 cm^{-1} band intensity

TABLE 22. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON RELAXATION OF THE 1160 cm^{-1} COMPONENT (CELLULOSE) IN BALSAM FIR LATEWOOD

Relax- ation time, min.	Delignification time, min.								
	0	30	60	90	120	180	240	240 (5%)	240 (17.5%)*
	Lignin content, %**								
	100	96	79	72	55	41	19	8	0
0	0.48	0.52	0.56	0.55	0.52	0.62	0.56	0.66	0.68
1	0.44	0.46	0.52	0.42	0.42	0.50	0.54	0.64	0.62
3	0.41	0.50	0.52	0.44	0.46	0.58	0.50	0.66	0.69
6	0.42	0.48	0.47	0.44	0.48	0.61	0.52	0.72	0.70
9	0.42	0.45	0.46	0.45	0.48	0.64	0.54	0.68	0.69
12	0.45	0.42	0.48	0.48	0.54	0.57	0.52	0.70	0.65
15	0.38	0.44	0.46	0.43	0.50	0.58	0.52	0.70	0.63
18	0.36	0.44	0.48	0.39	0.48	0.62	0.50	0.67	0.63
21	0.44	0.46	0.48	0.46	0.46	0.59	0.54	0.69	0.68
24	0.50	0.54	0.48	0.46	0.48	0.58	0.58	0.66	0.68
27	0.56	0.50	0.50	0.53	0.50	0.62	0.54	0.70	0.69
30	0.48	0.50	0.52	0.49	0.46	0.66	0.54	0.67	0.62
33	0.48	0.49	0.56	0.60	0.49	0.57	0.50	0.70	0.68
36	0.47	0.38	0.48	0.46	0.46	0.54	0.52	0.69	0.61
39	0.49	0.42	0.50	0.53	0.46	0.58	0.52	0.69	0.69
42	0.50	0.42	0.55	0.55	0.48	0.63	0.48	0.67	0.68
45	0.40	0.44	0.52	0.58	0.59	0.57	0.48	0.66	0.65
48	0.45	0.42	0.54	0.48	0.56	0.58	0.48	0.64	0.68
51	0.38	0.36	0.50	0.53	0.57	0.58	0.50	0.66	0.68
54	0.40	0.38	0.50	0.50	0.51	0.56	0.52	0.65	0.66
57	0.36	0.40	0.50	0.46	0.53	0.62	0.50	0.68	0.64
60	0.40	0.42	0.58	0.45	0.56	0.64	0.50	0.69	0.64
63	0.36	0.44	0.50	0.40	0.52	0.56	0.50	0.68	0.69
66	0.42	0.40	0.48	0.40	0.54	0.58	0.53	0.65	0.65
69	0.40	0.42	0.46	0.45	0.54	0.63	0.52	0.65	0.65
72	0.46	0.42	0.54	0.45	0.58	0.58	0.48	0.67	0.69
75	0.40	0.45	0.46	0.36	0.50	0.54	0.50	0.67	0.70
78	0.44	0.46	0.52	0.36	0.54	0.58	0.48	0.67	0.68
81	0.44	0.45	0.58	0.45	0.54	0.58	0.50	0.68	0.64

* Caustic treatments at 25°C **Based on the 1500 cm^{-1} band intensity

TABLE 23. EFFECT OF REMOVING LIGNIN ON RELAXATION OF THE 1730 cm^{-1} COMPONENT (HEMICELLULOSE) IN BALSAM FIR LATEWOOD

Relaxation time, min.	Delignification time, min.					
	30	60	90	120	180	240
	Lignin content, % *					
	96	79	72	55	41	19
0	1.28	1.32	1.28	1.31	1.26	1.26
1	1.20	1.27	1.20	1.02	1.16	1.22
3	1.25	1.24	1.14	1.16	1.12	1.16
6	1.16	1.20	1.15	1.04	1.06	1.08
9	1.12	1.15	1.18	1.08	1.14	1.14
12	1.18	1.15	1.12	1.22	1.20	1.18
15	1.20	1.10	1.13	1.28	1.24	1.24
18	1.18	1.18	1.27	1.33	1.18	1.26
21	1.16	1.17	1.25	1.26	1.10	1.22
24	1.15	1.12	1.30	1.30	1.12	1.18
27	1.19	1.26	1.17	1.24	1.18	1.28
30	1.18	1.30	1.19	1.24	1.20	1.26
33	1.26	1.31	1.10	1.30	1.14	1.18
36	1.26	1.28	1.11	1.37	1.24	1.32
39	1.34	1.26	1.22	1.24	1.16	1.26
42	1.30	1.30	1.18	1.35	1.18	1.22
45	1.26	1.24	1.26	1.22	1.12	1.18
48	1.18	1.31	1.30	1.17	1.12	1.24
51	1.18	1.30	1.23	1.12	1.19	1.22
54	1.20	1.22	1.25	1.18	1.20	1.20
57	1.22	1.18	1.22	1.14	1.16	1.17
60	1.20	1.30	1.20	1.14	1.18	1.26
63	1.13	1.16	1.26	1.16	1.20	1.17
66	1.18	1.16	1.20	1.18	1.20	1.22
69	1.24	1.20	1.20	1.24	1.21	1.14
72	1.20	1.22	1.28	1.14	1.26	1.25
75	1.18	1.24	1.28	1.16	1.15	1.14
78	1.18	1.24	1.28	1.18	1.17	1.13
81	1.20	1.22	1.26	1.18	1.20	1.18

* Based on the 1500 cm^{-1} band intensity

TABLE 24. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON STRESS DECREMENT
OF DOUGLAS FIR EARLYWOOD DURING RELAXATION

Relax- ation time, min.	Delignification time, min.								
	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%) *
	Lignin content, % **								
	78	68	56	43	30	23	0	0	0
0	0	0	0	0	0	0	0	0	0
0.2	12.3	11.4	18.2	14.5	14.2	18.4	21.4	24.6	26.1
0.4	13.9	12.9	22.1	16.4	15.6	22.6	25.8	29.4	29.9
0.6	15.4	14.3	24.1	17.6	17.8	25.3	28.3	31.9	32.8
0.8	16.9	15.7	25.9	18.3	18.8	26.3	30.0	33.3	34.7
1.0	17.7	15.7	26.5	18.9	19.3	27.4	31.5	34.8	35.7
1.5	18.5	15.7	27.9	20.5	20.5	29.5	33.7	37.3	38.9
2	20.0	15.7	29.1	21.1	21.4	31.6	35.1	38.7	40.5
3	20.8	16.5	30.3	22.1	22.4	33.2	37.2	40.7	42.8
4	20.8	17.1	31.5	22.7	23.4	35.3	38.6	42.4	44.7
5	20.8	17.1	31.1	22.9	23.7	36.3	40.0	43.5	45.7
6	20.8	15.7	32.1	23.2	24.2	37.4	40.7	44.6	47.0
7	20.8	15.5	32.4	23.2	24.2	37.9	41.8	45.5	47.9
8	20.8	15.0	32.7	23.2	25.1	38.4	42.5	46.1	48.6
9	20.0	14.5	32.7	23.2	25.6	38.4	42.8	46.3	49.5
10	20.0	14.3	32.9	23.7	25.9	38.9	43.3	46.9	50.8
11	19.2	14.3	33.2	23.7	25.6	39.5	43.9	47.2	51.1
12	19.2	14.3	33.2	24.4	26.3	40.0	44.2	48.0	51.8
13	20.0	14.3	33.8	24.4	26.3	40.5	45.1	48.6	52.1
14	20.0	14.3	33.8	24.4	26.3	40.5	45.6	49.2	52.1
15	20.8	14.3	34.4	25.1	26.3	41.1	45.9	49.4	51.8
16	21.5	14.3	34.4	25.1	26.3	41.1	46.1	50.0	52.4
17	21.5	17.0	34.4	25.1	26.3	41.6	46.5	50.3	52.7
18	20.8	18.6	34.4	25.1	26.3	41.6	46.8	50.6	53.4
19	20.8	18.6	34.4	25.1	26.6	42.1	47.0	50.9	53.4
20	20.8	18.6	34.1	25.1	26.6	42.1	47.2	50.9	54.0
21	20.8	18.6	34.1	24.8	26.6	42.1	47.4	51.1	55.0
22	20.0	18.6	34.1	24.8	26.8	42.6	47.4	51.1	55.3
23	19.2	18.6	34.1	24.8	26.8	42.6	47.5	51.4	55.6
24	18.4	19.5	34.1	25.1	27.1	42.6	47.7	51.4	56.3
25	18.1	20.0	33.8	25.3	27.1	43.2	47.9	51.7	56.6

(continuing)

Relax- ation time, min.	Delignification time, min.								
	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%)*
	Lignin content, %**								
	78	68	56	43	30	23	0	0	0
26	18.5	20.0	33.8	25.3	27.1	43.2	48.1	51.7	56.9
27	19.2	21.0	34.1	25.5	27.1	43.2	48.3	52.0	56.9
28	20.0	21.0	33.4	25.8	27.1	43.2	48.3	52.0	57.2
29	20.8	21.0	34.7	25.8	27.1	43.2	48.6	52.0	57.2
30	20.8	20.0	35.0	25.5	26.8	43.2	49.0	52.0	57.2
31	20.8	20.0	35.0	25.5	26.8	43.2	49.1	52.0	57.2
32	20.0	19.1	35.0	25.5	26.8	43.7	49.3	52.2	57.6
33	20.0	18.2	35.0	25.3	27.1	43.7	49.5	52.2	57.6
34	20.0	18.2	35.0	25.3	27.1	44.2	49.5	52.5	57.6
35	18.5	17.1	35.0	25.3	27.3	44.2	49.7	52.8	57.9
36	17.7	17.1	35.0	25.3	27.3	44.7	50.0	53.1	57.9
37	17.7	17.1	35.0	25.3	27.3	44.7	50.0	53.7	58.2
38	16.9	17.1	35.0	25.3	27.3	45.3	50.0	59.0	58.2
39	16.9	17.1	35.0	25.3	27.3	45.3	50.0	59.0	58.5
40	16.9	17.1	35.0	25.3	27.3	45.3	50.2	59.0	59.2

* Caustic treatments at 25°C

** Based on the 1500 cm⁻¹ band intensity

TABLE 25. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON STRESS DECREMENT OF DOUGLAS FIR LATEWOOD DURING RELAXATION

Relax- ation time,	Delignification time, min.									
	0	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%)*
	Lignin content, %**									
	100	97	86	72	60	46	20	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0.2	11.2	11.2	7.3	10.4	9.9	10.0	24.1	14.0	25.7	30.4
0.4	13.8	14.2	8.0	12.1	11.9	12.6	30.4	16.0	31.1	34.7
0.6	15.0	15.0	9.5	13.0	12.9	14.0	33.5	17.5	33.2	37.3
0.8	15.8	16.7	9.9	13.8	13.7	15.0	35.4	18.7	35.4	39.0
1.0	16.5	17.5	10.9	14.4	14.1	15.7	36.7	19.3	36.8	40.4
1.5	17.7	18.3	11.7	15.5	15.4	16.8	39.2	20.8	39.3	42.8
2	18.1	19.2	12.4	16.3	16.0	17.5	41.1	22.3	41.1	44.7
3	18.8	20.4	14.6	17.1	16.8	18.9	43.7	23.4	43.6	47.1
4	19.6	20.8	15.3	17.7	17.2	19.5	44.9	24.6	45.4	49.0
5	19.6	21.7	15.3	18.0	17.4	19.9	46.8	25.8	46.5	50.2
6	20.0	22.1	15.3	18.8	17.8	20.4	47.5	26.4	46.8	51.7
7	20.4	22.5	15.3	19.0	17.8	20.6	48.1	27.3	47.5	52.6
8	20.4	22.9	15.0	19.2	18.0	20.8	48.7	28.2	47.9	53.6
9	20.8	23.3	14.6	19.4	18.0	21.4	49.4	28.5	48.6	54.1
10	21.2	23.8	14.4	19.4	18.0	21.5	50.0	28.8	48.9	54.6
11	21.2	23.8	14.6	19.6	18.2	21.9	50.6	28.8	49.3	55.0
12	21.2	23.8	15.0	19.6	18.2	22.2	50.6	29.1	49.3	55.3
13	21.9	23.8	15.0	19.6	18.4	22.5	51.9	29.1	50.0	55.5
14	21.9	23.3	15.0	19.6	19.0	22.6	52.5	29.4	50.0	55.7
15	21.9	23.3	16.8	19.6	19.0	22.6	53.2	29.7	50.4	56.2
16	21.7	23.3	16.8	19.6	19.0	22.6	53.2	29.7	51.1	56.5
17	21.7	22.9	16.8	19.6	19.0	22.8	53.2	30.0	51.4	56.7
18	21.5	22.9	16.8	19.6	19.0	22.6	53.7	30.0	51.8	57.2
19	21.5	22.9	16.8	19.6	19.0	22.6	53.8	30.3	52.1	57.4
20	21.5	22.9	16.8	19.6	18.8	22.6	53.8	31.2	52.5	57.7
21	21.5	23.3	16.0	19.6	18.6	22.8	53.8	31.5	52.5	58.1
22	21.5	23.8	15.3	19.6	18.6	22.8	53.8	31.8	52.5	58.9
23	21.5	23.8	15.3	19.6	18.6	23.2	54.4	32.6	52.1	58.9
24	21.9	24.2	15.3	19.6	18.6	23.3	54.4	32.6	52.1	58.9
25	22.3	24.2	15.3	19.8	18.6	23.5	55.1	32.4	52.5	59.1

(continuing)

Relax- ation time, min.	Delignification time, min.										*
	0	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%)	
	Lignin content, % **										
	100	97	86	72	60	46	20	0	0	0	
26	22.7	24.2	16.0	20.0	18.6	23.8	55.1	33.0	52.5	59.1	
27	22.7	24.2	16.8	20.2	18.8	23.9	55.1	33.0	52.5	59.1	
28	22.7	24.2	16.8	20.3	19.0	24.0	55.7	33.0	52.5	59.1	
29	22.7	24.2	17.5	20.3	19.2	24.0	55.7	33.0	52.9	59.1	
30	22.7	24.2	16.8	20.3	19.2	24.0	55.7	33.0	53.2	59.1	
31	22.7	24.2	16.8	20.3	19.2	24.0	56.3	33.0	53.6	59.3	
32	22.7	23.8	16.0	20.3	19.2	23.9	56.3	33.0	53.6	59.6	
33	22.3	22.8	16.0	20.3	19.2	23.9	56.3	33.0	53.9	59.8	
34	22.3	23.3	16.8	20.3	19.2	24.0	56.3	33.2	53.9	60.1	
35	21.9	24.2	16.8	20.3	19.2	24.2	56.3	33.2	53.6	60.5	
36	21.9	24.2	16.8	20.3	18.8	24.5	56.3	33.2	53.6	61.0	
37	21.9	24.6	16.8	20.3	18.8	24.6	56.3	33.5	53.9	61.0	
38	21.9	24.6	16.8	20.3	18.8	24.6	56.3	33.5	53.9	60.8	
39	21.9	24.6	16.8	20.3	18.8	24.9	57.0	33.5	53.9	60.8	
40	21.9	24.6	16.8	20.3	18.8	24.9	57.0	33.5	53.9	60.8	

* Caustic treatments at 25°C ** Based on the 1500 cm⁻¹ band intensity

TABLE 26. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON STRESS DECREMENT OF BALSAM FIR EARLYWOOD DURING RELAXATION

Relaxation time, min.	Delignification time, min.									
	0	30	60	90	120	180	240	240 (5%)	240 (17.5%) *	
	Lignin content, %**									
	100	78	62	55	52	45	30	14	0	
0	0	0	0	0	0	0	0	0	0	
0.2	5.8	4.1	7.7	11.2	6.6	6.7	11.2	15.1	28.7	
0.4	7.6	5.5	7.7	13.0	8.7	8.0	13.8	17.1	33.6	
0.6	8.5	4.8	9.2	14.9	10.1	9.3	14.5	18.7	36.8	
0.8	10.3	6.2	9.2	15.8	10.8	10.0	15.8	19.7	38.6	
1.0	10.8	6.2	9.2	16.7	11.6	10.0	16.5	20.4	40.4	
1.5	12.2	6.2	9.2	18.6	11.6	11.0	17.8	22.4	42.6	
2	12.6	6.9	10.8	19.5	11.6	11.7	19.1	23.4	45.3	
3	14.3	8.9	10.8	20.7	11.6	12.3	19.7	25.1	47.9	
4	14.7	8.3	10.8	21.7	15.1	13.0	19.7	26.1	49.8	
5	15.2	9.0	12.3	22.3	15.1	13.3	20.4	27.1	51.1	
6	15.6	9.0	12.3	22.3	15.6	13.3	20.4	27.4	52.0	
7	15.9	9.7	12.3	23.2	15.9	13.3	21.1	28.8	53.8	
8	16.1	9.7	10.8	23.2	16.3	13.3	21.1	29.1	54.3	
9	16.8	9.7	10.8	23.2	16.4	13.7	21.1	29.8	54.7	
10	17.0	10.3	10.8	23.8	16.7	13.7	21.1	29.8	55.2	
11	17.5	10.3	12.3	24.2	16.7	13.7	21.7	30.4	56.1	
12	17.9	10.3	13.9	24.2	16.7	13.7	22.4	30.8	57.0	
13	18.9	10.3	15.4	24.2	16.7	13.3	22.4	31.1	58.3	
14	18.9	10.3	15.4	24.2	17.5	13.3	23.0	31.4	58.7	
15	18.2	10.3	15.4	24.8	17.5	13.0	23.0	31.8	59.2	
16	18.4	9.7	13.9	24.8	17.5	13.0	22.4	31.8	59.2	
17	17.9	9.0	13.9	24.8	19.1	13.0	22.4	31.8	59.2	
18	17.9	8.3	13.8	24.8	19.3	13.7	22.4	31.8	59.6	
19	18.2	8.3	12.3	24.8	19.3	14.3	22.4	32.1	59.6	
20	18.4	6.9	13.6	25.7	19.3	14.7	21.7	32.1	59.6	
21	18.2	7.6	13.9	25.7	19.3	14.7	22.4	32.4	59.6	
22	18.2	9.0	12.3	25.7	19.3	14.7	22.4	32.4	60.1	
23	18.2	8.3	12.3	25.7	19.8	14.3	23.0	32.8	60.1	
24	17.9	9.7	10.8	25.7	19.8	14.3	23.0	33.1	60.5	
25	17.9	10.3	10.8	25.7	19.8	14.3	23.7	33.1	61.4	

(continuing)

Relax- ation time, min.	Delignification time, min.								
	0	30	60	90	120	180	240	240 (5%)	240 (17.5%) *
time, min.	Lignin content, % **								
	100	78	62	55	52	45	30	14	0
26	17.9	10.3	10.8	25.7	19.8	14.0	23.7	34.4	61.9
27	17.7	10.3	10.8	25.7	19.8	14.0	23.7	34.4	62.8
28	18.2	10.3	10.8	25.7	19.8	14.3	23.0	34.4	63.2
29	17.9	10.3	10.8	25.7	19.8	14.3	23.0	34.4	63.7
30	17.7	10.3	10.8	25.7	19.6	14.7	23.0	34.4	63.7
31	17.9	10.3	9.2	25.7	19.3	14.7	22.4	34.4	63.7
32	17.9	9.7	9.2	25.7	19.8	14.7	22.4	33.8	63.7
33	17.9	9.7	9.2	25.7	20.4	14.7	22.4	33.8	63.7
34	17.7	9.7	9.2	25.7	20.6	14.7	22.4	33.8	63.7
35	17.7	8.3	9.2	26.7	20.9	14.7	22.4	33.8	63.7
36	17.5	8.3	7.7	26.6	20.9	14.7	23.0	34.1	63.7
37	17.5	6.9	7.7	26.6	20.9	14.7	23.7	34.1	63.7
38	17.5	6.9	7.7	26.6	20.6	14.7	24.3	34.1	63.7
39	17.5	6.9	7.7	26.6	20.6	14.7	24.3	34.5	64.1
40	17.5	6.9	7.7	26.9	20.6	14.7	24.3	34.5	64.5

* Caustic treatments at 25°C

** Based on the 1500 cm⁻¹ band intensity

TABLE 27. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE ON STRESS DECREMENT OF BALSAM FIR LATEWOOD DURING RELAXATION

Relax- ation time, min.	Delignification time, min.							Lignin content, % **		
	0	30	60	90	120	180	240	240 (1%)	240 (5%)	240 (17.5%)*
	100	96	79	72	55	41	19	13	8	0
0	0	0	0	0	0	0	0	0	0	0
0.2	6.7	5.9	9.2	8.3	8.6	7.6	8.8	9.4	14.1	27.3
0.4	8.3	7.3	11.3	9.7	10.7	10.1	11.1	11.6	17.4	32.11
0.6	9.3	8.4	12.2	10.4	12.1	11.5	12.5	12.7	19.6	35.6
0.8	10.3	9.4	13.0	11.1	13.0	12.4	13.2	14.0	21.1	37.1
1.0	10.6	9.8	13.7	11.1	13.7	13.0	14.0	14.7	22.0	38.7
1.5	11.7	10.0	14.0	11.8	15.2	14.5	14.5	15.8	24.1	41.2
2	12.7	10.2	14.7	12.5	15.9	15.2	16.0	16.5	25.9	42.6
3	13.3	10.2	15.5	13.9	17.2	16.2	17.2	17.4	29.1	45.3
4	13.7	11.5	15.5	14.6	18.1	17.0	17.9	18.3	30.4	47.2
5	14.0	11.8	15.8	15.3	18.7	17.7	18.6	18.6	30.9	48.9
6	15.0	11.8	15.8	15.3	19.1	17.7	18.9	18.7	31.9	49.9
7	15.0	11.8	15.5	15.3	19.1	17.7	19.0	18.8	32.4	50.9
8	15.0	11.8	15.5	15.3	19.1	18.8	19.1	19.0	32.8	51.3
9	15.0	11.8	15.1	16.7	20.0	19.0	19.1	19.1	33.0	51.9
10	15.7	12.2	15.1	16.7	20.2	19.0	19.1	19.1	33.7	52.6
11	15.7	12.2	15.1	16.7	20.2	19.3	19.0	19.3	34.1	52.8
12	15.7	11.8	16.1	16.7	20.9	19.3	19.0	19.4	34.6	53.2
13	15.7	11.8	16.1	16.7	20.9	19.7	19.0	19.5	35.0	53.6
14	16.0	11.8	17.8	16.7	21.2	19.8	18.9	19.8	35.7	53.8
15	16.0	11.8	17.8	16.7	21.2	15.0	19.1	20.0	35.9	54.0
16	16.3	11.8	17.5	16.0	21.5	20.0	19.3	20.1	36.1	54.2
17	16.3	11.8	17.5	16.0	21.7	20.2	19.3	20.1	36.5	54.7
18	16.3	11.8	17.1	15.3	21.7	20.2	19.4	20.1	36.5	55.3
19	16.3	11.8	17.1	15.3	21.7	20.6	19.4	20.1	36.5	55.5
20	16.3	11.8	16.8	16.0	22.2	20.6	19.4	20.0	36.7	55.9
21	16.3	11.8	16.4	16.0	22.2	20.6	19.4	20.0	36.8	55.9
22	16.3	11.8	16.1	16.0	22.2	20.6	19.25	19.8	37.0	56.7
23	16.0	11.8	15.8	15.3	22.3	21.0	19.11	19.8	37.0	56.7
24	16.0	11.8	15.5	15.3	22.4	21.0	18.9	20.0	37.0	56.7
25	16.0	11.8	15.5	16.0	22.6	21.2	19.0	20.0	37.2	56.9

(continuing)

Relax- ation time, min.	Delignification time, min.							240 (1%) 240 (5%) 240 (17.5%)*		
	0	30	60	90	120	180	240			
	Lignin content, % **									
	100	96	79	72	55	41	19	13	8	0
26	16.0	11.8	15.1	15.3	22.8	21.2	19.1	20.0	37.2	56.9
27	16.0	11.8	15.1	15.3	22.8	21.2	19.1	20.0	37.2	57.1
28	16.0	11.8	15.5	15.3	23.4	21.3	19.3	20.3	37.4	57.1
29	16.0	11.8	16.1	15.3	23.4	21.3	19.3	20.4	37.4	57.3
30	16.0	11.8	16.1	15.3	23.4	21.3	19.4	20.4	37.4	57.3
31	16.0	11.8	17.1	16.0	23.5	21.5	19.6	20.8	37.6	57.5
32	16.0	11.8	17.1	16.0	23.5	21.5	19.7	21.0	37.8	57.6
33	16.0	12.2	16.8	16.0	23.5	21.5	19.5	20.8	37.8	58.0
34	16.0	12.2	16.8	16.0	23.5	21.5	19.4	20.8	38.0	58.2
35	16.3	12.2	16.4	16.7	23.6	21.7	19.2	20.8	38.0	58.6
36	16.3	12.2	15.8	16.7	23.6	21.7	19.3	20.8	38.0	58.8
37	16.3	12.2	15.5	16.7	23.6	21.7	19.4	21.0	38.3	58.8
38	16.3	12.2	15.5	16.7	23.6	21.8	19.4	20.8	38.7	58.8
39	16.3	12.2	15.5	16.7	23.6	21.8	19.3	21.0	38.9	58.9
40	16.3	12.5	15.5	16.7	23.6	21.8	19.3	20.8	39.4	59.0

* Caustic treatments at 25°C

** Based on the 1500 cm⁻¹ band intensity

A₀ Radiant heating rods A₃ Aluminium rod
 A₁ Insulated copper tubing A₄ Fixed blocks
 A₂ Guides A₅ Specimen

C₀ Spring C₃ Micrometer
 C₁ Release clutch C₄ Specimen
 C₂ Sliding plate

FIGURE 1. PHOTOGRAPHS SHOWING THE RAMP-LOADING APPARATUS (A) AND ITS POSITION IN THE INSTRUMENT (B), AND THE STEP-LOADING APPARATUS (C) AND ITS POSITION IN THE INSTRUMENT (D).

FIGURE 2. INFRARED POLARIZATION SPECTRA ($\parallel$ AND $\perp$) OF DOUGLAS FIR "REGULAR" AND COMPRESSION WOOD TISSUES (ARROW INDICATES THE 1160 cm^{-1} BAND).

FIGURE 3. RELATIONSHIP BETWEEN LIGNIN (1500 cm^{-1}) AND CELLULOSE (1160 cm^{-1}) ORIENTATION FOR VARIOUS WOOD TISSUES.

FIGURE 4. ELECTRON PHOTOMICROGRAPHS OF BALSAM FIR LATEWOOD CROSSSECTION FOLLOWING DELIGNIFICATION (a, 0 MIN; b, 60 MIN; AND c, 240 MIN) AND FAILURE IN TENSION PARALLEL TO GRAIN. CELL WALL LAYERS (P, S₁, S₂ AND S₃) AND MIDDLE LAMELLA (ML).

DOUGLAS FIR

BALSAM FIR

FIGURE 5. DEPENDENCE OF DICHOIC RATIOS AT 1160 AND 1730 cm^{-1} ABSORBANCES ON LIGNIN CONTENT OF DOUGLAS FIR AND BALSAM FIR WOOD TISSUES.

FIGURE 6. X-RAY DIFFRACTION PATTERNS OF DOUGLAS FIR WOOD TISSUES FOLLOWING DIFFERENT LEVELS OF CHLORITE DELIGNIFICATION.

FIGURE 7. EFFECT OF DELIGNIFICATION LEVEL ON CRYSTALLINITY OF WOOD TISSUES.

FIGURE 8. RELATIONSHIP BETWEEN X-RAY TOTAL CRYSTALLINITY AND ORIENTATION ANGLE OF THE WOOD CELLULOSE 1,4- β -D-LINKAGE.

FIGURE 9. INTRA-INCREMENTAL RELAXATION OF THE 1160 cm^{-1} COMPONENT (CELLULOSE) IN DOUGLAS FIR WOOD TISSUES.

FIGURE 10. INTRA-INCREMENTAL RELAXATION OF THE 1730 cm^{-1} COMPONENT (HEMICELLULOSE) IN DOUGLAS FIR WOOD TISSUES.

FIGURE 11. INTRA-INCREMENTAL RELAXATION OF THE 1500 CM⁻¹ COMPONENT (LIGNIN) IN DOUGLAS FIR WOOD TISSUES.

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FIGURE 12. MOLECULAR MOTION OF WOOD CARBOHYDRATE COMPONENTS DURING CREEP TEST OF BALSAM FIR WOOD TISSUES.

FIGURE 13. EXCITATION TIME EFFECTS ON THE MOLECULAR RELAXATION OF THE 1730 CM-1 COMPONENT IN BALSAM FIR WOOD TISSUES.

FIGURE 14. THE EFFECT OF REMOVING LIGNIN, THEN HEMICELLULOSE, ON RELAXATION OF THE 1160 cm^{-1} COMPONENT (CELLULOSE) IN DOUGLAS FIR EARLYWOOD TISSUES.

FIGURE 15. THE EFFECT OF REMOVING LIGNIN ON RELAXATION OF THE 1730 CM^{-1} COMPONENT (HEMICELLULOSE) IN DOUGLAS FIR EARLYWOOD TISSUES.

FIGURE 16. THE EFFECT OF REMOVING LIGNIN, THEN HEMICELLULOSE ON RELAXATION OF THE 1160 cm^{-1} COMPONENT (CELLULOSE) IN DOUGLAS FIR LATEWOOD TISSUES.

FIGURE 17. THE EFFECT OF REMOVING LIGNIN ON RELAXATION OF THE 1730 cm^{-1} COMPONENT (HEMICELLULOSE) IN DOUGLAS FIR LATEWOOD TISSUES.

FIGURE 18. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE, ON PHYSICAL STRESS RELAXATION OF DOUGLAS FIR EARLYWOOD TISSUES.

FIGURE 19. EFFECTS OF REMOVING LIGNIN, THEN HEMICELLULOSE, ON PHYSICAL RELAXATION OF DOUGLAS FIR LATEWOOD TISSUES.