ELEMENTS OF WOOD FIBER STRUCTURE AND FIBER BONDING

U.S. FOREST SERVICE
RESEARCH PAPER

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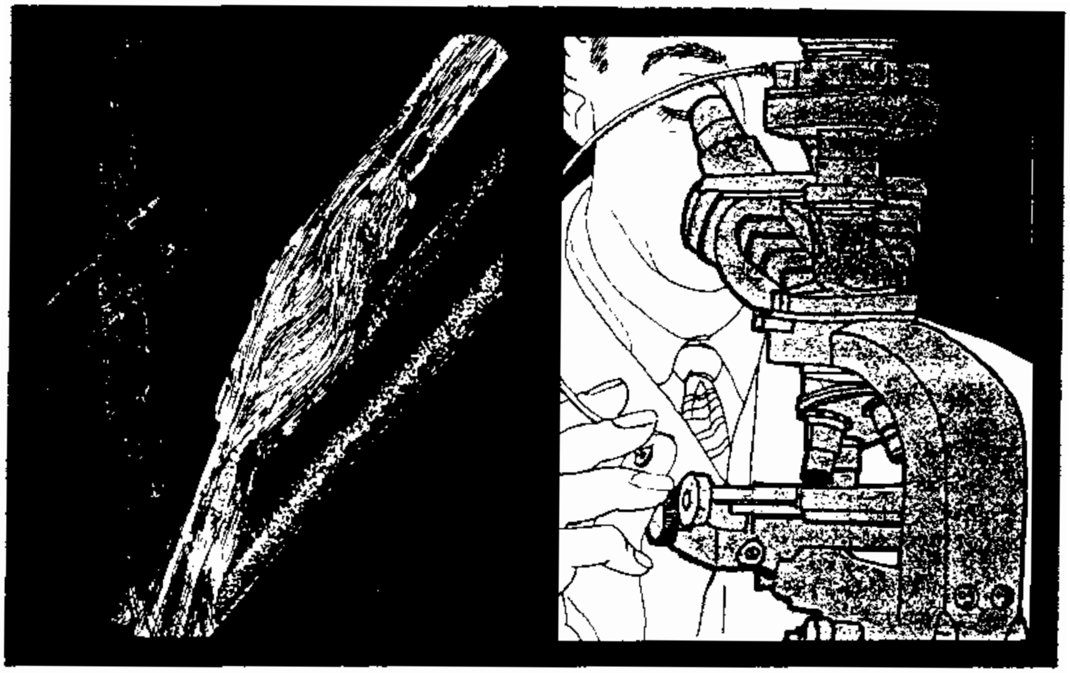
MAY
1963



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SUMMARY

Current concepts of the chemical composition and physical organization of wood fibers are reviewed. The use of cellulose solvents in studies of the microscopic structure of the cell wall is discussed and illustrated. Types of natural fiber-to-fiberbonding are pictured in color as well as current work on the distribution of additives in linerboard applied for chemical bonding.

ELEMENTS OF WOOD
FIBER STRUCTURE AND FIBER BONDING

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INTRODUCTION

Wood fibers are highly complex in chemical composition, distribution of chemical components, and physical organization. Their complex structure has a strong bearing on their papermaking qualities. In pulp made from any one species, the fibers can vary widely, depending on the pulping process used. Manufacturers of pulp and paper are confronted daily with the need for a complete understanding of the significance of these varying characteristics when striving to introduce scientific and engineering principles into their processes.

At the macroscopical level, fiber length, fiber width, and the thickness of the fiber wall are important. Long fibers improve tearing strength. Short, thin-walled fibers contribute to the smooth surfaces required of modern printing papers. Thick-walled fibers add bulk, opacity, and tearing strength.

At the microscopical level, the cell wall consists of several layers of cellulose embedded in lignin and hemicelluloses. These layers, made up of fibrils differently oriented, comprise three distinct walls--the primary, the secondary, and the tertiary. In turn, the secondary wall consists of two layers, S-1 and S-2. The S-2 layer is the thickest of the three; it comprises the bulk of the secondary wall, This physical organization is shown schematically in figure 1, in which the relative thickness of the walls is depicted according to present consensus, the ranges of values in microns being 0.23 to 0.34, 0.12 to 0.35, 1.77 to 3.68, and 0.10

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[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

to 0.15 (9).[2]

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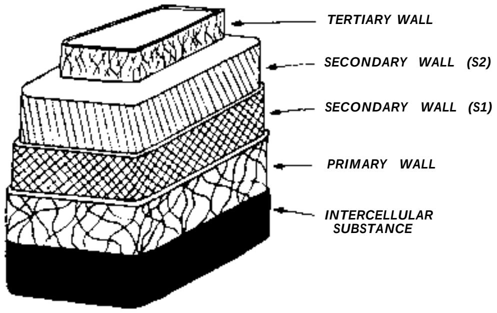

Figure 1.--The physical organization of a typical softwood fiber (relative thickness of walls to scale).

The term "tertiary wall" refers herein to the inner layer of the secondary wall in agreement with Bucher (2) and with Liese (11). The latter has demonstrated that the fibrillar orientation of this layer is interwoven or meshlike in contrast to those of the S-1 and S-2 layers. He also mentioned that the tertiary wall is more resistant to enzymatic decomposition and differs in its behavior to chemicals. The S-2 layer is the richest in cellulose (13) and is the most reactive with respect to fiber bonding. The physical structure is especially critical in the manufacture of high-strength pulps and in subsequent pulp beating and papermaking.

At the submicroscopical level, the structure is somewhat less well defined. It includes the crystalline, the amorphous, and the "in-between" regions of the cellulose, and the hemicelluloses and lignin. The hydrogen bond cross linkage between the cellulose molecules is generally considered to be also the principal bond between fibers in paper. They form between the fibers and fibrils when these are dried during the papermaking operation as explained by Campbell (3).

SOLVENT SEPARATION OF CELL WALL LAYERS

One technique long used in the study of fiber physical structure is the swelling of fibers with a cellulose solvent to loosen and separate fibrils and cell wall layers. About 1926 at the Forest Products Laboratory, Ritter used sulfuric acid in his pioneering work on the separation of the layers of the mature cell walls (17). He was cognizant of the work of the German botanist Dippel. who had observed primary, secondary, and inner layers of the cell wall by means of polarized light more than 50 years earlier (4). Recently, Jurbergs (10) discussed this use of swelling agents in some detail and also demonstrated the value of homogeneous acetylation in morphological studies.

Structural features of a Douglas-fir kraft pulp fiber swollen with cadmium ethylenediamine are shown in figure 2, upper left. This solvent, prepared according to Henley (8), was diluted with water to a cadmium concentration of about 4.2 percent and used for all swelling treatments reported herein. For the photographs, polarized

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[2] Underlined numbers in parentheses refer to Literature Cited at the end of this report.

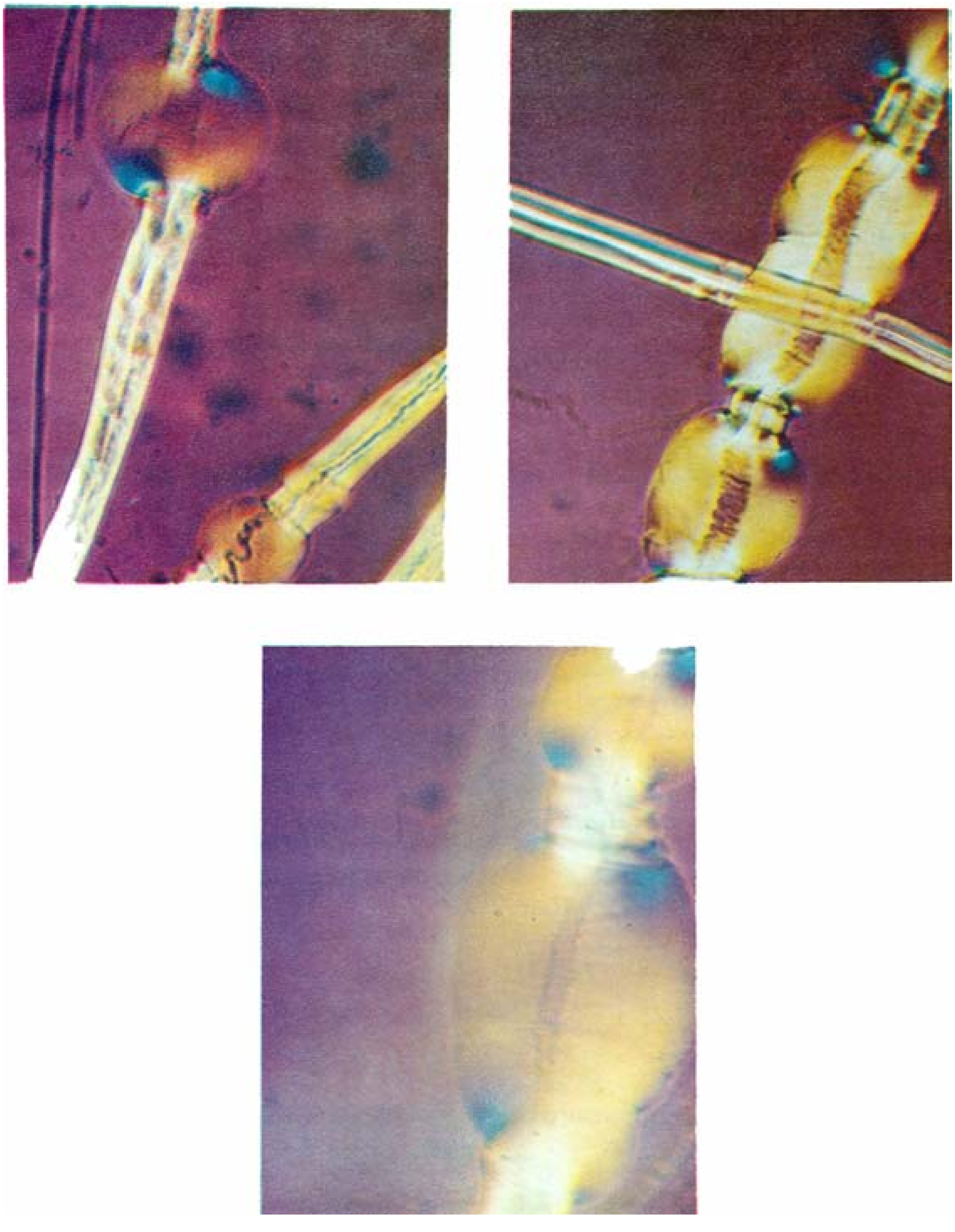


Figure 2. ––Upper left, chemically swollen Douglas-fir kraft pulp fiber showing the tertiary layer within the balloons of the S-2 layer and the intact S-1 layer at the ends of the balloons (magnification 190X). Upper right, southern pine kraft fiber showing same foregoing structure details (95X). Bottom, sweetgum kraft fiber showing foregoing structure details and lesser resistance to swelling (190X).

light with crossed polars in conjunction with, for the most part, a first order redplatewas used. The balloons are areas where the outer layer of the secondary wall, S-1, was ruptured, which permitted the less resistant inner layer, S-2, to swell grossly. A fibrillar strand of S-1can be seen at one end of the smaller balloon. Microscopical studies of the effects of various types of mechanical processing on this S-1 layer are useful in paper manufacture. Hemicelluloses in this layer have been said to cause nonuniformity of reactions during the chemical conversions of dissolving pulps (7). More information is needed on the effects of pulping andbleaching processes on both the chemical and physical qualities of S-1.

The tertiary wall is seen as the pronounced screw- or spiral-like structure within the fiber and parallel to the long axis of the fiber. This layer in pines, and many other conifers, is characterized by a wart structure that is highly resistant to chemicals (12, 24). It is plausible that these bodies also cause difficulties such as haze in cellulose acetate solutions in the chemical usage of wood pulps,

The S-1, S-2, and tertiary layers of southern pine and sweetgum kraft pulp fibers are shown clearly in figure 2, upper right and bottom. In the sweetgum, the tertiary wall is, in this instance, less pronounced than in the Douglas-fir and pine pulps.

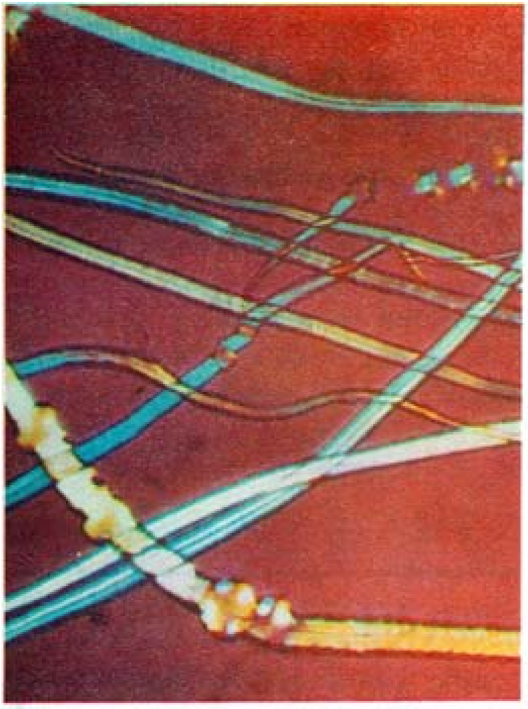
Chemical swelling is useful for qualitative comparisons of pulps produced with controlled variations in characteristics. Ritter and Chidester (18) found that with decreasing yield and increasing bursting strength, spruce and hemlock sulfite pulps became less resistant to the swelling action of phosphoric acid. Also, for a given pulp, swelling increased during beating.

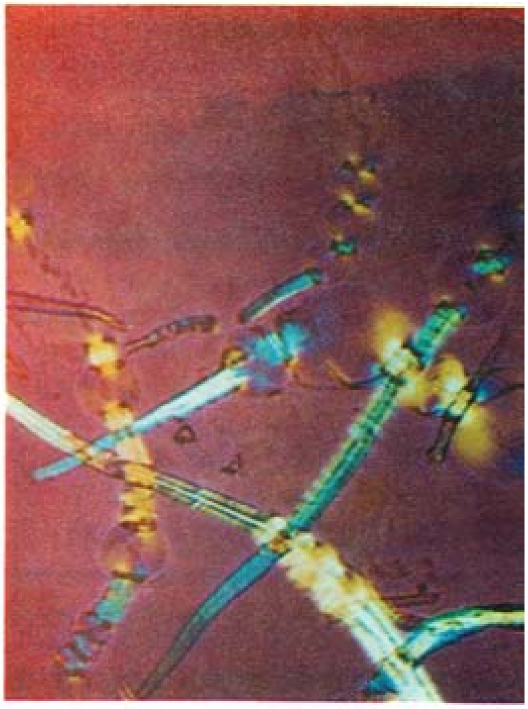
In a comparison based on the tertiary wall as revealed by swelling with cupriethylenediamine, Meier and Yllner (14) reported that this wall "is largely destroyed in sulfite pulp, but in sulfate pulp, it seems as well preserved as in holocellulose. Prehydrolyzed sulfate pulp shows, if any, a very weak tertiary wall." This generalization apparently stems from observations made on a single pulp of each type bleached without a caustic soda extraction stage.

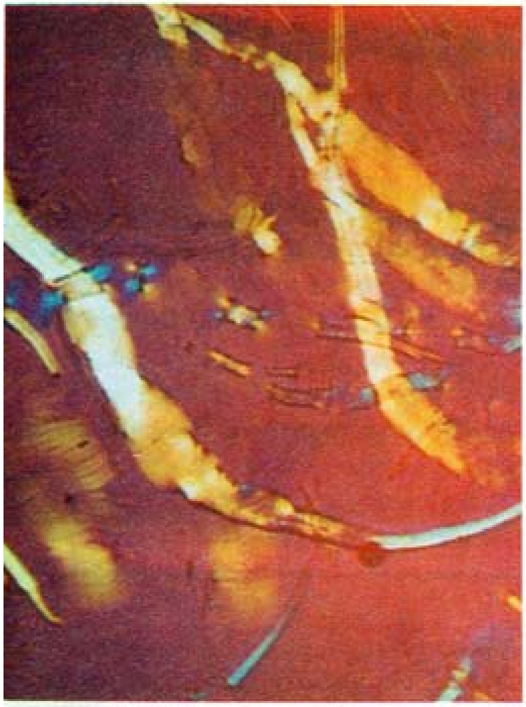
Rodgers and coworkers (19) used swelling with this reagent (0.18 molar) as a qualitive measure of how uniformly and completely dissolving pulp fibers (presumably southernpine) could be expected to react in the viscose process. The criterion was essentially the simultaneous dissolution of the tertiary and secondary layers of the cell walls. These investigators found, and it seems remarkable, that this dissolution did not occur when the concentration of caustic soda during cold extraction was up to 6 percent but at 7 percent, it did.

The relative resistance to swelling of samples of sweetgum bleached kraft and cold-purifiedprehydrolysis-kraft pulps produced and described previously (22) is shown in figure 3. The controlling variable

Figure 3.--Relative resistance to swelling of sweetgum bleached kraft and purified prehydrolysis-kraft pulps. Upper left, kraft (130X). Upper right, prehydrolysis-kraft, 60-min. hydrolysis (130X). Lower left and right, 150-min. hydrolysis (130X and 200X).







was duration of water-prehydrolysis at 170° C. Hydrolysis periods of 60 and 150 minutes are shown. The hydrolysis greatly decreased resistance to swelling. Although the 60-minute hydrolysis pulp was only about 100 lower in degree of polymerization than the kraft pulp, its pentosan content was only about a tenth as much. Compared to this pulp, the 150-minute pulp was about 500 lower in degree of polymerization but only about half lower in pentosan content. The effects of interfibrillar bonding and chain shortening are evident.

In contrast to the spruce prehydrolysis-kraft pulp examined by Meier and Yllner (14), there was extensive persistance of the tertiary wall, eventhough a cold extraction with 5 percent caustic soda solution was included in the purification treatment.

Another phase of chemical swelling worthy of investigation, especially for hardwood pulps, is a very mild action to rupture hydrogen bond cross linkages in varying degree as a sort of internal fibrillation. Effects of this treatment on fiber stiffness, strength, and bonding capacity are of great interest.

MECHANICAL SEPARATION

Mechanical processing, such as beating, is another means for revealing wall structure. Microscopical studies of the effects of various types of mechanical processing on the S-1 layer and their correlation with paper properties are of practical value.

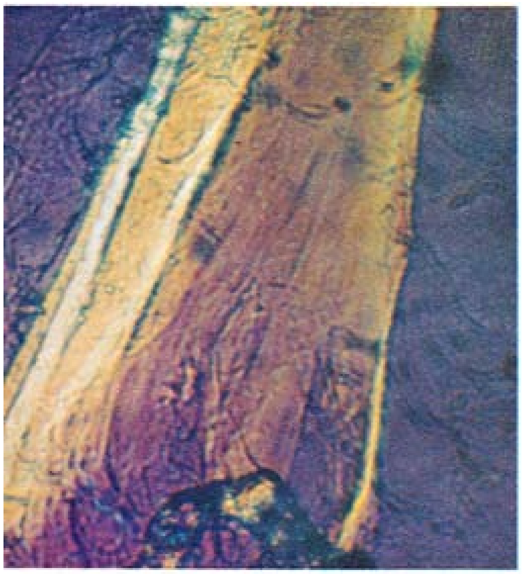
The micrograph in figure 4, upper left, of a ponderosa pine kraft fiber beaten to a Canadian standard freeness of 270 milliliters shows that the fiber wall was split open longitudinally, thus revealing the tertiary wall. A gross, slightly angled fibrillar orientation can be seen. The bright left edge is the S-2 layer, as is shown by the fairly parallel fibrillar orientation. Adjacent to this edge is a separated area of an S-1 layer, identifiable by the coaxial orientation of fibrils. Clearly, the external surface or potential bonding area of this fiber was increased considerably. Presumably, however, the inherent tensile strength and stiffness were decreased.

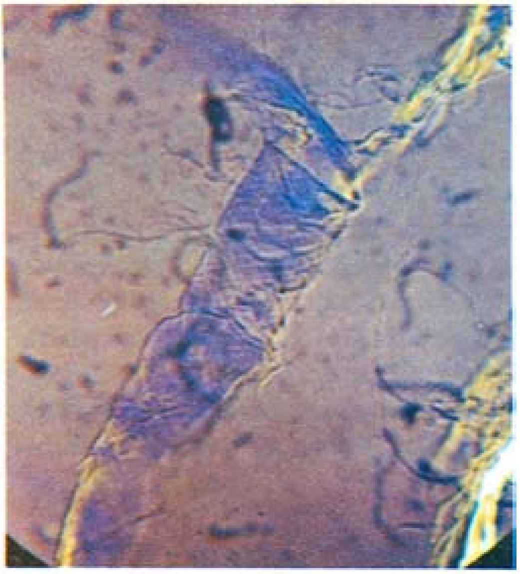
An S-1 layer completely separated from a ponderosa pine fiber is shown in figure 4, upper right. The evidence is that this type of sleeve-like separation is characteristic of pine kraft pulps.

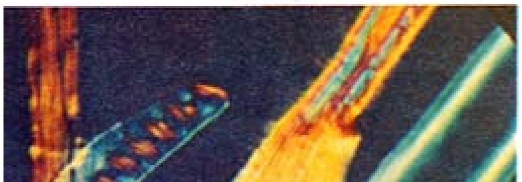
EFFECT OF PULPING PROCESS ON BEHAVIOR OF FIBER DURING BEATING

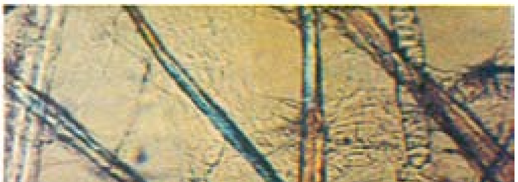
The pulping process used for separating wood fiber affects profoundly not only its chemical composition, strength, and bonding capacity but

Figure 4.--Upper left, ponderosa pine kraft fiber showing cell wall layers revealed by beating (500X). Upper right, the S-1 layer from a beaten ponderosa pine kraft pulp fiber (magnification 500X). Lower left, jack pine two-stage sulfite pulp fiber swollen by beating (260X). Lower right, larger field of the beaten jack pine sulfite pulp (125X).









also its behavior during beating.

A micrograph of a two-stage neutral sulfite acid sulfite pulp made from jack pine in a pulping investigation at the Forest Products Laboratory by Sanyer and others (20) is shown also in figure 4, lower left.

This pulp had been bleached and beaten to a freeness of 235 milliliters, Canadian standard. The point of interest is the central summerwood fiber in which a gross swelling of the S-2 layer occurred over an area where the S-1 layer was removed during beating. The typical orientation of the S-2 fibrils is evident. This balloonlike swelling occurred extensively in this pulp. The micrograph in figure 4, lower right, shows a larger area of the pulp and the extensive fibrillation induced by the beating.

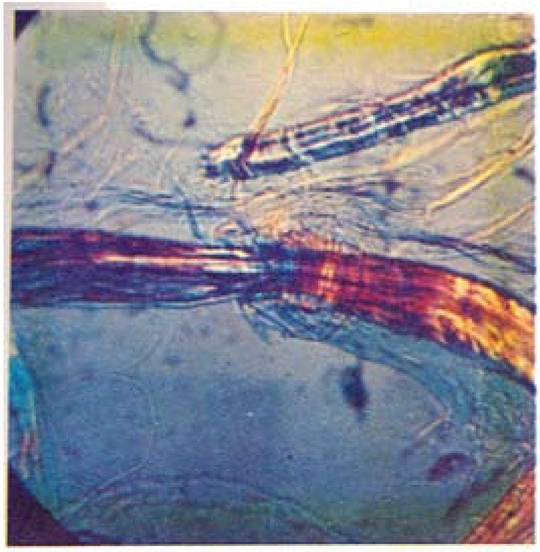
Kraft pulp made from the jack pine (20) bleached and beaten to a freeness of 210 milliliters is shown in figure 5, upper left. This pulp was much stronger than the sulfite pulp. Here, the S-1 layer has been fibrillated and peeled from the S-2 layer which, in contrast to the weaker sulfite, did not exhibit balloonlike swelling. A larger field of the beaten kraft pulp is shown in figure 5, upper right. The lesser degree of fibrillation is evident, as well as the preponderance of intact fiber--a manifestation of the strength superiority of the pulp.

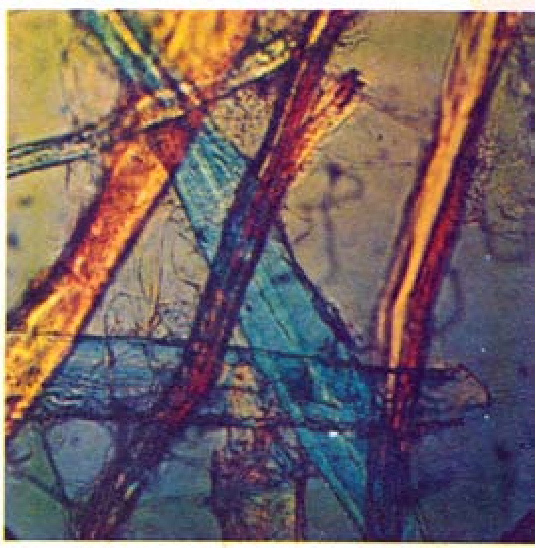
This difference in swelling characteristics was attributed (20) largely to the higher glucomman content of this sulfite pulp. Further discussion on certain differences between acid sulfite and kraft pulps are quoted from this paper (20) as follows: "The fibrillar bundles of kraft pulps have been shown to be larger in diameter than those of sulfite pulps. In addition, the crystallites are wider and more perfectly developed, and the cellulose has a wider lateral order distribution in prehydrolysis kraft than in dissolving grade sulfite pulp. Consequently, it is more resistant to swelling and has greater mechanical strength. The S-3 layer of the secondary wall in sulfite pulp was found to be greatly weakened and that the cell wall expands or swells inwardly without change in external fiber diameter. Consequently, the apparent density of sulfite fiber is lower than that of kraft fiber and the wall is therefore weaker."

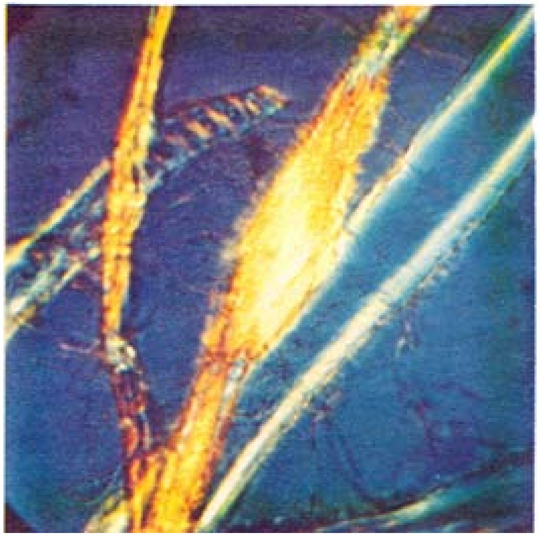
FIBER-TO-FIBER BONDING

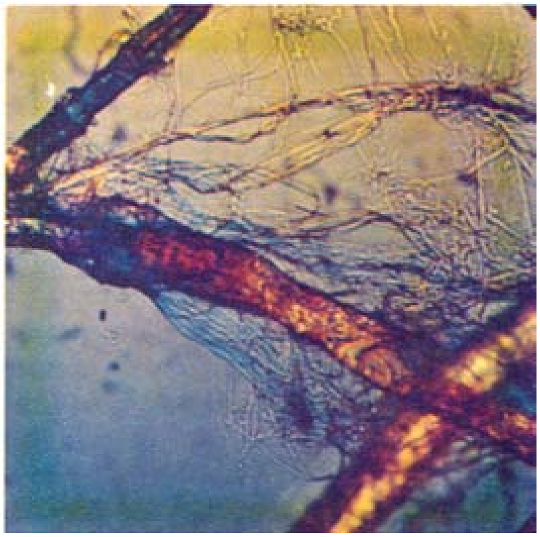
As was mentioned, pulping process affects the capacity of fibers to bond to one another. For example, in the manufacture of groundwood pulp, the lignin of the wood is retained, but it is largely removed in the production of chemical pulp. No known mechanical processing technique can yield groundwood pulp approaching chemical pulp in strength. The lignin in the groundwood pulp lacks the bonding capacity of the cellulose and hemicelluloses.

Figure 5.--Upper left, jack pine kraft pulp fibrillated by beating (260X). Upper right, a larger field of the beaten jack pine kraft pulp opposite (magnification 260X). Lower left, the jack pine sulfite fiber of figure 3 shrunken upon drying (260X). Lower right, the shrunken jack pine kraft pulp fiber above, left (260X).









Before fiber-to-fiber bonds can form, fiber surfaces must come close enough to one another to be within the minute distance through which a molecular force such as the hydrogen bond can act. This is brought about by the shrinkage of the fibrous system when dried in the presence of a strongly polar liquid, such as water. A point is reached when the surface tension of the water provides the force needed to bring the surfaces within the sphere of molecular attraction--3 to 5 Angstroms for the hydrogen bond (3).

The micrograph in figure 5, lower left, shows the shrinkage of the jack pine sulfite fiber specimen of figure 4 when it was dried on a glass slide without restraint, other than what might have resulted from adhesion of fiber to glass. The transverse shrinkage of the summerwood fiber just at the point of the swollen area was 25 percent. The similar shrinkage of the pine kraft fiber is shown at the lower right in figure 5.

A fibrillar type of fiber-to-fiber bonding between two beaten sweetgum kraft pulp fibers is shown in figure 6, upper left. A lamellar or film type of bond between two of the gum fibers is shown at the upper right. Here the fiber at the left was split open during beating but not fibrillated and formed the filmlike bond clearly evident. The relative quality of these types of bonds, that exist in papers made from pulps so beaten is not known.

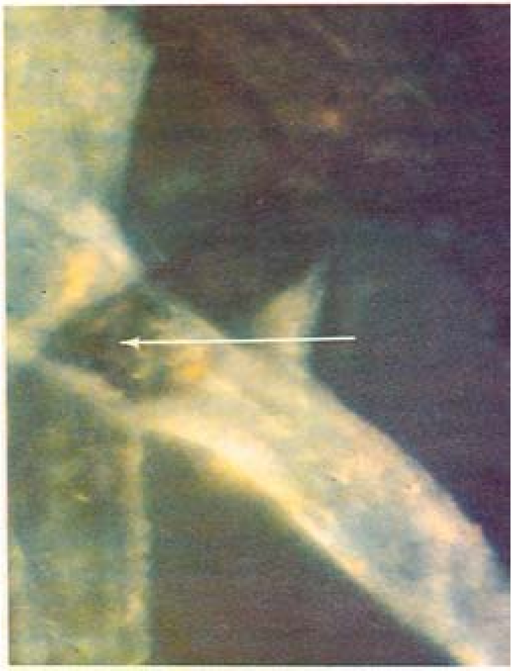
An example of the fibrillar type of bond observed in a very thin sheet of paper (actually, a handsheet) is shown in figure 6, lower left. The dynamic behavior of these fibrillar and lamellar bonds during the drying of extremely thin sheets of papers with and without restraint, using the cinnematic technique is under consideration.

Vertical polarized illumination, as proposed by Page (15), shows promise for the study of areas of fiber bonding between crossed fibers in paper. In accordance with his technique, a micrograph of the surface of a handsheet made from a mixture of dyed and undyed fibers to accentuate visibility of bonded areas is shown at the lower right in figure 6. It may be seen that the bright fiber centrally located crosses a dyed fiber at an angle of about 60°. According to hypothesis (15), dark areas like those at which fibers cross one another are areas in which bonds occur. It is not thought, however, that such areas are completely filled with bonds.

LONGITUDINAL SHRINKAGE OF FIBERS IN PAPER

From the pristine wet condition, wood pulp fibers may shrink during drying as much as 25 percent in width but only slightly in length--

Figure 6. --Upper left, fibrillar bond between two sweetgum kraft pulp fibers (725X). Upper right, lamellar bond between two sweetgum kraft pulp fibers (magnification 1,250X). Lower left, fibrillar bonds between fibers in a very thin paper (500X). Lower right, area of fiber bonding (arrow) between two crossed fibers in paper (500X).



about 1 to 2 percent.

In a paper by Smith (23) on the relation of curling and cockling of paper to dried-in strains, the practical and hypothetical aspects of fiber and sheet shrinkage are dealt with on the basis of his own data and those of others. Upon consideration of recoverable dried-in strains he supposed that when a cross-machine direction fiber bridges across several in-machine direction fibers and natural shrinkage can occur over the length of the bridging fiber, then this may be shortened much more than 2 percent owing to the diametrical shrinkage of the supporting in-machine direction fibers. This was confirmed later by Page and Tydeman (16) who observed fibers in the surface of a paper to shrink lengthwise as much as 10 percent.

BONDING WITH CHEMICAL ADDITIVES

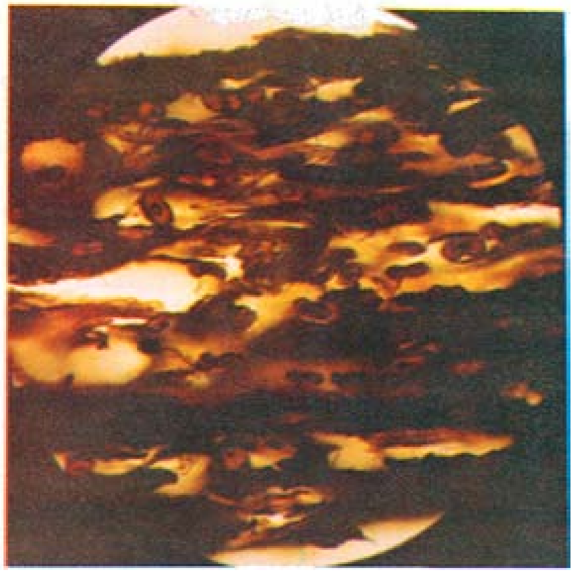
Military needs for special papers and container boards in World War II stimulated research on the use of chemical additives for improving the bonding of fibers, and this field has expanded greatly. Currently, the Forest Products Laboratory is developing, with the use of additives, a container board of improved stiffness under high humidity for the Air Force (5).

The distribution of the chemicals within the boards is being studied microscopically. The need for work in this area is recognized widely (21, 6, 1), since differences between treated boards or papers with respect to strength and other qualities can often be explained by the results obtained with this technique.

An example of this is shown in figure 7 by means of photomicrographs of cross sections across the machine direction of linerboards--wire side down. When a starch-phenol resin was added to relatively dry board at the size press, a considerably higher strength was obtained than when the chemicals were added to the wet board at the smoothing press, The photomicrographs show that in the stronger board the chemical, as revealed by staining with iodine, penetrated only a little way below each surface, but in the weaker board the penetration was consistent through the sheet. The superiority of the boards only partially penetrated is plausibly explained by considering them as sandwich constructions.

The resin-coated layers of fibers on the two surfaces act as "skins." The center, or core, which had little or no chemical, apparently had sufficient strength at 90 percent relative humidity to prevent these skins from buckling. The micrograph at the lower left of figure 7 shows the starch did not penetrate the cell walls of the fibers.

Figure 7. --Micrographs of cross-sections showing chemical distribution in linerboard (Iodine stain shows starch-phenol resin as dark areas). Upper left, unstained cross-section (110X). Upper right, location of chemical when added at size press of paper machine--30 percent strength increase (110X). Lower left, field from lower right at higher magnification showing no starch in fiber cell wall (230X). Lower right, location of chemical when added at smoothing press--6 percent strength increase (110X).



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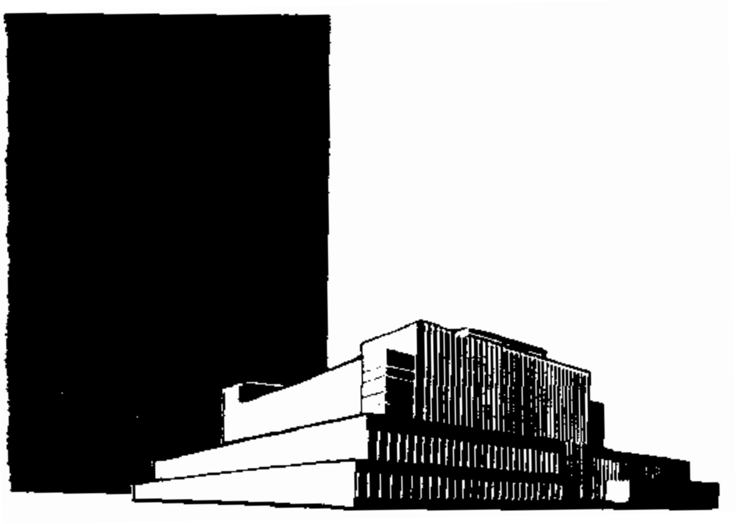

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