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# MECHANISMS OF FIBRE BOND FORMATION

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## ABSTRACT

The structure of interfibre bonding in hand sheets made of a hardwood BKP was investigated throughout the sheet formation stages using a transmission electron microscope (TEM), a scanning electron microscope (SEM) and a scanning laser microscope (SLM). The sample preparation techniques for TEM and SLM were newly developed for observation of the bond formation and bond structure.

Observations were made on couched wet webs, pressed wet webs, drying stages of the wet webs and dry sheets. Structures of the bonded zone and bonded fibres were characterized based on these observations. In this paper we discussed how the structures are affected by beating, couching, pressing and drying. We also discussed the roles of these structures in the physical properties of the fibre bonding.

## INTRODUCTION

The subject of interfibre bonding is the most fundamental basis of paper making. The nature of interfibre bonding is extremely complex, for it is affected by nearly all the treatments applied to pulp fibres in the course of paper making. These treatments include beating, wet pressing, drying, calendering etc. Interfibre bonding is also affected by the physical and chemical properties of pulp fibres. In order to

clarify the mechanism of how these treatments affect the nature of interfibre bonding, the structure of the interfibre bonding should be understood throughout its formation stages. We need to know the mechanisms of structure formation in the course of paper making and how the structure is affected by the various treatments. To date, very little is known about these mechanisms. The purpose of the present investigation is to obtain basic information on the structure of interfibre bonding for deeper understanding of the paper properties.

Knowledge of the structure of the interfibre bonding increased considerably during the 1950s and 1960s supported by the development of sample preparation techniques for TEM and SEM observation (1, 2, 3). A Polarized vertical illumination method developed by Page et al. (4) contributed greatly to visualization of the shape of the bonded area in the paper sheet by a light microscope. However, knowledge of fibre bond structure has increased very little since the 1960s, because the new microscopic techniques had not been developed for the further study of interfibre bonding. It was apparent from the outset that technique development was necessary before further progress could be made. Therefore, we started the development of observation techniques to study the structure of interfibre bonding. First we developed a formaldehyde cross-linking technique (5) which enabled the preparation of the ultrathin sections from the paper sample made of BKP. By this technique we first observed interfibre bonding in cross section using TEM. A specific method for staining external fibrils for TEM observation was also developed in order to visualize the location of external fibrils in the bonded zone (5). We also observed the drying process of wet webs under a scanning laser microscope (SLM) using high magnification (6). These techniques were further modified and were combined in this study.

## EXPERIMENTAL

### Pulp

A laboratory-made bleached kraft pulp of Buna (Japanese Beech, Fagus crenata) was used since Buna is one of the most widely used species for printing and writing papers in Japan. Fibres of Buna pulp are relatively small in diameter and rather thick-walled (Table 1). The Runkel Ratio of the fibre is about 0.6.

The pulp was beaten in a PFI mill to various freeness levels. The beaten pulps were fractionated by a Bauer McNett classifier to obtain a fine-free fraction (24 mesh pass / 80 mesh on). The fractionated and unfractionated pulps were used in the following processes.

## Specific Staining of External Fibrils and Secondary Fines

Using the method of Nakao and Kaeriyama (7), the colloidal palladium and the colloidal gold were prepared in the presence of a cationic surfactant. These colloids have the specific characteristic of sticking to fibre surfaces without penetration into fibre wall. External fibrils of the fine-free beaten pulps were stained with these colloids according to the method of Nanko et al. (5) for the specific staining of external fibrils. The unfractionated beaten pulps were also treated with the palladium colloid for staining of secondary fines as well as external fibrils.

## Preparation of Ultrathin Sections of Wet Web

Using a laboratory sheet mold, wet webs were prepared from the pulps stained with the metal colloids or from the unstained pulps. After couching, the wet webs were sandwiched between blotters and pressed using the TAPPI standard method for the first pressing. A piece of the wet web, 1 cm x 2 cm in size, was cut out with its blotters using a razor blade. They were placed between a pair of slide glasses and pinched by paper clips to maintain pressure. In this state, the wet webs were dehydrated by ethanol and then substituted by an epoxy resin in this state. Finally the webs alone were embedded in the epoxy resin. Ultrathin transverse sections were cut from the embedded samples, and they were observed under a TEM (JEM 100SX) with and without post-staining by lead citrate.

## Preparation of Ultrathin Sections of Dry Sheet

As previously reported we have shown that intact ultrathin section of BKP paper could be successfully prepared by a formaldehyde cross-linking treatment (5). According to the method of Minato et al. (8) hand sheets were treated by a vapour phase system of formaldehyde without catalyst. The

cross-linked paper samples were embedded in an epoxy resin for ultrathin sectioning. The sections were post-stained with lead citrate and observed under the TEM.

### Negative Staining Method of External Fibrils

External fibrils were observed under the TEM using the negative staining method. The wet beaten fibre was placed on a copper grid with a carbon evaporated supporting film. The fibre was negatively stained with 2 % aqueous solution of uranyl acetate. Even the cellulose microfibrils which form the external fibrils can be visualized by this method.

### Scanning Laser Microscopy of the Wet Web in Drying Process

An SLM was used to the observe the drying process of wet webs. The SLM used in this study was a Scanning Laser Microscope 1LM11 made by Lasertec Corporation. The laser light source is a 1.5 mW He-Ne at 632.8 nm.

The wet webs were prepared from the fine-free fraction of beaten and unbeaten pulps using a laboratory sheet mold. After couching, the wet webs were pressed against cover glasses using the TAPPI standard method for the first pressing. A piece of the pressed wet web with its cover glass firmly attached was fixed on a glass slide using an adhesive tape as described in the previous paper (6). The glass slide was set on the stage of the SLM and was left in the air for drying. The glass slide was weighed with an electronic balance immediately after taking a photograph of each drying stage. The bone dried webs were weighed in order to calculate the solids content of the webs at each drying stage.

## EFFECTS OF BEATING AND PRESSING ON STRUCTURE OF THE WET WEBS

The structure of the couched and pressed wet webs made of Buna BKP was observed in cross section under the TEM. Buna BKP is mainly composed of fibres, vessel elements and ray cells. When the sections are cut perpendicularly to the web surface, these elements are cut transversely, longitudinally or obliquely to the cell axis because they are arranged in various directions in the web. It is necessary to identify these

TABLE 1. Characteristics of major cell types composing Buna Wood

| | Fibre* | Vessel element | Ray cell |
|---|---|---|---|
| Cell size (9) | | | |
| diameter (um) | 13 - 25 | 20 - 110 | 20 |
| length (mm) | 0.5 - 1.8 (Av. 1.1) | 0.4 - 0.8 | 0.025 |
| Wall thickness (um) (10) | | | |
| P + S1 | 0.58 | 0.25 | 0.50 |
| S2 | 4.32 | 0.50 | 0.92 |
| S3 | 0.10 | 0.25 | 0.32 |
| Total | 5.00 | 1.00 | 1.79 |

* Tension wood fibres of S1+S2+G structure are also mixed with ordinary fibres.

constituents cut in various directions in order to understand wet web structure. In this study the pulp elements were identified basically by the size and shape of the cells. The cell wall characteristics of each element, such as the thickness and the proportion of constituting layers, were also very useful for identification (Table 1). In addition to these pulp elements, the fibrils generated by beating were observed in the wet webs made of beaten pulp. They were easily identified morphologically within the sections post-stained by lead citrate.

**Structural Characteristics of Beaten Fibre**

As previously reported (5), morphological changes of fibres due to beating proceeded as follows.

early stage: destruction and removal of the primary wall; partial separation of the S1 from the S2.

advanced stage: complete separation of the S1 from the S2; delamination and external fibrillation of the S1;
crack formation and delamination of the S2.

final stage: swelling and destruction of the S1;
progress of delamination of the S2.

Vessel elements and ray cells were more or less damaged by beating. Their cell wall layers, S1, S2 and S3, were easily delaminated and became swollen by beating. The external surface of vessel elements were fibrillated as well as the fibres'.

## Structure of Wet Web after Couching

In the couched wet web the beaten fibres were relatively close together, although they were not in tight contact (Fig. 1). The fibres were more or less round in cross section, and were not conforming to each other. This pattern suggests that couching is not strong enough to give irreversible deformation to the fibres. There were many large vacant spaces which were surrounded by pulp elements in the couched wet web (Fig. 1). The secondary fines were located along the inner margin of the space (Fig. 1, arrows) and also filling the spaces between pulp elements. This suggests that the secondary fines were attracted to the other pulp elements in the process of couching as water was removed.

## Structure of Wet Web after Pressing

The pressed wet web structure was more tightly packed as compared with the couched wet web. Fibres, vessel elements and ray cells were pressed against each other and flattened to form close contact. The structure of the wet web varied with the degree of beating of pulps.

In the case of the wet web made of unbeaten pulp, fibres became rather flattened and were making close contact with each other. The S1 of the fibre wall was often forced by pressure to be separated from the S2 at the non-contact sides of flattened fibres (Fig. 2, arrows). This type of separation probably gives the fibre wall some plasticity. On the other hand, the S2 remained almost undamaged and still appeared to have enough rigidity. In some cases, the lumen of fibres and vessel elements were collapsed. The surface of pulp elements was very smooth and unfibrillated. Most of the fibres, vessel elements and ray cells had intact primary walls on the surface and they were making contact on the primary wall (Fig. 2).

In the pressed wet web made of beaten pulp, fibres were very much flattened. The degree of flattening of fibres increased by progressive beating. It appeared that damage of fibres by beating increased conformability and plasticity of the fibre wall (Figs. 3-6). The S1 of the fibres was often separated from the S2 forming a space between the two layers (Fig. 6, arrows). Space were formed at the noncontact region of the fibres. The number of fibres with such spaces increased by progressive of beating. As we have reported (5), the S1 of the beaten fibres are more or less swollen and the circumference of the S1 is generally longer than that of the S2. Therefore, it is probable that, when fibres are pressed, the excessive part of the S1 is squeezed out to the noncontact region to form the space. On the other hand, in the web made of excessively beaten pulp, many fibres without S1 layer were observed (Fig. 5, arrows).

Vessel elements which are long and thin walled were very flexible and made good contact with fibres (Figs. 4, 6). Ray cells which are short and thin walled were found in the space between fibres as well as on the surface of fibres (Fig. 5).

The amount of secondary fines observed in the pressed wet web increased considerably by progressive beating of pulp (Figs. 2-5). The fines were filling the spaces between fibres or were found on the fibre surface (Figs. 5, 6).

The primary walls of fibres were almost completely removed from the surface of pulp elements by beating. The fibres and other pulp elements made contact with one another by the more or less fibrillated surface of the S1. The secondary fines were often sandwiched between the fibres.

Based on these experimental observations, a structure model of the pressed wet web is schematically shown in Fig. 7.

**Structure of Bond Forming Zone**

There have been many discussions of the role of external fibrillation of fibres to the bond formation and to bond strength. Emerton (11) maintained that the external fibrillation was not essential to development of paper strength. On the other hand, Clark (12) claimed that the external fibrils were the most important agents in causing

TABLE OF SYMBOLS USED IN FIGURES

B: bonding layer
C: covering layer
F: fibre
L: lumen
P: primary wall
R: ray cell
S1: S1 layer
S2: S2 layer
Sk: skirt structure
V: vessel element
W: wrinkle

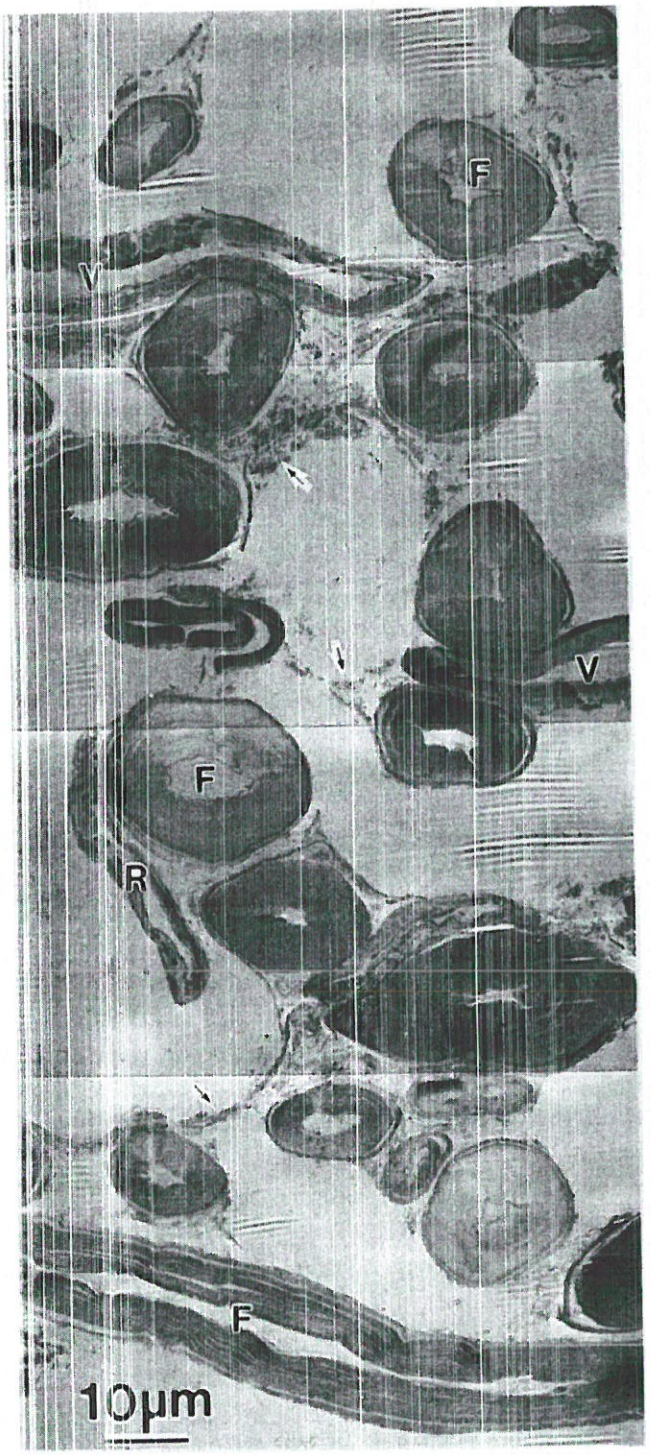


Fig. 1 Cross section of couched wet web made of beaten pulp (315 ml CSF). Post-stained with lead citrate.

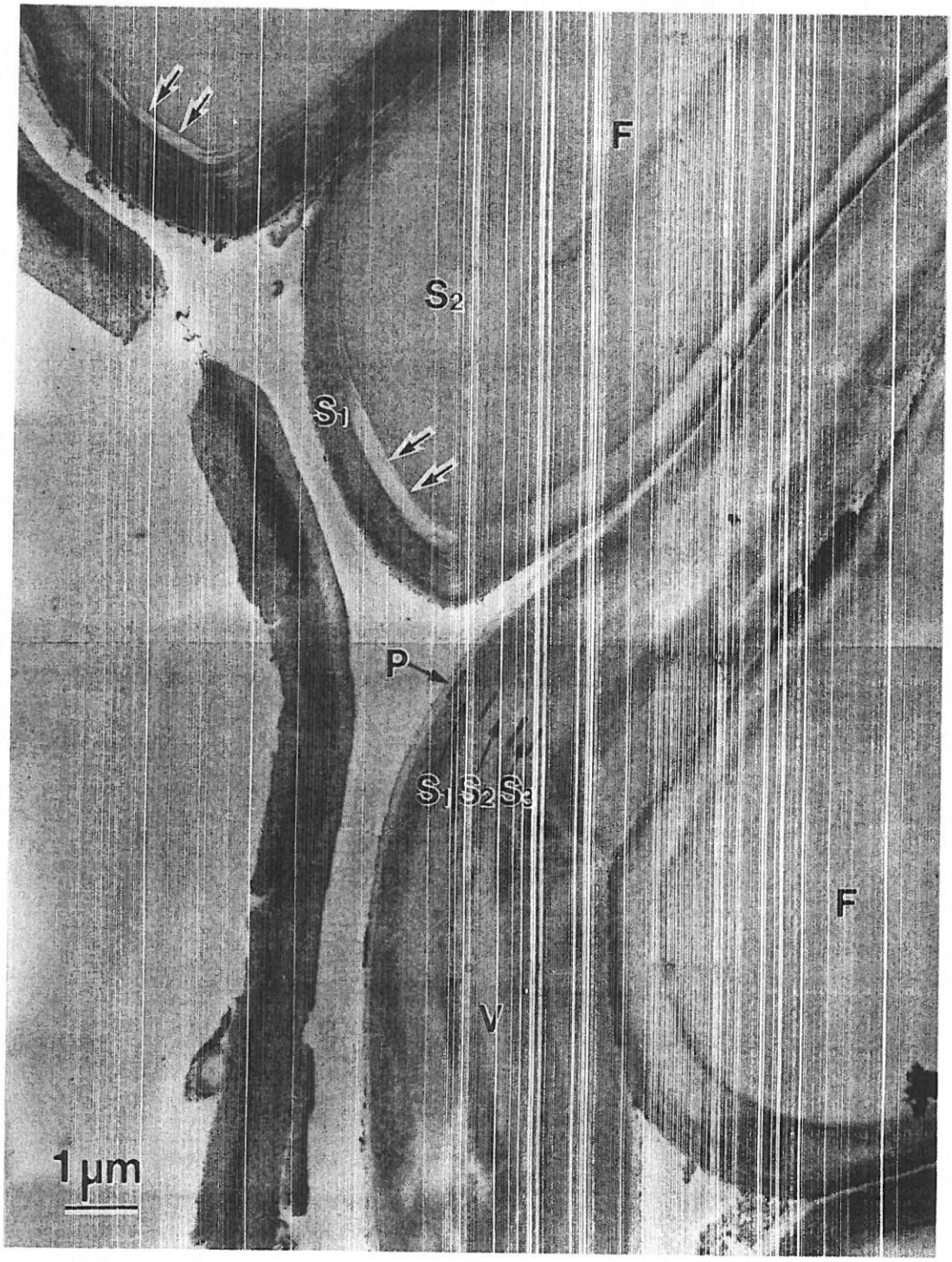


Fig. 2 Cross section of pressed wet web made of Pd-colloid stained unbeaten pulp. Post-stained with lead citrate.

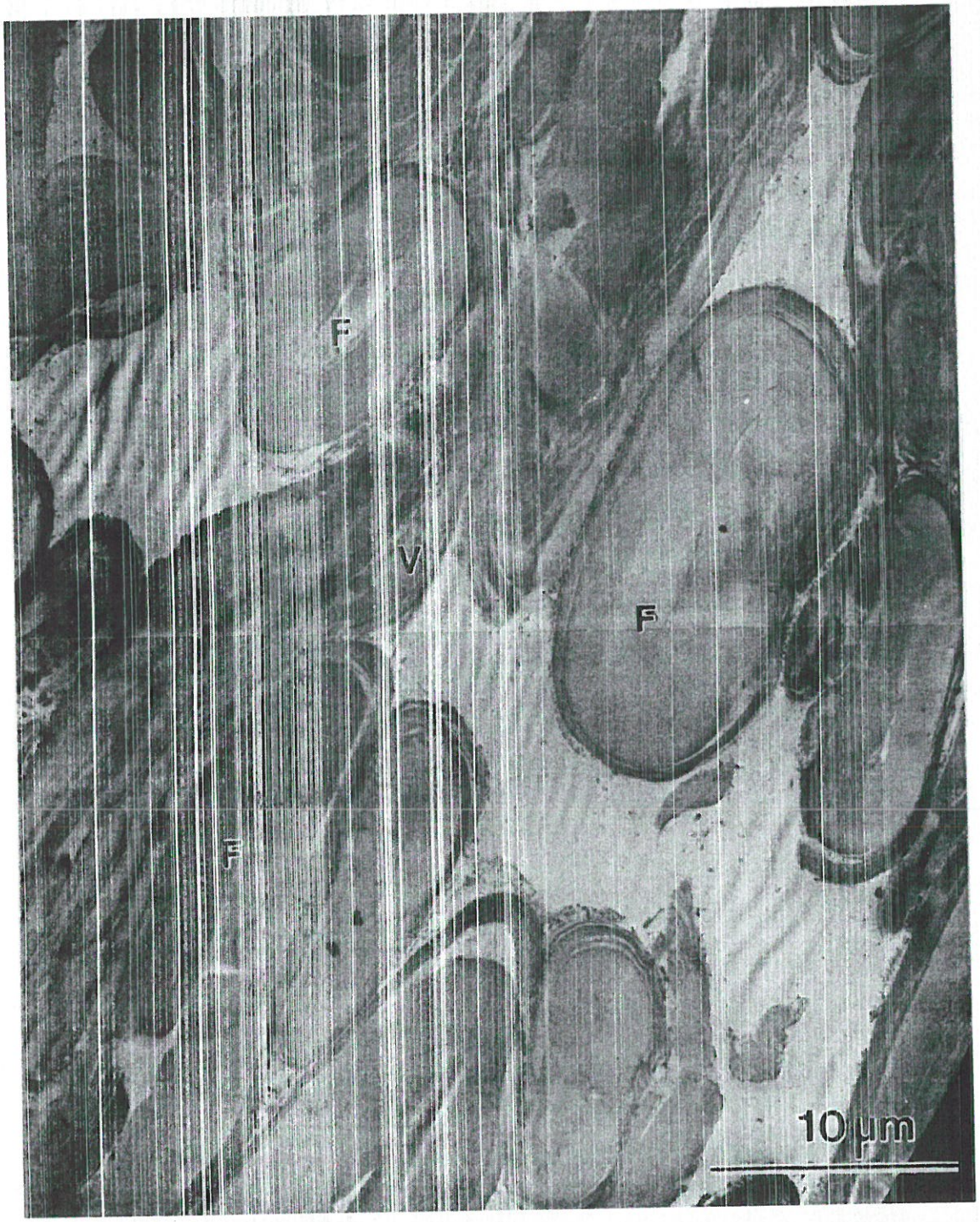


Fig. 3 Cross section of pressed wet web made of Pd-colloid stained beaten pulp (500 ml CSF). Post-stained with lead citrate.

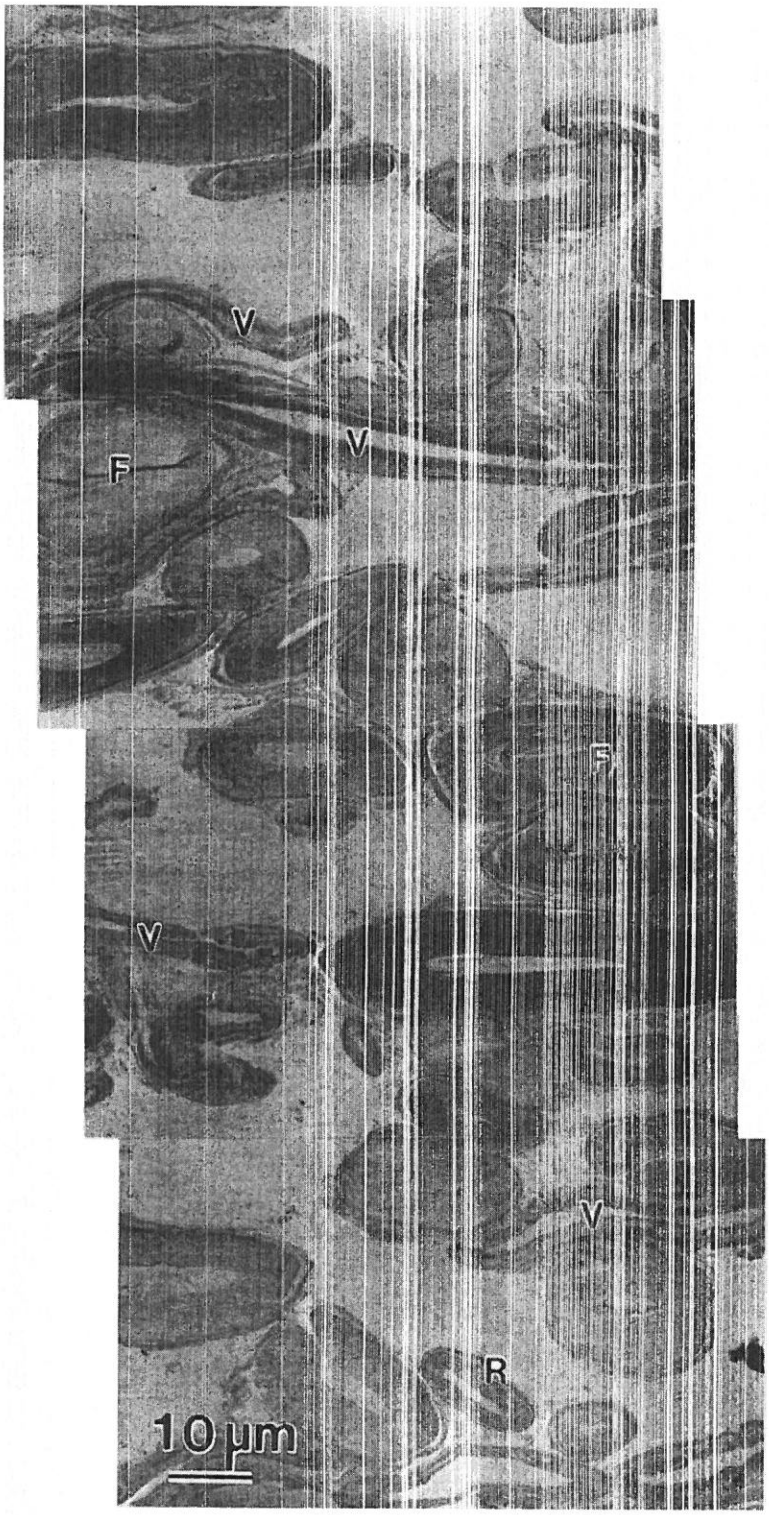


Fig. 4 Cross section of pressed wet web made of beaten pulp (400 ml CSF). Post-stained with lead citrate.

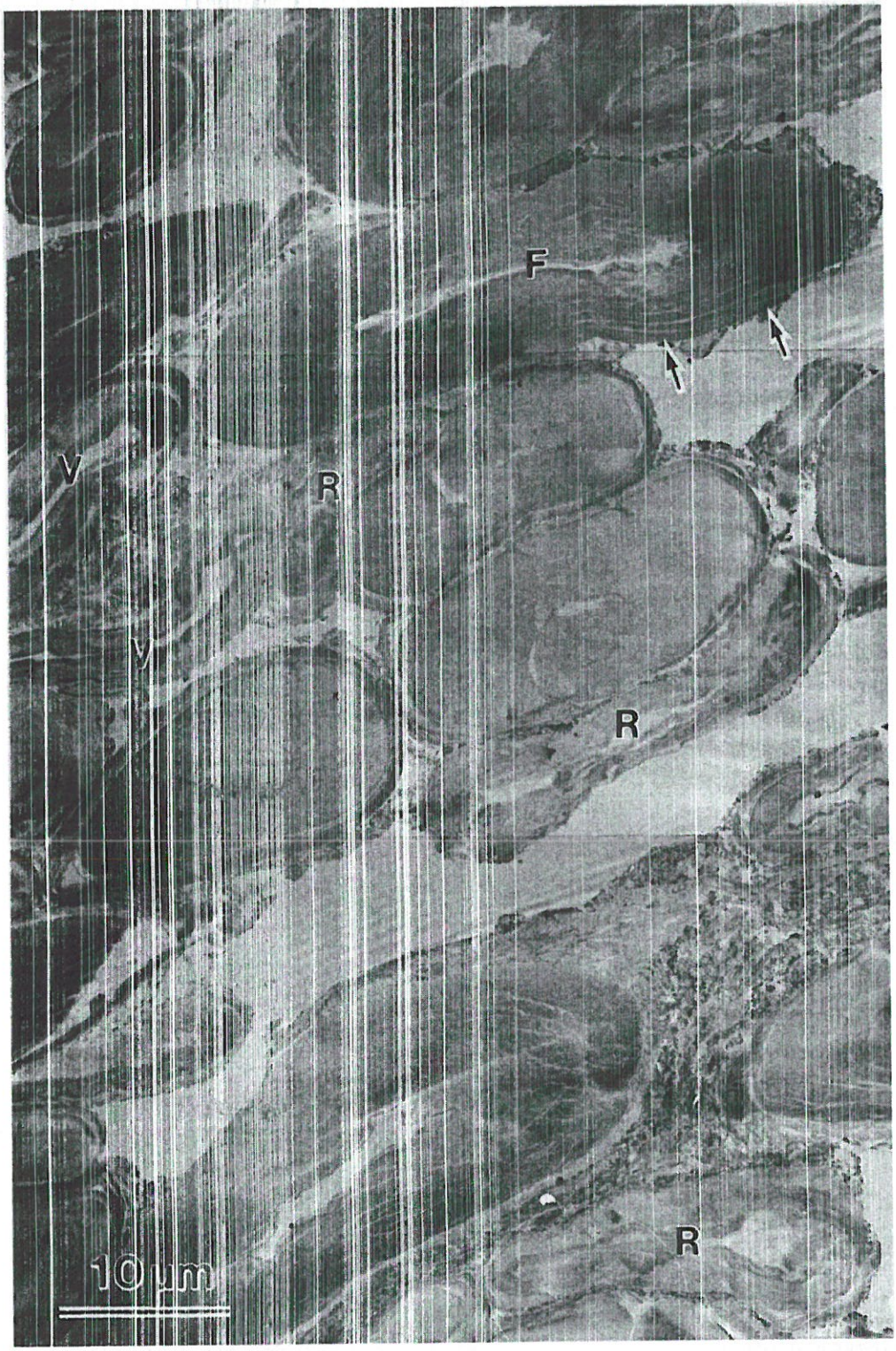


Fig. 5 Cross section of pressed wet web made of Pd-colloid stained beaten pulp (300 ml CSF). Post-stained with lead citrate.

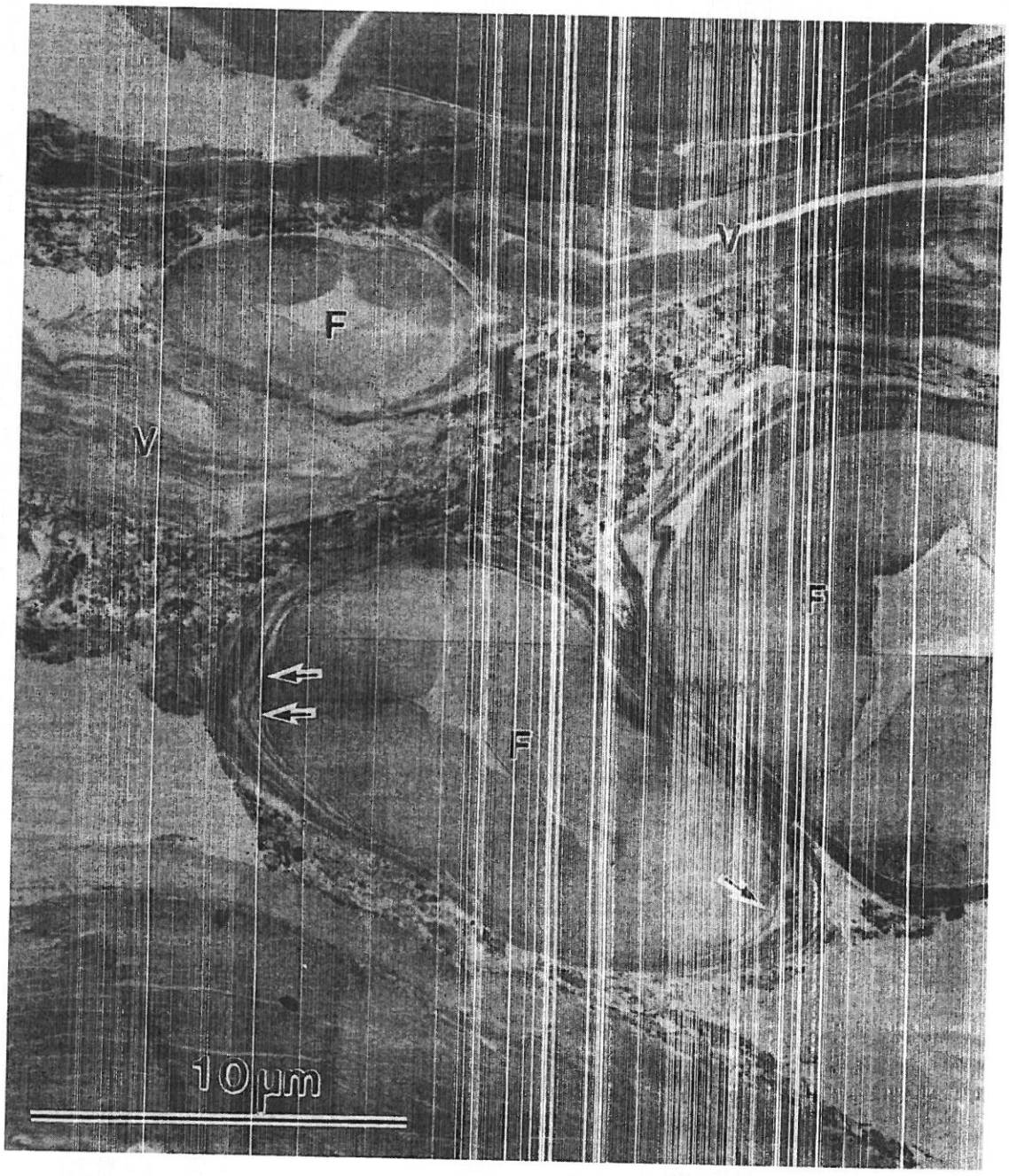


Fig. 6 Cross section of pressed wet web made of Pd-colloid stained beaten pulp (300 ml CSF). Post-stained with lead citrate.

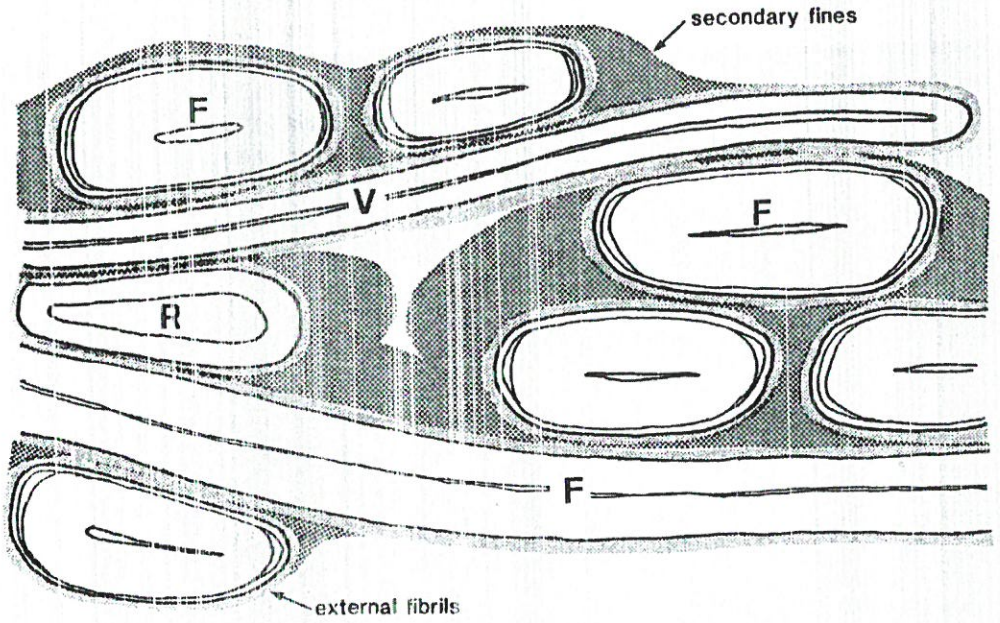


Fig. 7 Schematic illustration of structure of pressed wet web made of beaten pulp.

interfibre bonding. However, these discussions are not based on any direct observation of bond formation. Therefore, it is necessary to directly observe how the external fibrils exist at the bond forming area, and to clarify their role in bond formation.

The external fibril were very difficult to distinguish morphologically from the secondary fines. In order to find the location of the external fibrils, the pressed wet webs were prepared from the made of fine-free pulps which were stained with palladium colloid. In properly beaten pulp (around 400 ml CSF) colloidal particles were often distributed between fibres forming a layer (Fig. 8). Figure 8 shows that the external fibrils exist as a layer between the contact fibres. However, in some cases, the layer of external fibrils was very thin and sometimes was not observed (Fig. 9, arrows).

As shown in Figs. 8 and 10 (arrows), most of the external fibrils were arranged parallel to the fibre surface in the bond forming zone. Some paper scientists have estimated that external fibrils are entangled or intermingled in the bonding zone. The arrangement of the external fibrils in the bond

forming zone may affect the bond strength. Therefore, the following experiment was made. A wet web was prepared from a mixture of two kinds of stained fibres from the same fine-free beaten pulp: one stained with colloidal palladium and the other stained with colloidal gold. In the cross section of the pressed wet web, the contact zone of the palladium colloid stained fibre and the gold colloid stained fibre were observed under TEM. The palladium and gold colloidal particles can be easily distinguished under TEM, for the gold colloid is much larger in diameter and much higher in electron density than the palladium colloid. In the bond forming zone, the palladium and the gold colloid were not distributed uniformly forming a very clear border around the middle (Fig. 11). This may suggest that the external fibrils are not deeply entangled throughout the bonding zone, although small scale entanglement of cellulose microfibrils might exist near the border.

Morphology of external fibrils itself seems to be very important in bond formation. We directly observed the external fibrils by the negative staining method. They consisted of thick bundles of cellulose microfibrils and of more or less loose and swollen masses of cellulose microfibrils (Fig. 12-A). In the swollen regions, cellulose microfibrils were in the form of individual cellulose microfibrils and bundles of several microfibrils; they were very tangled (Fig. 12-B). In this paper, for convenience, the thick bundles of cellulose microfibrils are termed "macrofibrils" and the cellulose microfibrils in the swollen regions of external fibrils are termed "microfibrils". When the external fibrils were stained with the colloidal palladium, considerable amounts of colloidal particles stuck to the cellulose microfibrils in the swollen regions, but did not penetrate into the macrofibrils. Figure 8 is the cross section of the bond forming zone of the palladium colloid stained fibres. The dark areas where more colloidal particles were distributed correspond to the microfibrils, whereas the white threads correspond to the macrofibrils. This electron micrograph suggests that the microfibrils are filling the spaces between the macrofibrils and they are closely packed in the bond forming zone. Thus, the role of the microfibrils must be very important in strong bond formation.

External fibrils were found on the exposed fibre surface. They often cover the contact edges of fibres forming a continuous layer (Fig. 13). Sometimes, they form bridges between neighboring fibres (Fig. 14).

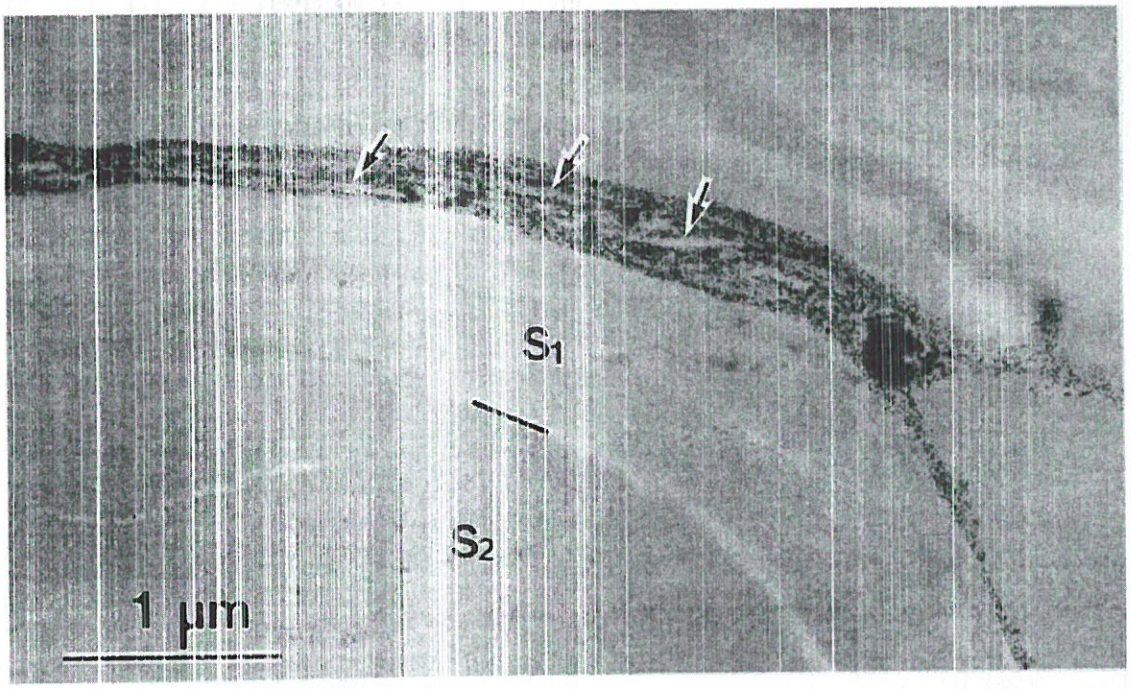


Fig. 8 Cross section of pressed wet web made of Pd-colloid stained fine-free beaten pulp showing a layer of external fibrils between contact fibres.

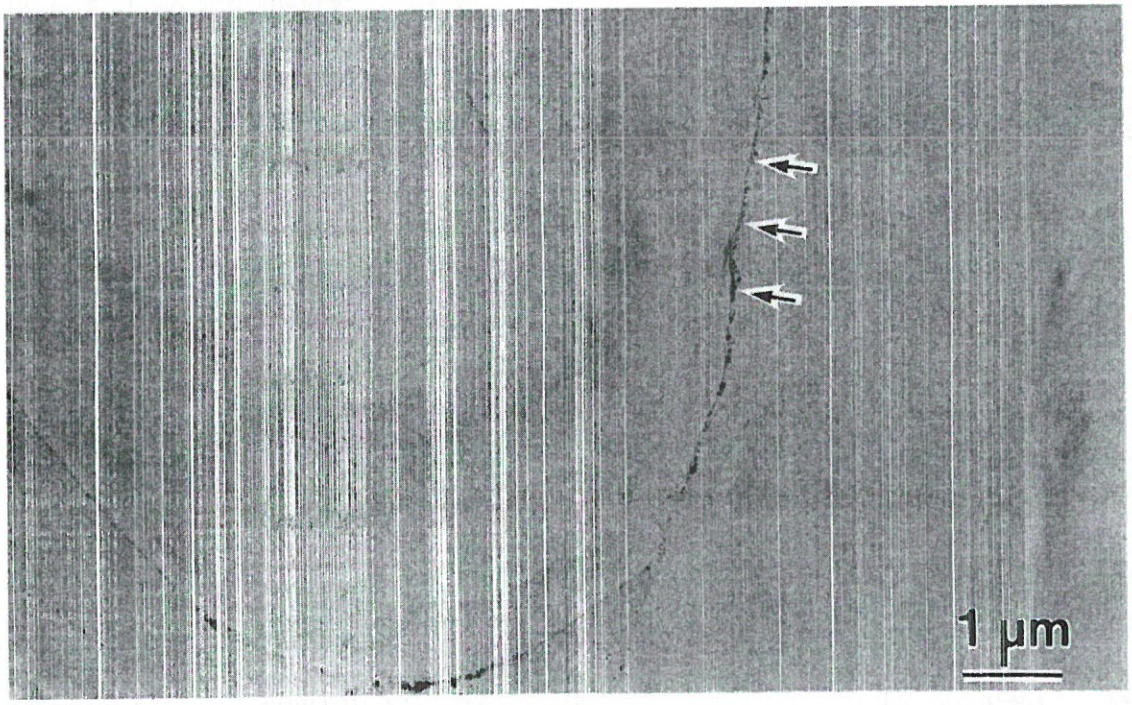


Fig. 9 Same as Fig. 8 showing the bond forming zone without a layer of external fibrils.

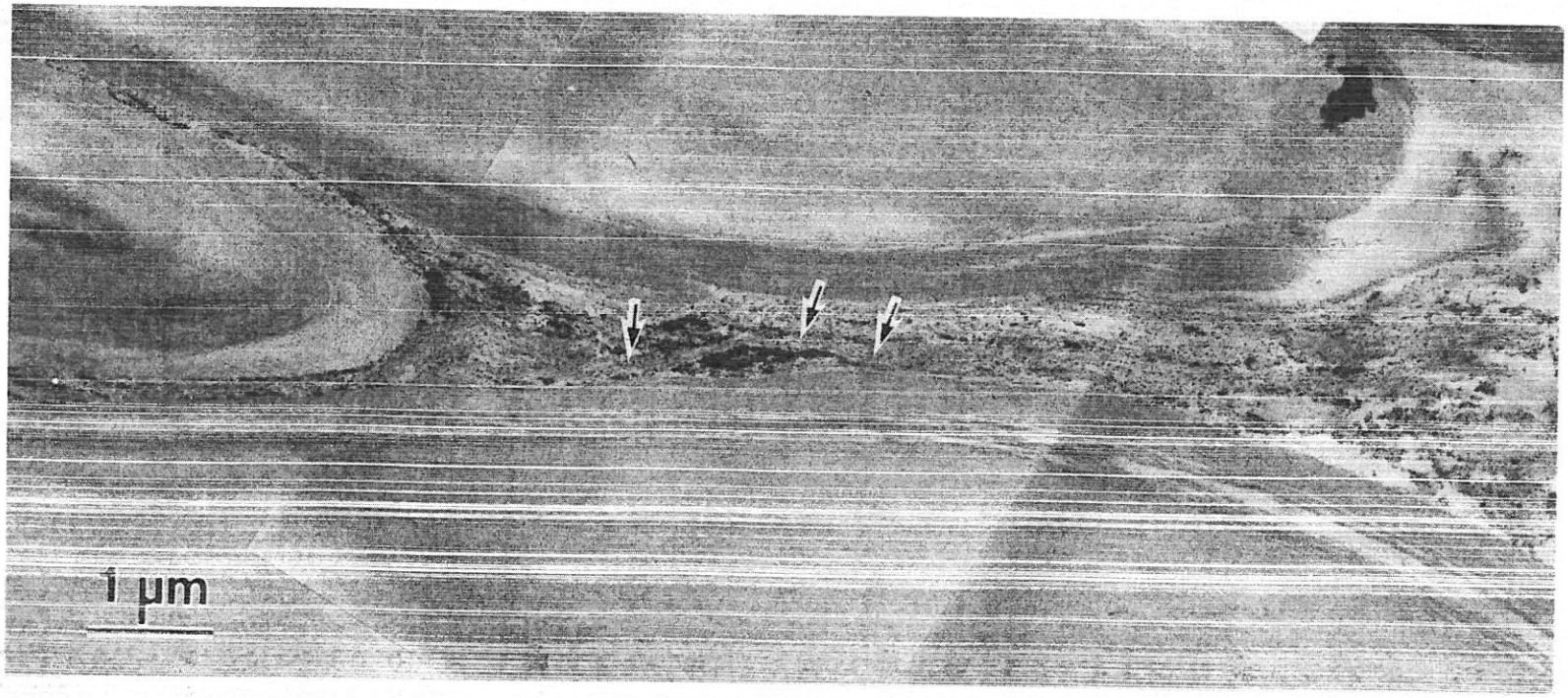


Fig.10 Cross section of pressed wet web made of Pd-colloid stained pulp. Post-stained with lead citrate.

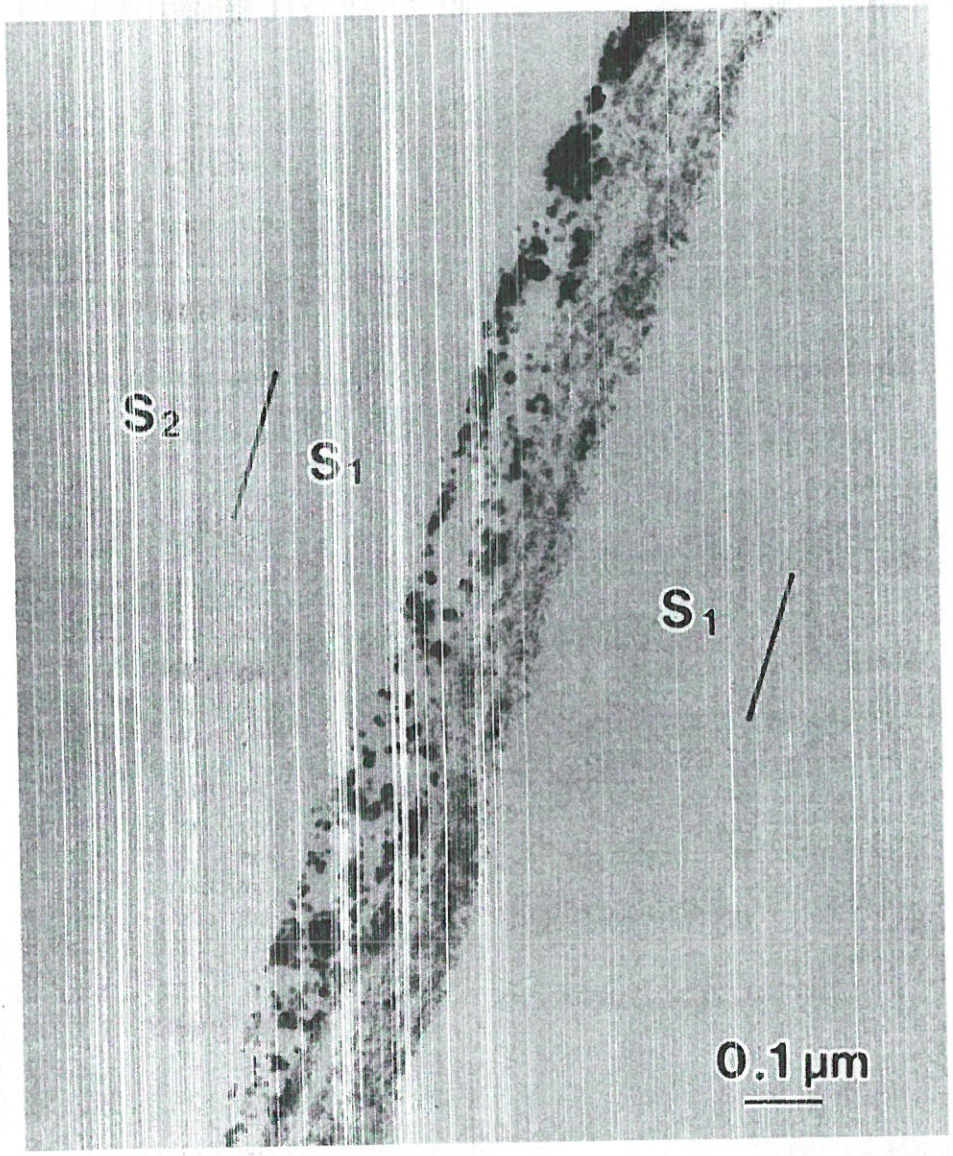


Fig.11 Cross section of bond forming zone between a Pd-colloid stained fibre (right) and a Au-colloid stained fibre (left). Note: external fibrils of each fibre are localized in the bond forming zone forming a clear border in the middle.

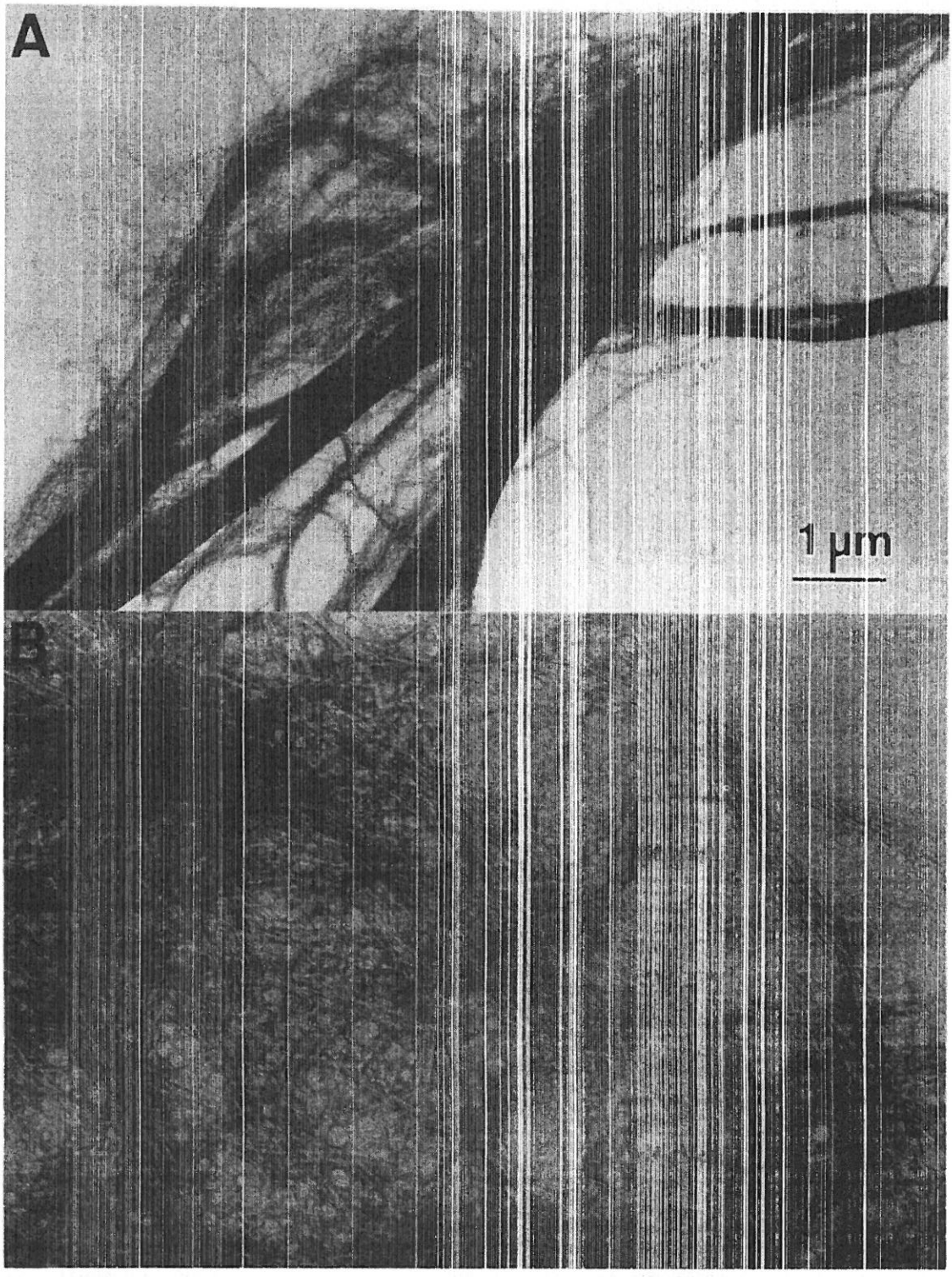


Fig.12 (A) External fibrils negatively stained with uranyl acetate. (B) Higher magnification of swollen region in (A).

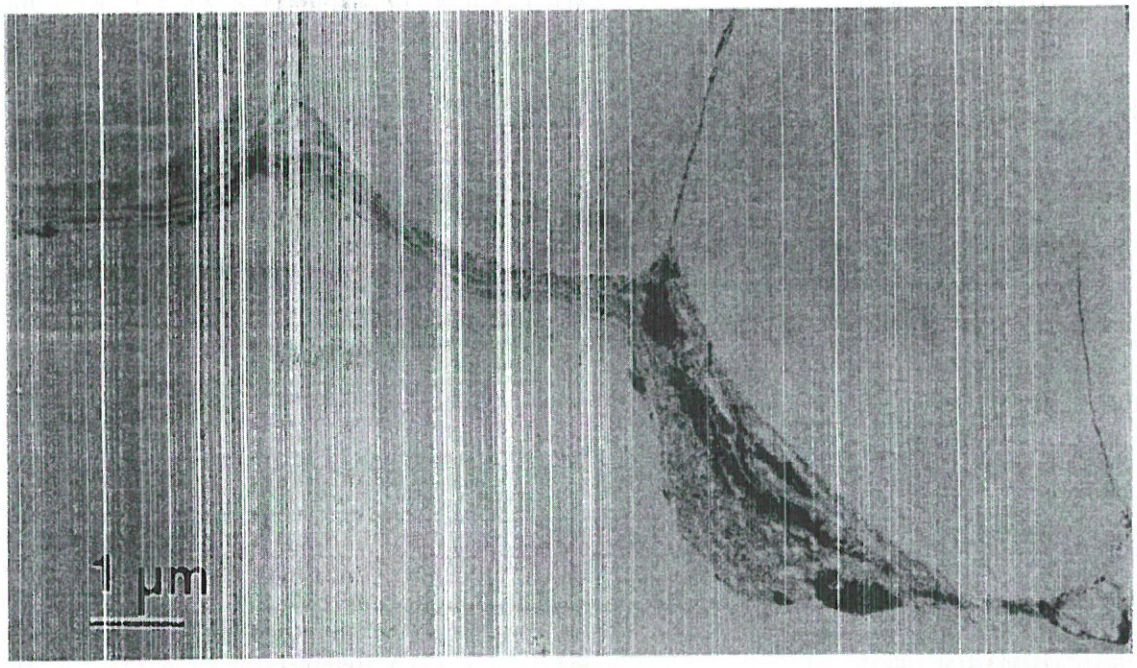


Fig.13 Cross section of pressed wet web made of fine-free pulp showing external fibrils covering the surface of contact fibres.

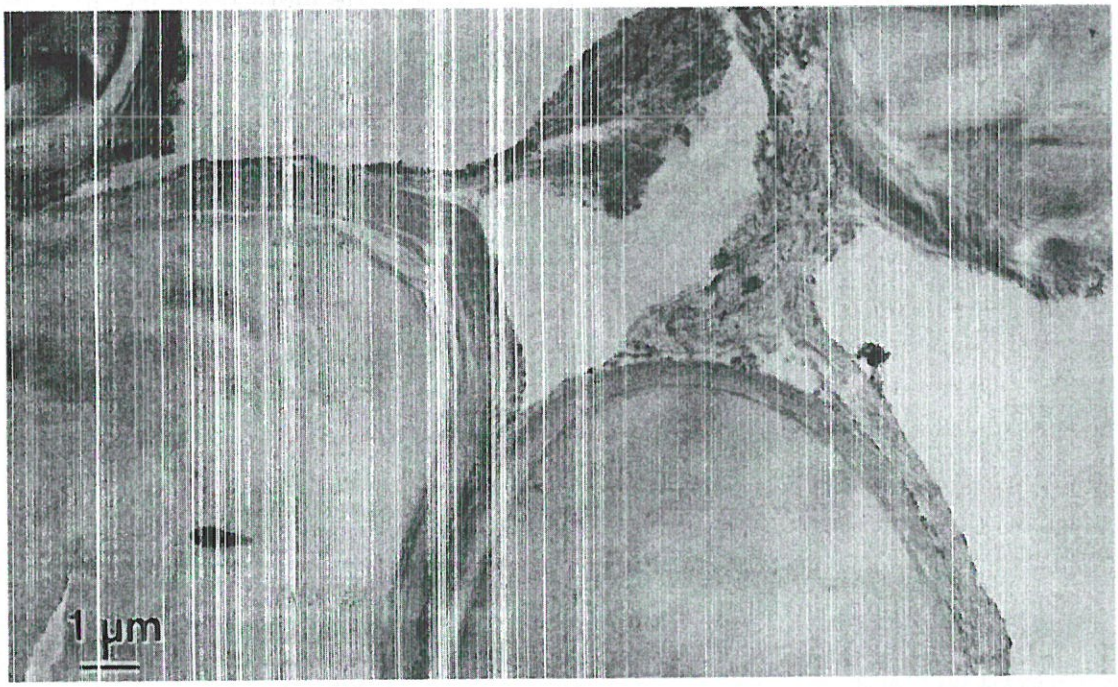


Fig.14 Same as Fig. 13. Post-stained with lead citrate. Note: external fibrils are forming bridges between neighboring fibres.

## DRYING PROCESS OF WET WEBS

The recent development of the scanning laser microscope (SLM) has made it possible to observe surface morphology of transparent samples in the air with high magnification. Using SLM, surface of pulp fibres can be observed even in the wet state. In the previous paper (6), we have applied a newly developed SLM for the observation of the drying process of pressed wet webs. The SLM revealed how fibres shrink and how they form interfibre bondings during drying.

In the present investigation, changes in weight of wet webs were measured during SLM observation in order to reveal how morphological changes were accompanied by solids content of webs. The effects of beating on morphological changes during drying were also examined. The webs were dried under the restrained condition by the cover glass.

The drying process of the pressed wet webs made of an unbeaten pulp, a slightly beaten pulp, a moderately beaten pulp and an excessively beaten pulp were shown in Figs. 15, 16, 17 and 18 respectively, with various solids contents of the wet webs of each drying stage.

The fibres of the couched wet webs were more or less round in cross section. After pressing, the fibres became flat in Z-direction. The effect of pressing was apparently strong enough to give irreversible deformation to the fibres. The beaten fibres looked much more conformable than the unbeaten fibres (Figs. 15-18). The unbeaten fibres had distinctive longitudinal ridges which correspond to the cell corner of fibres. The ridges became obscure by beating.

Drying process of the pressed wet web was divided into five stages from the morphological point of view.

1st stage (solids content: up to 50-55 %):
solids content increased without any changes of fibre morphology.

2nd stage (solids content: over 50 - 55 %):
flattening of fibres began at fibre crossings without changing the surface texture.

3rd stage (solids content: over 60 - 65 %):
formation of longitudinal wrinkles began on the fibre surface; flattening of the fibres progressed.

4th stage (solids content: over 70 - 75 %):
fibres started to shrink transversely at the unbonded region, which initiated "necking"; flattening of the fibres progressed and the longitudinal wrinkles increased.

5th stage (solids content: over 80 - 85 %):
fibres started to shrink transversely at the crossing regions; shrinkage of the fibres at the unbonded regions also progressed and the longitudinal wrinkles became more distinctive; the morphology of the webs became unchanged at the solids content of around 90 %.

The above mentioned morphological changes of wet webs during drying can be explained on the basis of water removal from the different locations in the pulp fibres as follows. Before drying starts, water is kept on the fibre surface, in the space between fibres, in the lumen, in the pit canals and in the cell walls of fibres. Drying starts with evaporation of the water located outside of the fibre wall (1st stage), which causes almost no deformation of the fibres. Even after water on the fibre surface disappears, water evaporation from the fibre surface continues. The water in the lumen as well as in the pits moves into the fibre wall to make up the loss. The removal of water from the lumen increases the force of water surface tension, which causes the fibre to collapse especially at the fibre crossings (2nd stage). When water disappears from the lumen, drying of the fibre wall begins. Water is removed from the space between cellulose microfibrils as well as from the cavities of the delaminated fibre wall, and makes the fibre wall shrink. Formation of the longitudinal wrinkles on the fibre surface can be an indication that shrinkage of the fibre wall has begun in the cell wall (3rd stage). The mechanism of the wrinkle formation will be discussed later. The progress of dewatering from the fibre wall causes the transverse shrinkage of the fibres at the unbonded areas where the fibre can shrink without restraint (4th stage). When the fibre wall loses most of the water, the fibre shrinks transversely even at the bonded regions (5th stage). Based on the above mentioned interpretation, morphological changes in the drying stages are schematically illustrated in Fig. 19.

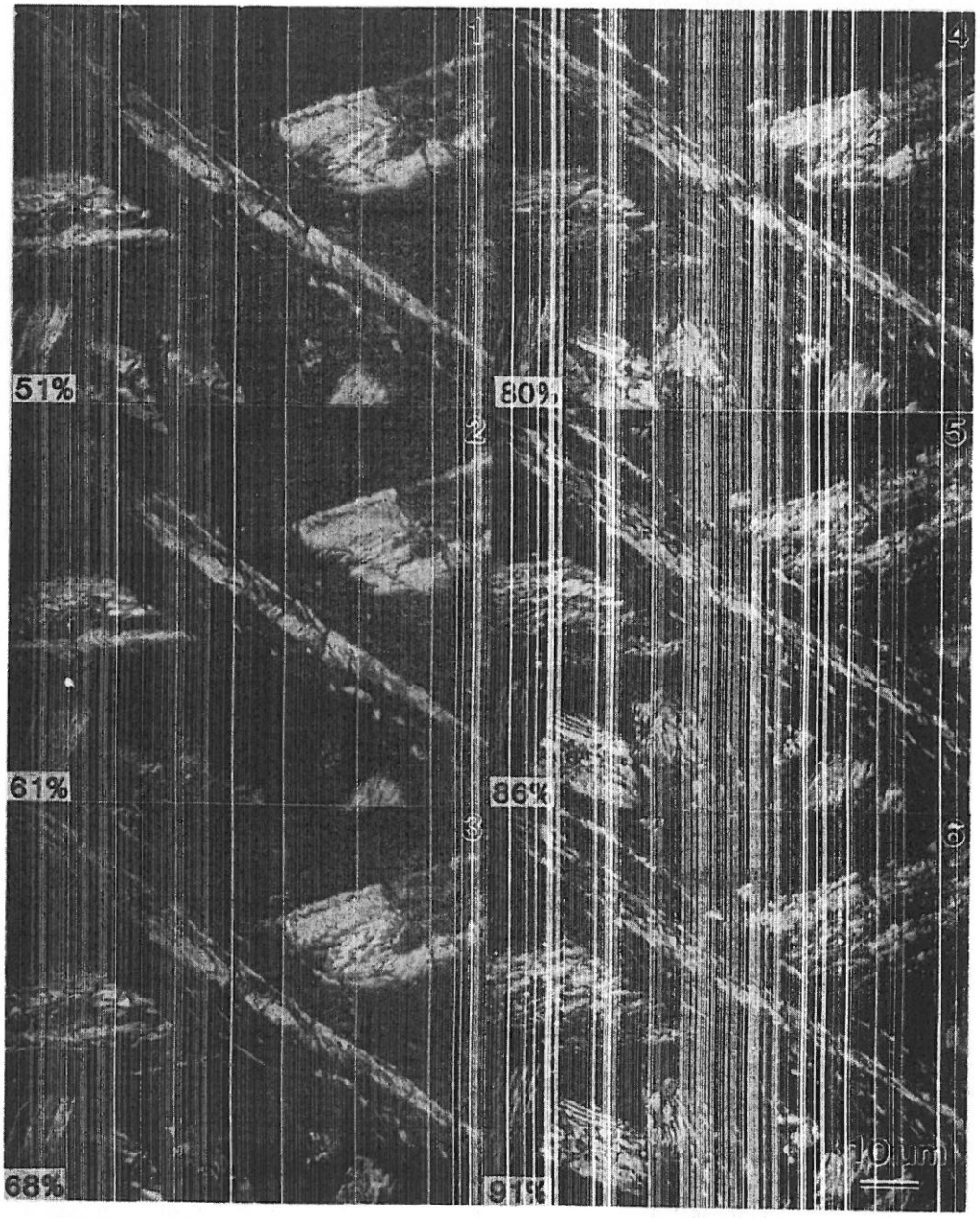


Fig.15 Series of scannig laser micrographs showing the drying process of pressed wet web made of unbeaten pulp. Number in each micrograph represents dry solids content of web.

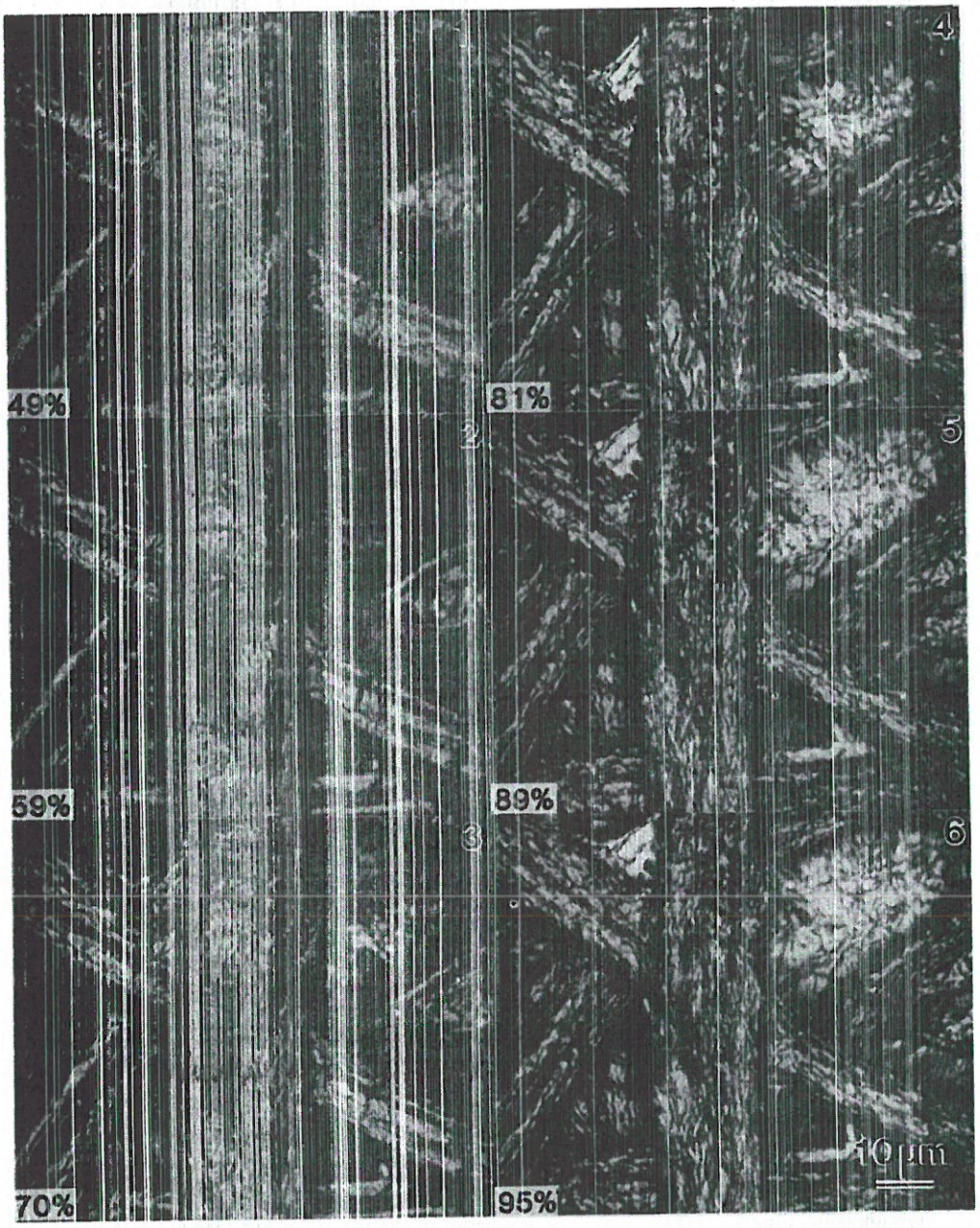


Fig.16 Same as Fig 15. Beaten pulp (525 ml CSF).

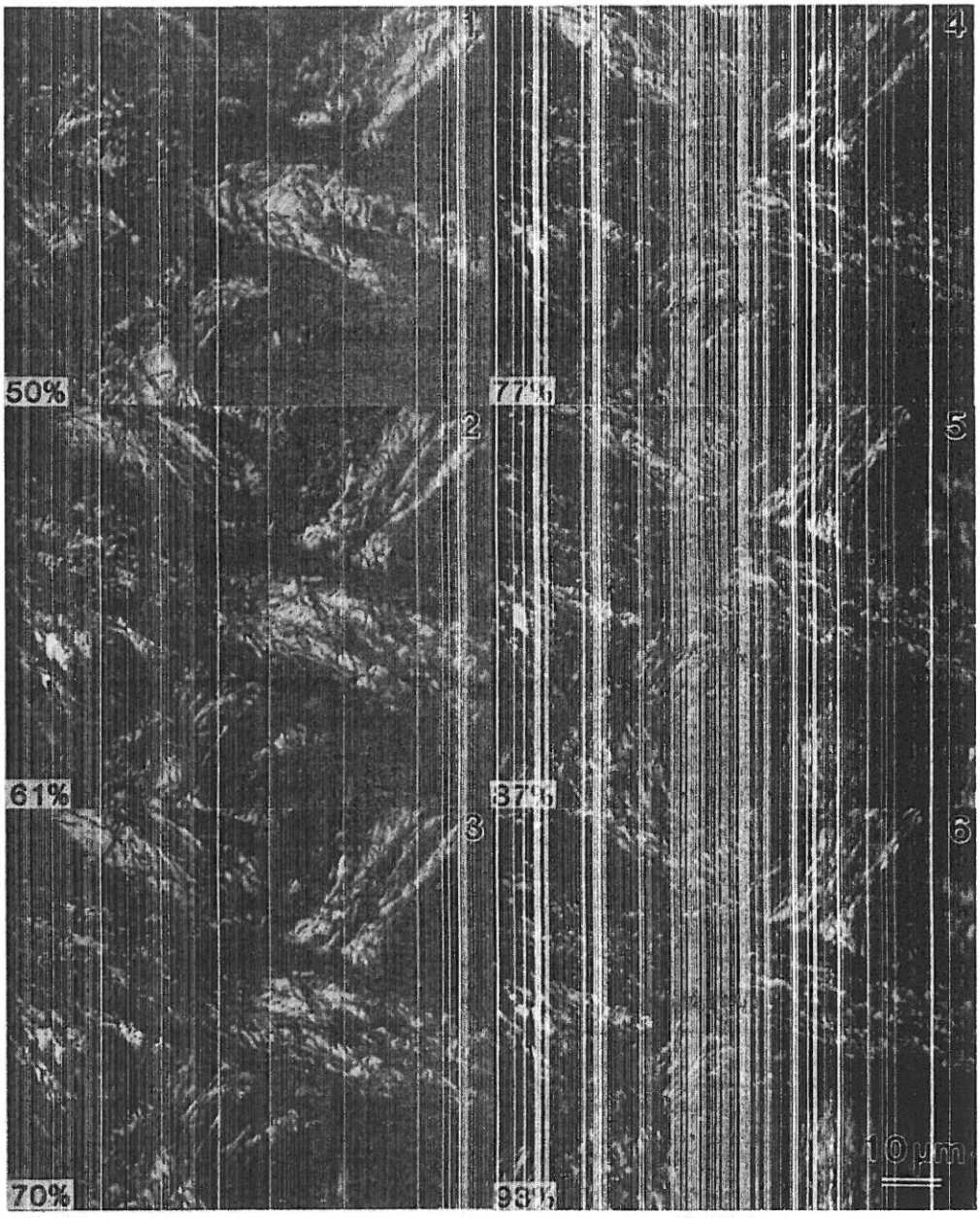


Fig.17 Same as Fig. 15. Beaten pulp (415 ml CSF).

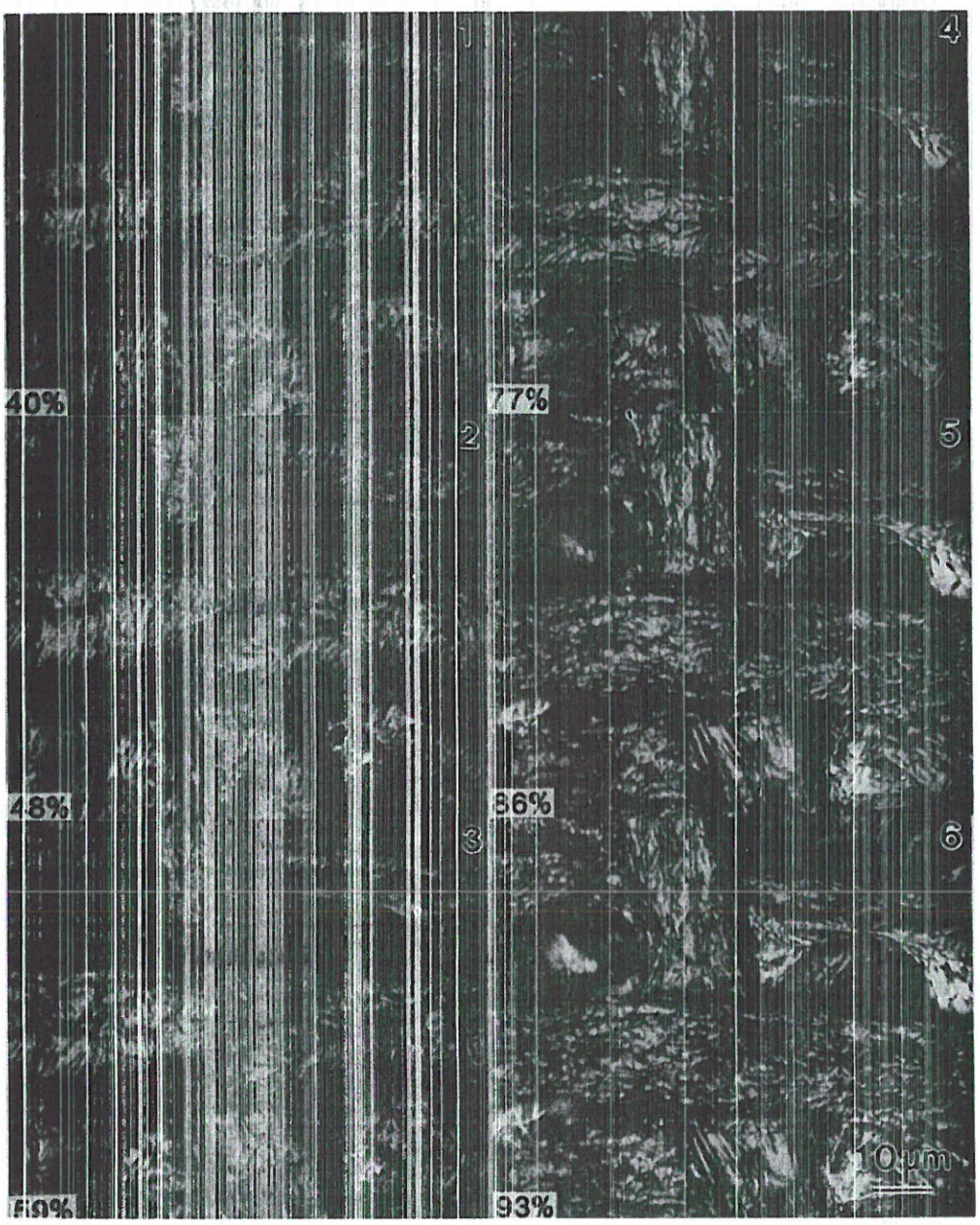


Fig.18 Same as Fig. 15. Beaten pulp (310 ml CSF).

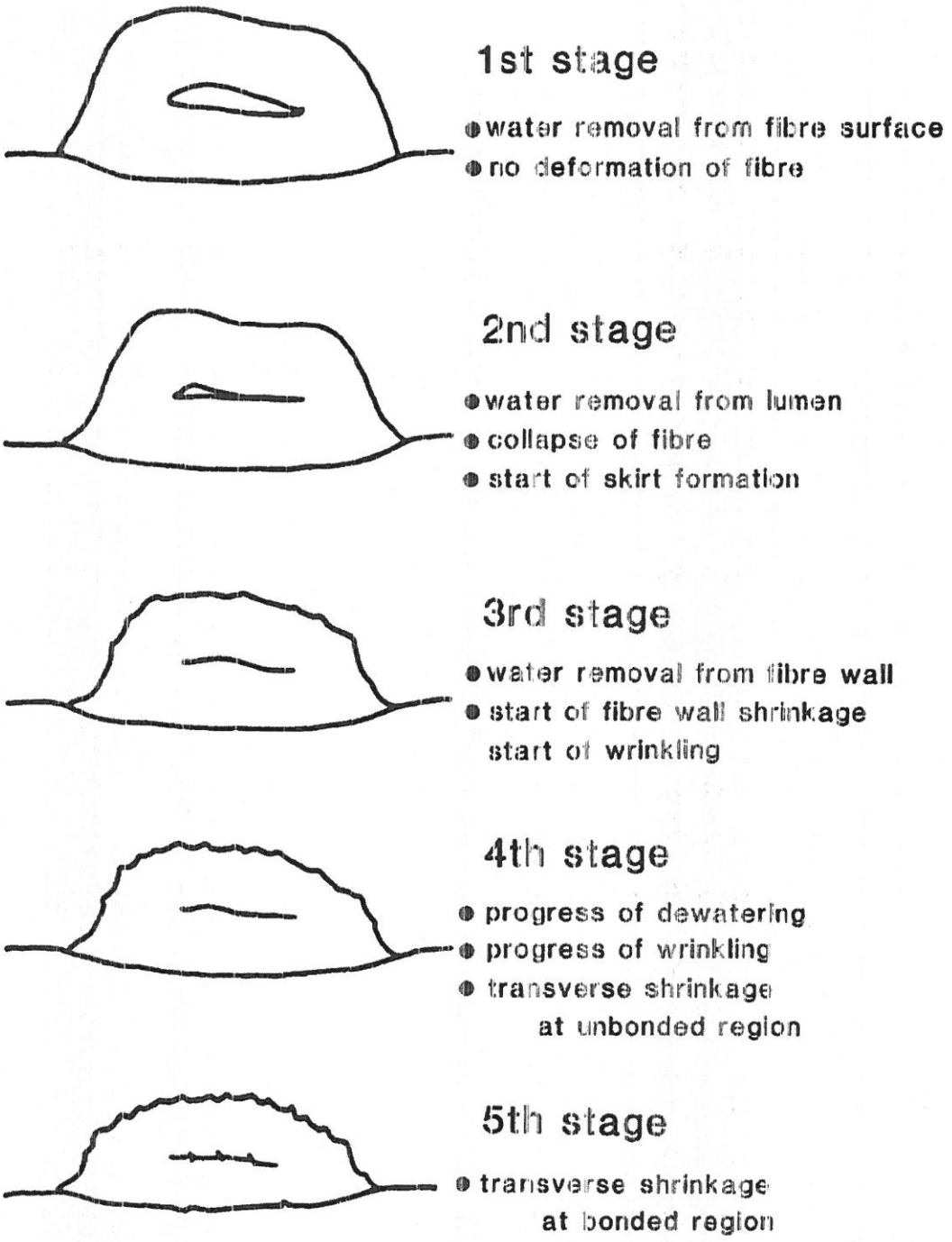


Fig.19 Schematic illustration of drying process of pressed wet web based on observation by SLM.

The pressing brought a plastic deformation of the fibre wall especially at the fibre crossing point as suggested by Pye et al. (3). Once the fibres were in close contact by pressing, the contact area neither shifted nor broke during drying. Fibre adhesion in the pressed wet web seems to be strong enough to tolerate the force of shrinkage of the fibres as Page and Tydeman (13) claimed in the "adhesion before shrinkage" hypothesis.

De Ruvo and Htun (14) investigated the effect of dryness on the reswellability of bleached kraft pulp. They showed that beaten fibres, dried to above 60 % solids content, did not recover the initial swollen state after rewetting. As observed in this experiment, formation of longitudinal wrinkles and shrinkage of the fibre wall began when solids content exceeded 60 %. This may not be just a coincidence but possibly the result of an irreversible decrease in size and number of accessible sites for water molecules when the fibre wall begins to shrink.

Page and Tydeman (13) have reported that the optical contact area between bond forming fibres slightly diminished in size without changing shape during the final drying phase. We noticed that the fibres shrank transversely at the crossing regions when solids content exceeded 80 %. These observations are very interesting, because Htun and de Ruvo (15) reported that the drying stress of the sheet increased slowly at first and then increased very rapidly after the sheet reached 80 % dryness with a bleached kraft pulp. The shrinkage of fibres which occurs at the final stage of drying may cause the extreme increase in the drying stress.

## STRUCTURE OF INTERFIBRE BONDING

### Structural Characteristics of Bonding Fibres

Figure 20 is a typical cross sectional view of bonding fibres which are crossing perpendicularly. The most of the important structural features of the bonded fibres can be seen in this photograph. In Fig. 20, the two fibres are bonding on the surface of the S1 layers. Between the S1 layers, there is an amorphous-appearing layer which is considered to originate from the external fibrils. This layer is termed a "bonding layer" in this paper as it is often observed between bonding fibres. At the bonding edges of the transversely sectioned fibre, the fibre wall often deformed to resemble the skirts of Mt. Fuji and smoothly merged with the bonding partner. This structure is termed "skirts" in this paper. Another specific feature observed in Fig. 20 is the "wrinkles" which formed on the fibre surface. The wrinkles are more or less parallel to the fibre axis. They are formed more on the free surface of the fibre and less in the bonded region.

### The Effects of Beating on the Bond Structure

The above mentioned structures varied with the degree of beating of pulp. The interfibre bonding between the unbeaten fibres had no bonding layer (Fig. 21). The fibres should be bonded on the surface of the primary wall, although the primary wall was not always distinguishable in the dry sheet. The bonding areas were relatively small. The unbonded regions often existed in the bonding areas (Fig. 21, an arrow). A few small wrinkles were also formed in the bonding region.

The morphological changes of the bonding region in the beating process were observed using hand sheets made of the fine-free pulps. Bonding areas were apparently increased by beating. Between the S1 layers of bonded fibres, a bonding layer was often observed (Figs. 20, 22). The bonding layers could be distinguished from the S1 since it looks amorphous, whereas the S1 has distinctive striations of highly oriented microfibrils). The thickness of the bonding layer varied considerably from bond to bond. In the case of the fine-free pulp which was prepared from the properly beaten pulp (about 400 ml CSF), the bonding layer was frequently discontinuous or often missing. When the pulps were beaten excessively to less

than 300 ml CSF, the S1 was destroyed to be thinner (Fig. 23-A). The fibres without the S1 layer were also often found in the sheet. In the damaged S1 layer, the striation of cellulose microfibrils became obscure and the border between the amolphous-appearing S1 and the bonding layer became indistinct (Fig. 23-B).

In the case of the hand sheet made of whole pulp of properly beaten pulp (about 400 ml CSF), the bonding layer was more continuous and more commonly observed than in the case of hand sheet made of the fine-free pulp. This is obviously the effect of the secondary fines which filled the space between fibres together with the external fibrils. The secondary fines made the bonding layer thicker. Another distinctive observation was that the secondary fines often covered the surface of the fibres, especially the edges of bonded fibres (Fig. 24). In Fig. 25 the bonded edge of the two crossing fibres is very obscure and any distinctive boundary cannot be observed (an arrow). This is apparently a covering effect of the secondary fines. The layer of the secondary fines and the external fibrils which covers the surface of fibres is termed the "covering layer" in this paper. The variation of the bond structure caused by beating is schematically shown in Fig. 26.

The skirt has distinctive characteristics and is formed at the bonding edges of crossing fibres (Figs. 20, 27). The skirts of the unbeaten fibre were mostly very short or often missing (Fig. 21). The skirt is distinctive at the bonding edges of the beaten fibres. The fibres in which the S1 layer were removed by beating did not form the skirt.

One of the most interesting features was the wrinkling formed on the fibre surface. As observed by SLM (Figs. 16-19), the wrinkles are formed during drying. The wrinkles consisted of the S1 and partly the S2 (Fig. 28). The wrinkles were formed more on the exposed surface than on the bonded surface (Fig.20-A). There were two types of wrinkles at the bonded surface of the fibres: the wrinkles which were formed on one side of the fibres, and a pair of the wrinkles which were formed on both side of the fibres (Fig. 20-B). The pair of wrinkles were just like geared cogs.

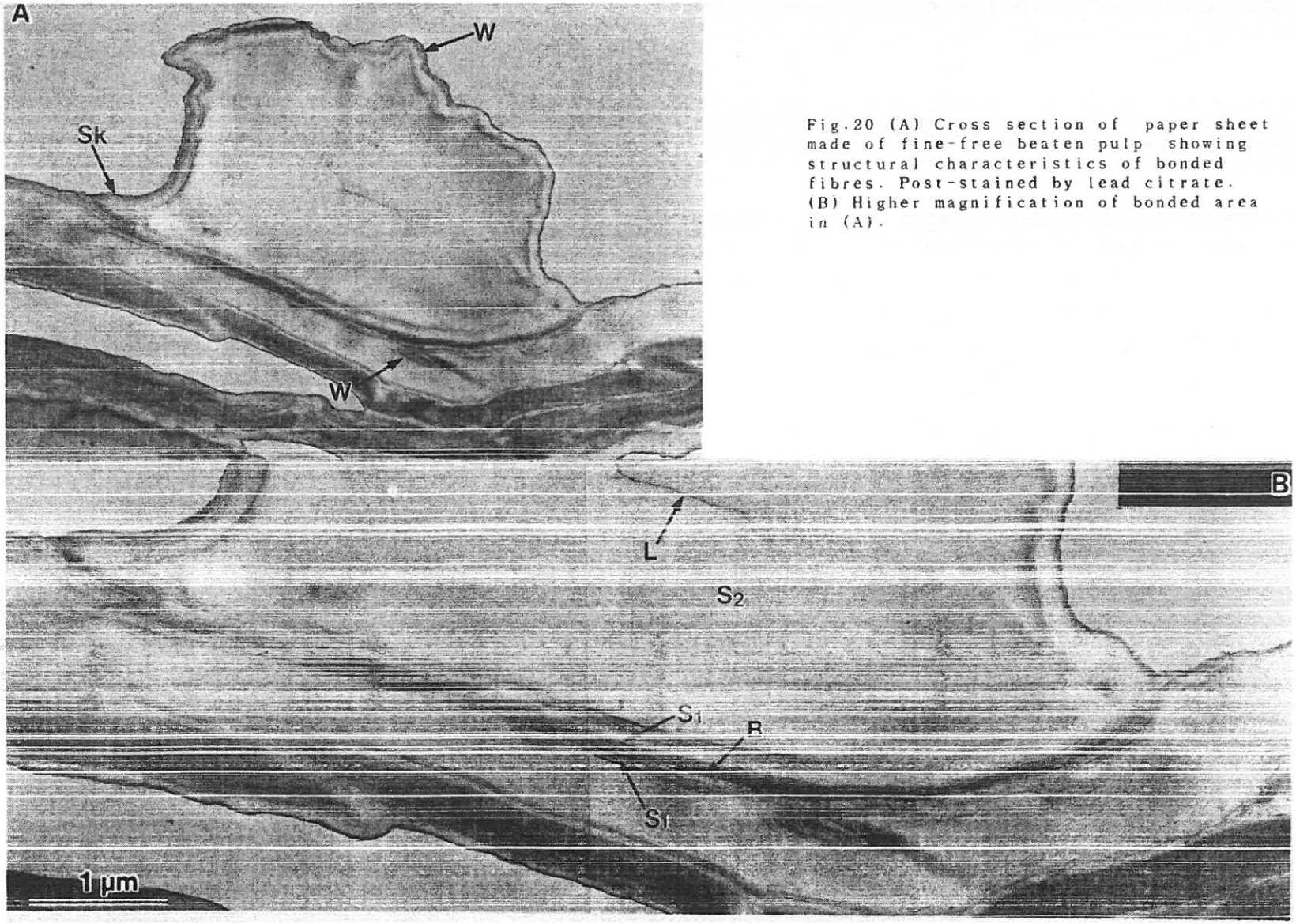


Fig.20 (A) Cross section of paper sheet made of fine-free beaten pulp showing structural characteristics of bonded fibres. Post-stained by lead citrate. (B) Higher magnification of bonded area in (A).

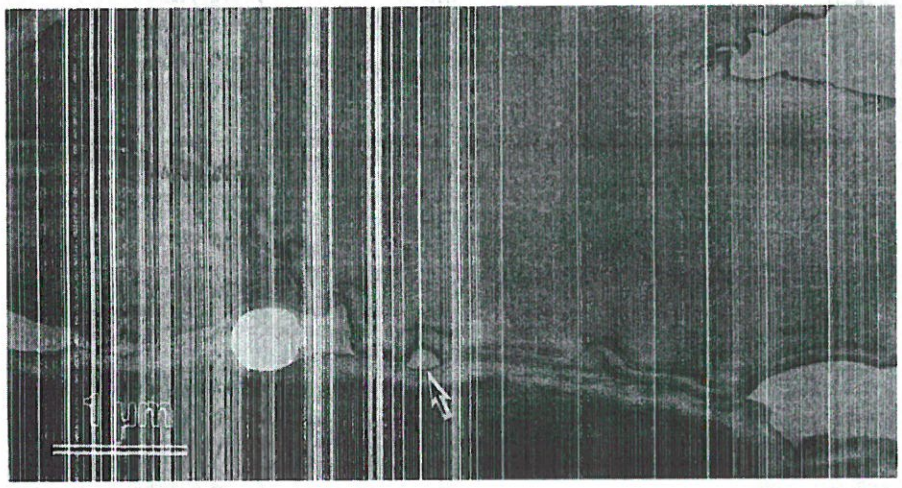


Fig.21 Cross section of paper sheet made of unbeaten fibre. Post stained by lead citrate.

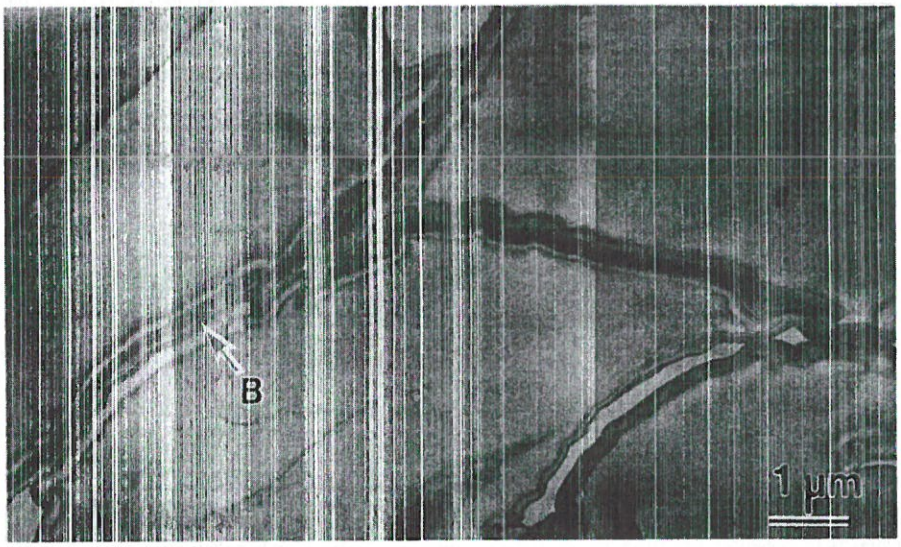


Fig.22 Cross section of paper sheet made of fine-free beaten pulp (500 ml CSF). Post-stained by lead citrate.

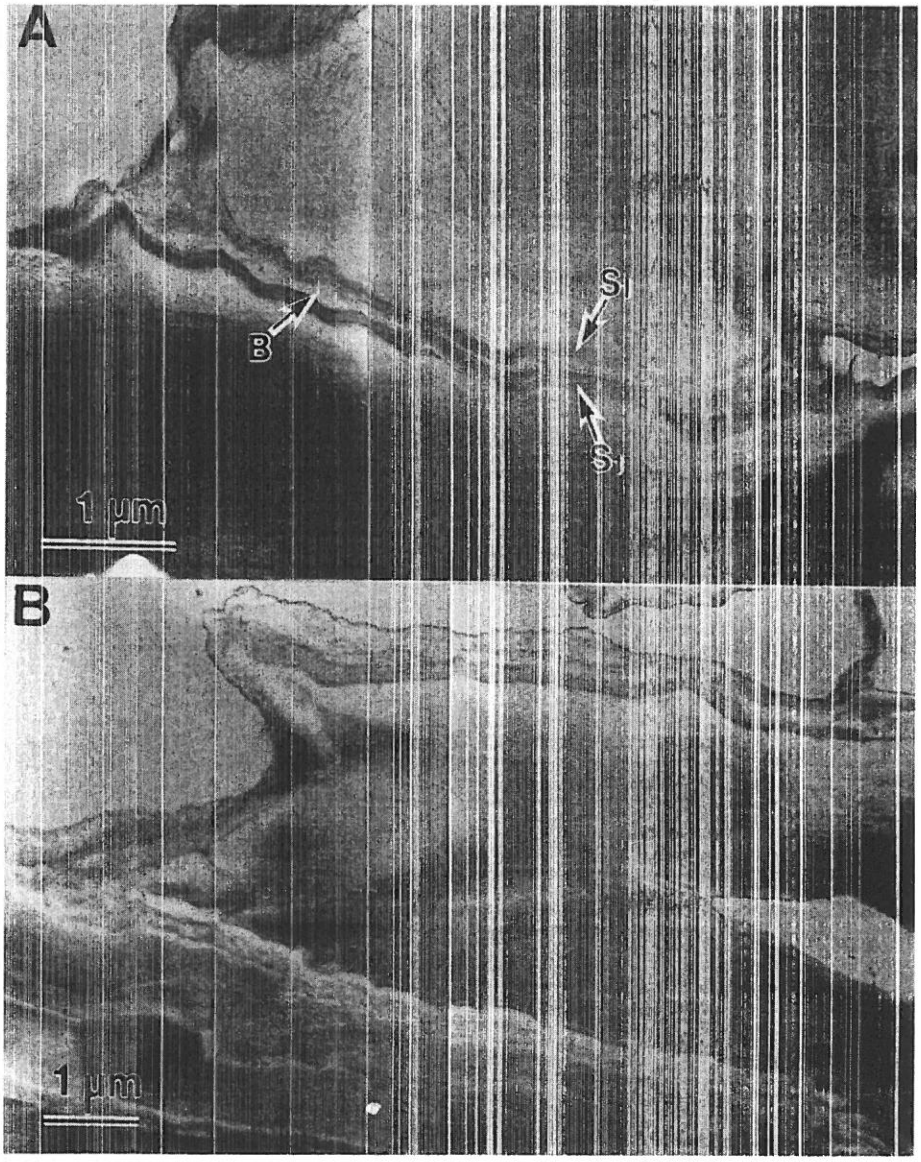


Fig.23 Cross section of paper sheet made of fine-free beaten pulp (160 ml CSF).


Fig.24 Cross section of paper sheet made of beaten pulp (375 ml CSF).

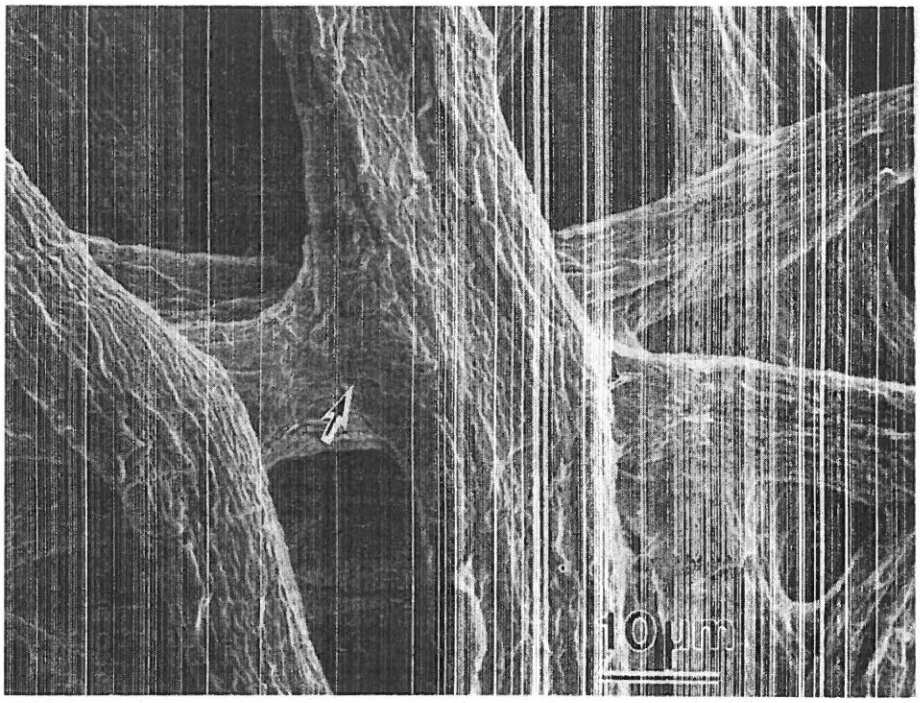


Fig.25 Surface of hand sheet made of beaten pulp showing effect of covering layer at bonding edge (an arrow).

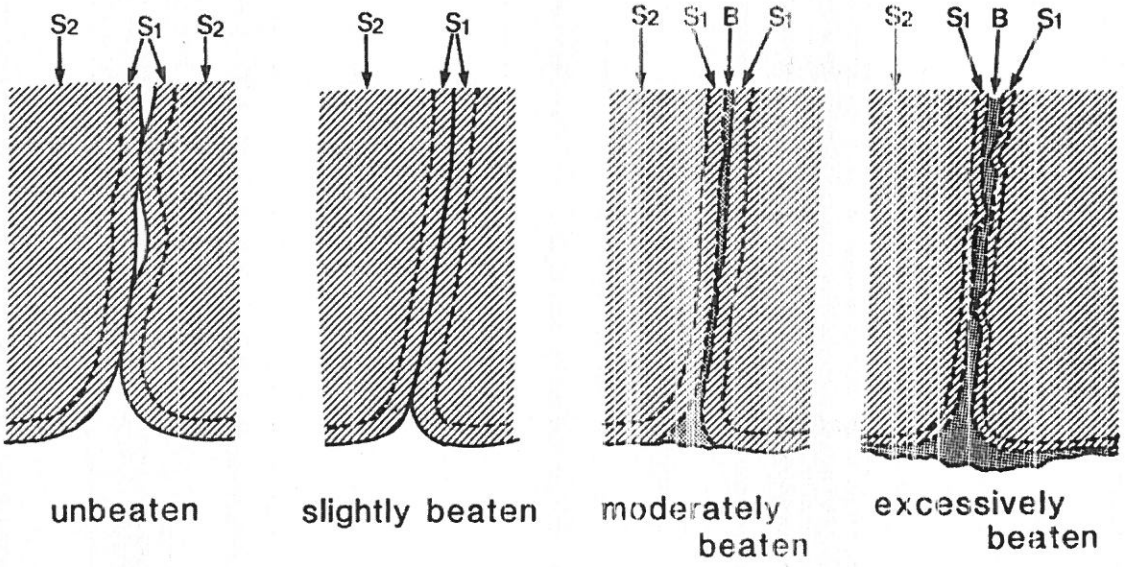


Fig.26 Schematic illustration of bond structure showing the effects of beating.

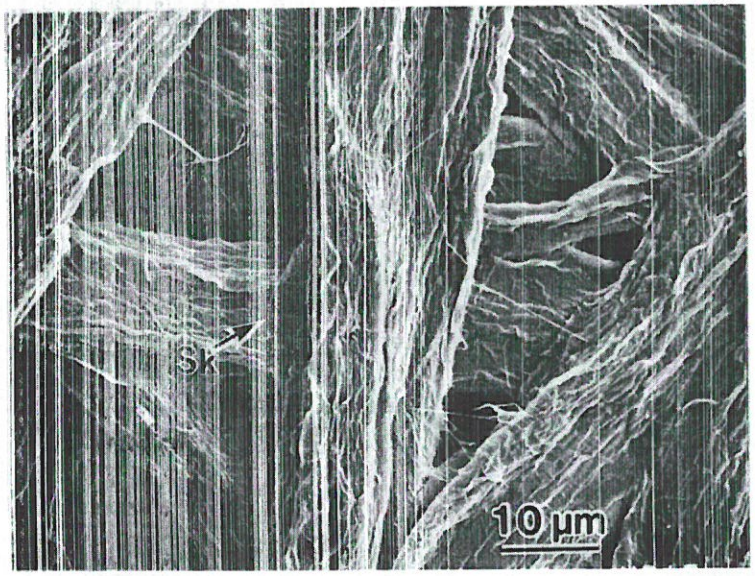


Fig.27 Surface of hand sheet made of fine-free beaten pulp showing skirt structure of bonded fibre.

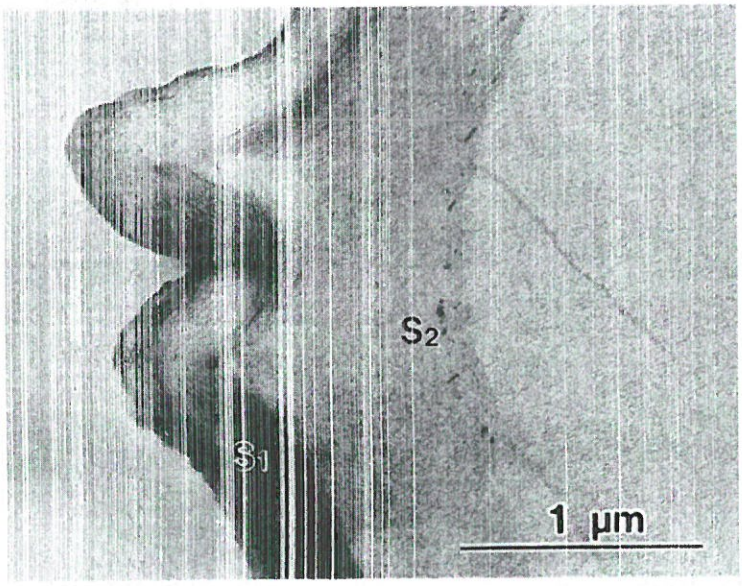


Fig.28 Cross section of wrinkles. Post-stained by lead citrate.

## MECHANISMS OF FIBRE BOND FORMATION

### Process of Fibre Bond Formation

The process of fibre bond formation in hand sheets made of the beaten pulp is summarized diagrammatically in Fig. 29.

Couching:

Fibres come close by couching but not close enough to make direct contact. Secondary fines are drawn to the fibres by the surface tension force of water.

Pressing:

Fibres are pressed together and the fibre wall becomes flattened making close contact to the bonding partner. Because of the plasticity of the S2, the contact of the fibres is very intimate. The S1, which is swollen and separated from the S2 by beating, is pressed against the S2 at the contact area, whereas the excess of S1 is squeezed out to the non-contact zone and a space is formed between the two layers. The external fibrils and the secondary fines are tightly packed together at the bond forming zone.

Drying:

Fibres collapse, and then shrink forming wrinkles on the fibre surface. The wrinkles are formed more on the free surface than on the bonded surface where shrinkage is restrained by the bonding partner. The contact area does not change until the fibres become dry. Therefore, when the fibres shrink, the skirt structure is formed at the bonding edges. The secondary fines and the external fibrils form a bonding layer between bonding fibres.

### Mechanism of Plasticization of Beaten Fibre

The bonding area between the fibres is increased by the effect of beating. It is generally thought that delamination of fibre wall which occurs during beating makes the fibre more flexible and more conformable. Page et al. (16) considered surface topography as an important factor for formation of large bonding areas. Page et al. (4) also suggested that the effect of surface topography is reduced by beating.

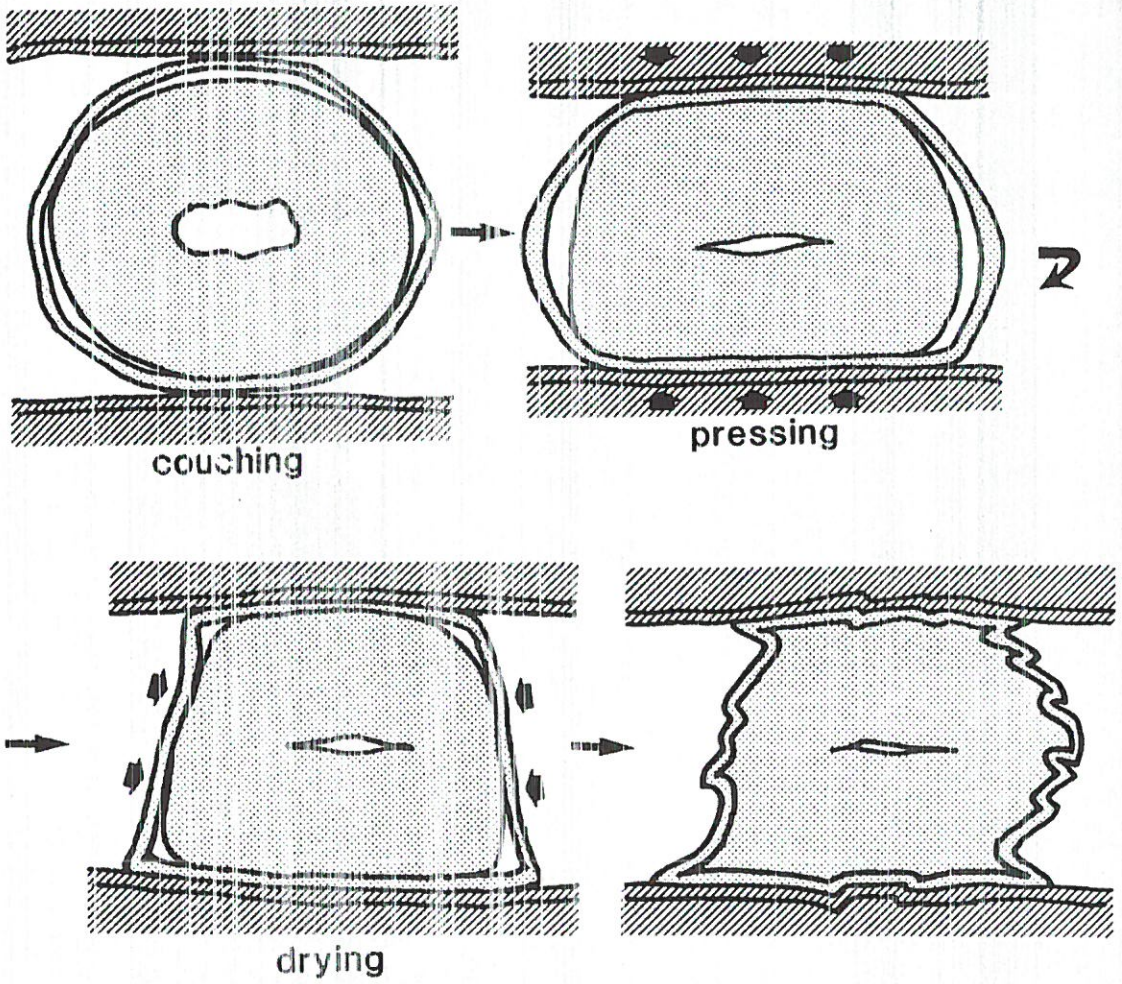


Fig.29 Summary of fibre bond formation process.

In this study, it was confirmed that the plasticity of the fibre wall increased by progressive beating. Especially the S2 layer, which occupies the major portion of the fibre wall, was more flattened by progressive beating. In addition to plasticization of the S2, the S1 also appears to play an important role in obtaining good contact between the fibres. Beating also easily separates the S1 and the S2 at the boundary between them. The S1 swells outwards and its circumference increases. Once they are separated, each layer can be deformed independently by an external force. Therefore, the separation of the S1 and the S2 contributes to the reduction of the rigidity of the fibre wall. Moreover, the separated S1 layer, which is more or less swollen and thin, can make good contact, conforming to the surface topography of the bonding partner when it is pressed. Thus, the separation of the S1 from the S2 seems to be an important factor in obtaining better contact of the fibre surface.

**Formation, Structure and Function of Bonding Layer**

In this study we found that a bonding layer did exist between bonded fibres. The bonding layer is made of the external fibrils and the secondary fines. The formation process of the bonding layer is diagrammatically illustrated in Fig. 30. The external fibrils and the secondary fines come close by dewatering and couching (A). These fibrils are pressed and packed between fibres. The macrofibrils lie mostly parallel to the fibre surface (B). When the web dries, the external fibrils and the secondary fines form a bonding layer together (C).

The structure of the bonding layer is schematically illustrated in Fig. 31 based on observations of the bond forming zone in the pressed wet webs. The macrofibrils, which are thick bundles of cellulose microfibrils, make a network structure, and the microfibrils fill the space between the macrofibrils. Thus a tightly packed structure is formed without voids. The microfibrils seem to contribute more to the strength of the bonding layer than do the macrofibrils, because the microfibrils have more chance to form mutual hydrogen bonding in the bonding layer. The bonding layer has a film-like structure which consists of randomly oriented macrofibrils and microfibrils. The bonding layer is hidden underneath the fibres, so its structure cannot be observed directly. Figure 32 shows the film-like structure made of the external fibrils and

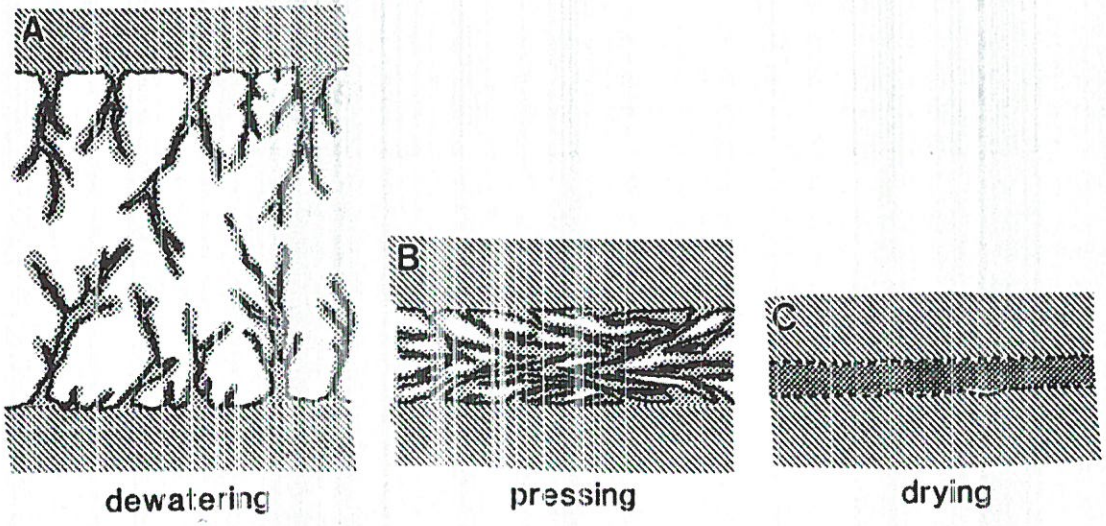


Fig.30 Schematic illustration of bonding layer formation process.

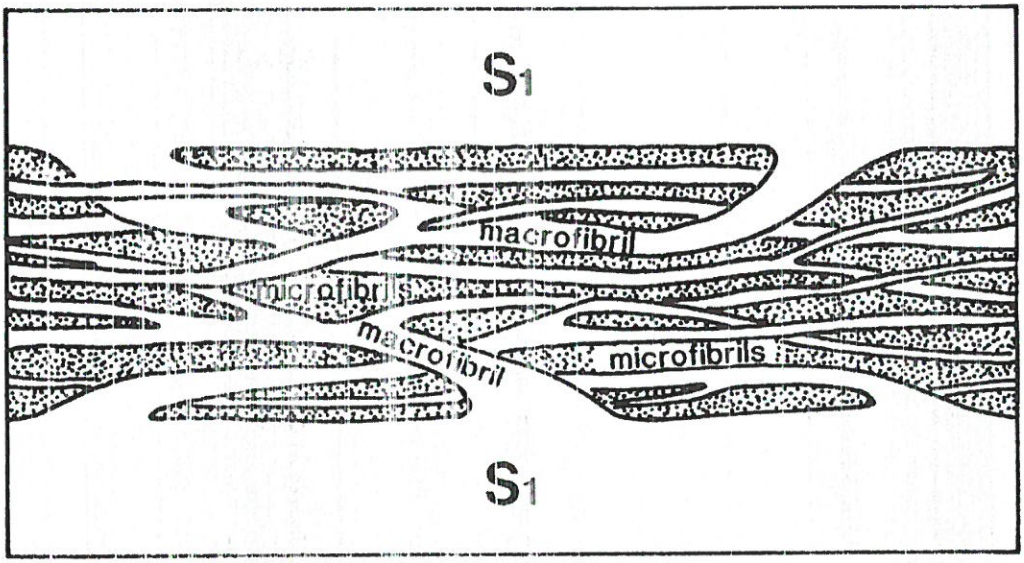


Fig.31 Structural model of bonding layer.

the secondary fines which are found in sheets made of excessively beaten pulp. The macrofibrils are embedded in the amorphous-appearance of microfibrils. The structure of the bonding layer must be very similar to this, because the bonding layer consists of secondary fines and external fibrils.

The bonding layer contributes substantially to the increase of contact area by filling gaps caused by the surface irregularity of bonded fibres. The S1 layer consists of highly oriented cellulose microfibrils, whereas the bonding layer has random orientation of cellulose microfibrils. In this sense the bonding layer is more durable for stress concentration than the S1 layer. Transition from the S1 layer to the bonding layer is continuous because of the anchoring effect of the external fibrils. Therefore, the stress is hard to be concentrated at the boundary between fibres. All of these nature of the bonding layer seems to affect the bond strength and, in consequence, the strength of the paper.

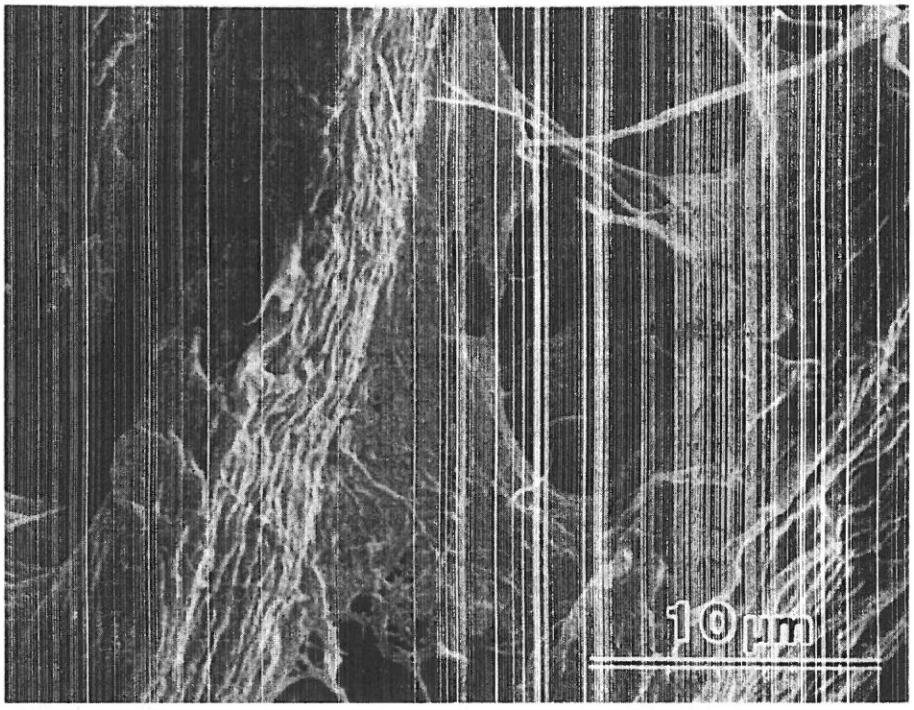


Fig.32 Surface of hand sheet showing film-like structure made of external fibrils and secondary fines.

**Influence of Shrinkage on the Formation of Fibre Bonding**

The most distinctive structure formed by drying is the longitudinal wrinkling on the fibre surface (Figs. 27, 28). The mechanism of wrinkle formation by drying can be explained as follows: as shown in Fig. 33, orientation of the cellulose microfibrils in the S1 is completely different from that of the S2. Each layer tends to shrink perpendicularly to the direction of its microfibril orientation. The S2 layer shrinks inwardly decreasing its cross sectional area as well as its perimeter, whereas the perimeter of the S1 remains almost unchanged even after drying. The S1 layer wrinkles to compensate for the difference of the perimeter of the two layers when the fibre becomes dry. The wrinkles of the beaten fibres were narrower and larger in number than those of the unbeaten fibres (Fig. 34). This probably occurs because the S1, which is separated from the S2 by beating, can form compensating wrinkles at the appropriate location without restriction by the S2.

At the bonded fibre crossing, wrinkles were formed more on the free surface than on the bonded surface (Fig. 20). The reason is that the shrinkage of the bond forming surface is restrained by the bonding partner which is resistant to the

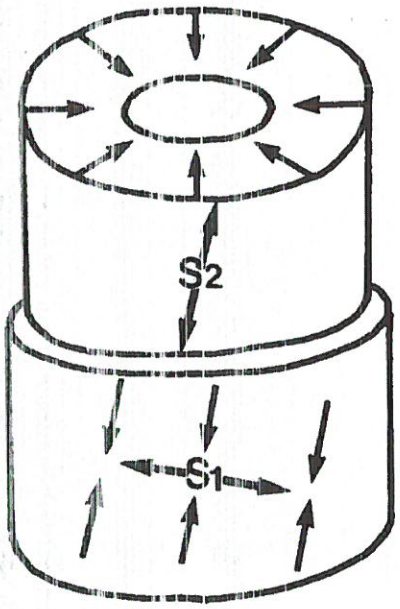


Fig.33 Structural model of wet pulp fibre showing microfibril orientation in S1 and S2 layers and direction of shrinkage of layers.

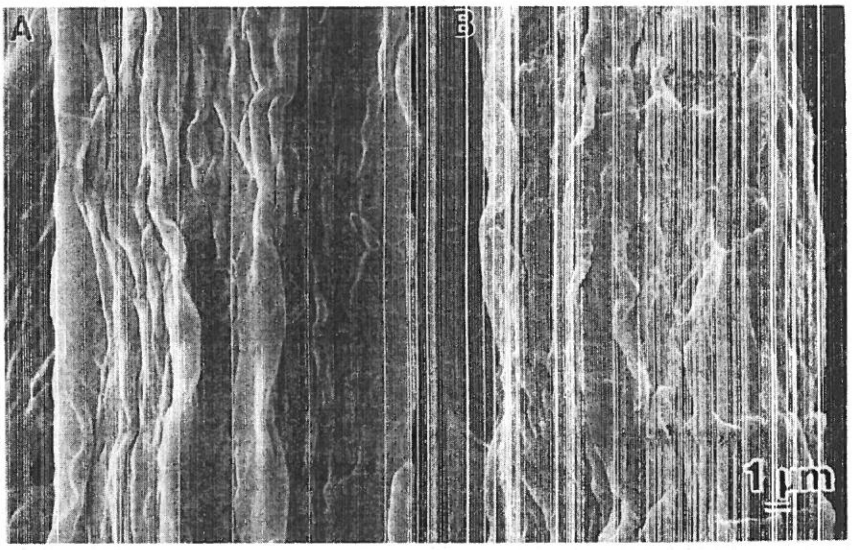


Fig.34 Surface of fibres showing wrinkles. (A) unbeaten fibre, (B) beaten fibre.

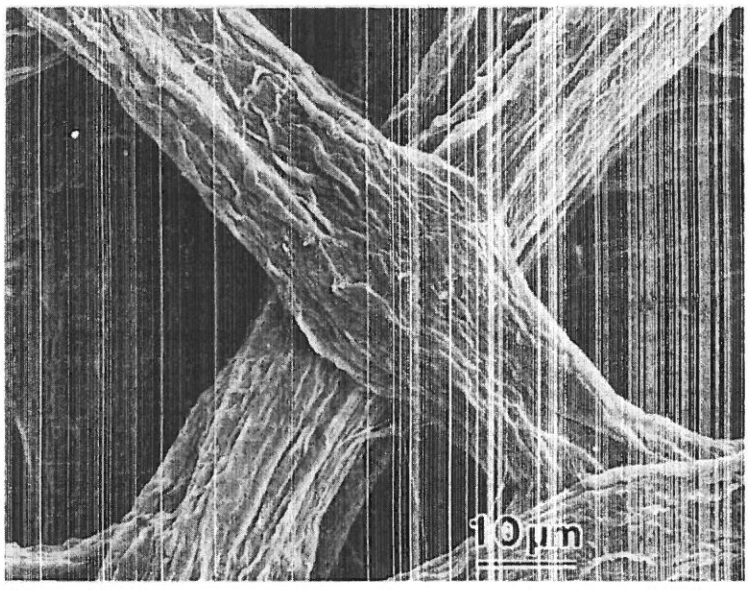


Fig.35 Surface of hand sheet showing necking of bonded fibre.

longitudinal compression, whereas the unbonded portion of the fibre can shrink freely. The fibre shrinks and becoms flattened towards the bonded surface. The fibre adhesion caused by pressing is strong enough, so the contact area does not change during shrinkage.

According to the microcompression hypothesis proposed by Page and Tydeman (17), the force of transverse shrinkage of one fibre give rise to a microcompression of the other fibre in its longitudinal direction at the bonded crossing and makes the fibre shorter. If their hypothesis is correct, many wrinkles should be formed at the bonded zone as schematically illustrated by Page (18). However, as shown in Fig. 20, only a few wrinkles were observed at the bonded zone in this study.

At the fibre crossing, the contact area does not change in size during the drying process, whereas the fibres shrink transversely at the both sides of the bonding zone (Fig. 35). This phenomenon has been known as "necking". According to Page and Tydeman (13), the reason why necking occurs is that the crossing fibres prevent transverse shrinkage of their bonding partner at the bonding zone. The mechanism of necking formation proposed by Page and Tydeman (13) seems to conflict with their microcompression hypothesis. If their proposed necking mechanism is correct, the wrinkles (microcompressions) are only sparingly formed at the bonded zone. Our present result (Fig. 20) supports this mechanism.

As shown in Fig. 20, the longitudinally cut fibre is bent into bowshape because only the bonded side of the fibre wall is forced to shrink by transverse shrinkage of the crossing fibre. This phenomenon may be closely connected to shrinkage of the sheet by drying, as it reduces the effective fibre length considerably.

The skirt is a characteristic structure which is found at the bonding edge of crossing fibres. The formation process of the skirt structure is shown schematically in Figs. 19 and 30 based on observations of the drying process of the wet web, the cross section of the wet web, and the cross section of bonded fibres. In the drying stages of the pressed wet web, formation of the skirt structure was noticed when shrinkage of the fibre wall started ( Fig. 19: 3rd stage, Fig. 16). The S1 layer which is separated from the S2 layer by beating appears to play an important role in the formation of the skirt structure. The

unbeaten fibre, in which the S1 layer is still in contact with the S2 layer, did not form skirts. Also the excessively beaten fibre without the S1 layer did not form skirts. The reason for the skirt formation, therefore, is understood as follows: the contact portion of the S1 layer can not shrink being restricted by the bond forming partner, while the free portion of the S1 layer is pulled inward by shrinkage of the S2 layer. In this case the adhesion between the S1 layer and contact fibres must be strong enough to withstand the stress generated by shrinkage.

Recent studies of adhesive bonding systems show that stress distribution in the bonded area is highly nonuniform and significantly affected by the geometry of the adherend (19). The region near the edge of the bonded area plays an especially important role in load transfer. The stress distribution shows a maximum value at the joint edge. The skirt structure appears to be effective in preventing stress concentration at the joint edge of the fibres. The "covering layer" consisting of the external fibrils which cover the bonding edge, probably has the same function as the skirt structure. Uesaka (19) suggested that the bond strength is the strength of the bond structure per se rather than the interface bond strength. In this sense, individual structures of the bonded fibres, such as the skirt structure, the covering layer and the bonding layer, are considered to be important factors which greatly influence bond strength. The formation of these structures must be one of the reasons why the tensile strength of paper increases by beating.

## CONCLUDING REMARKS

In the present investigation, the structure of interfibre bonding was examined throughout its developing stages. We found that a bonding layer made of the external fibrils and secondary fines exists between bonded fibres. We also found the following characteristic structures of bonded fibres: skirts, longitudinal wrinkles and covering layers. These structures are considerably affected by beating, by pressing and by drying. The importance of the bonding layer, skirt structure and covering layer for the bond strength was also suggested. The structures of interfibre bonding which were found in hand sheets made of laboratory beaten Buna BKP are summarized in Fig. 36.

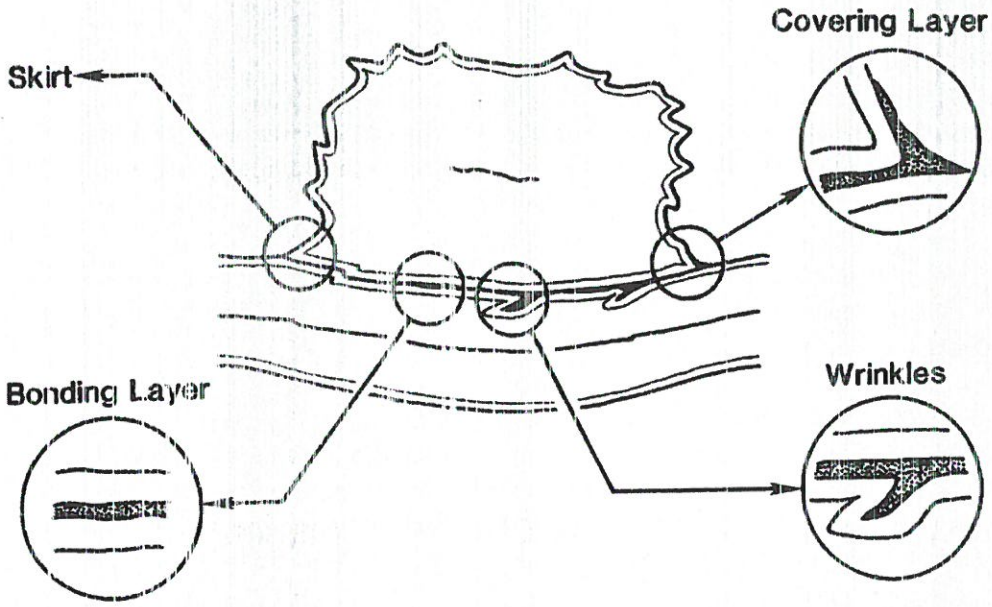


Fig.36 Basic structures of bonded fibres found in Buna BKP hand sheets.

The structure of interfibre bonding must be influenced by many other factors which we did not examine in this study, such as the fibre morphology (thick walled fibre or thin walled fibre, hardwood fibre or softwood fibre), the kind of pulp (chemical pulps or mechanical pulps), the beating equipment, the way of drying (free shrinkage drying or restrained drying) and so on. These are the subjects of future study.

The paper looks so complicated and so irregular in structure that it is not easy to find out the exact relation between the structural characteristics and specific properties of paper. In this study, we made an approach to the fibre bond structure throughout its formation stages. This way of approach was very successful and seems suitable for the analysis of the complex paper structure. This methodology has been commonly used in the field of anatomy, such as plant anatomy, wood anatomy and human anatomy, which is most effective for the study of the mechanism of structure formation as well as for the clarification of the relation between the structure and its function. Though paper is not a living organism, paper seems to be quite acceptable as an object of anatomy, if we regard the formation of paper as its ontogenetic process. "Paper Anatomy" deals with the structure and function of paper. The concept and

methodology of paper anatomy seems indispensable for the systematic study of the paper structure. Paper anatomy provides the methods for testing the theories and hypotheses of paper science. In this manner, paper anatomy can consolidate the foundations of paper science for its future development as a materials science.

**ACKNOWLEDGEMENT**

We wish to thank Dr. Akio Okagawa (JPRI, now with BASF Japan) and Mr. Hitoshi Sotobayashi (JPRI) for their helpful discussions and encouragement in the course of this study. For the preparation of metal colloids, we are deeply indebted to Dr. Yukimichi Nakao (Research Institute for Polymers and Textiles) and Dr. Kazuya Minato (Faculty of Agriculture, Kyoto University) for his suggestion on formaldehyde cross-linking treatment of paper sample. We are also greatly indebted to Lasertec Corporation for the use of the SLM. We are grateful to Mr. Masanori Arie (JPRI) for scanning electron micrographs. We would like to thank Professor Keizo Okamura (Faculty of Agriculture, Kyoto University) and Mrs. Virginia Lassiter for a critical reading of the manuscript.

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# MECHANISM OF FIBRE BOND FORMATION

H. Nanko and O. Oshawa

Unfortunately, due to an oversight three of the figures in Dr. Nanko's paper were not changed as requested. The correct figures are reproduced here.

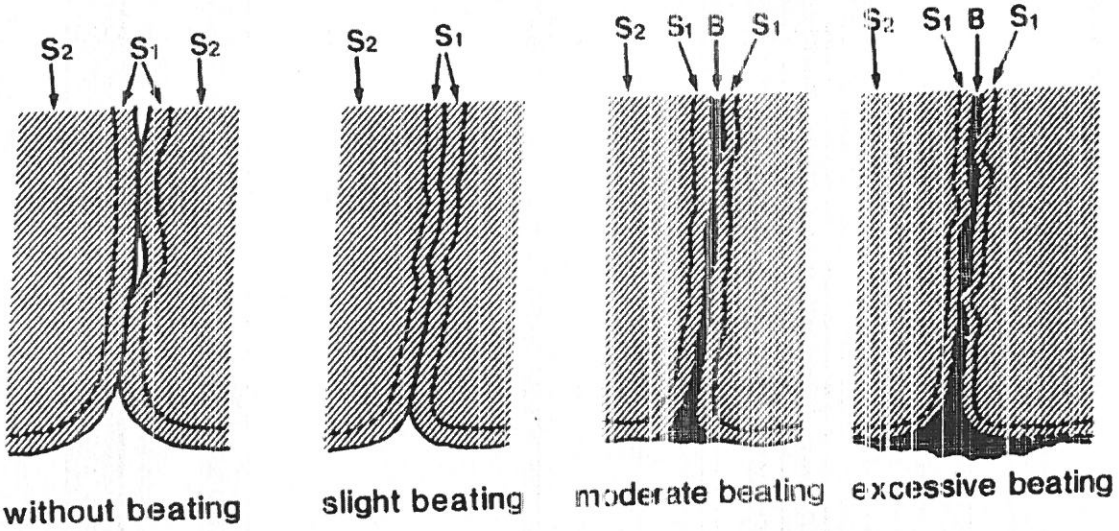


Fig.26 Schematic illustration of bond structure showing the effects of beating.

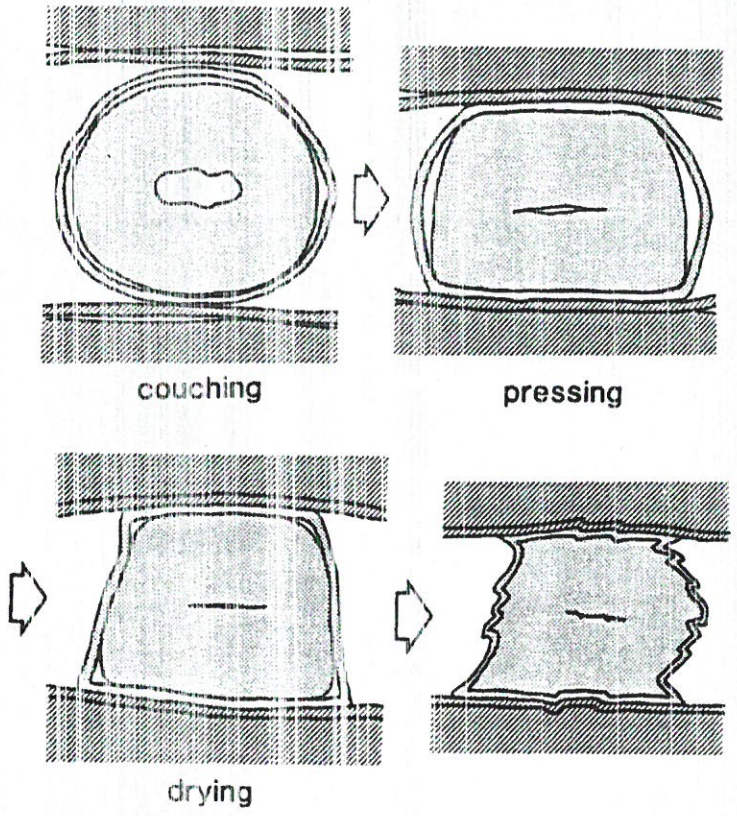


Fig.29 Summary of fibre bond formation process.

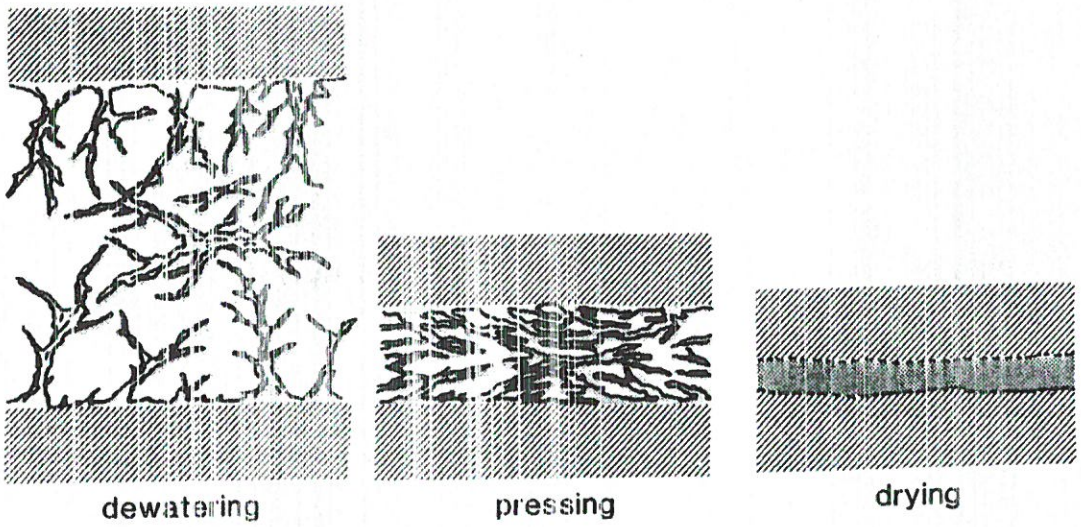


Fig.30 Schematic illustration of bonding layer formation process.

**Dr. D.H. Page Paprican Canada**

I feel I must get up and once again congratulate you on your wonderful work. However, from your text it appears that there is a misunderstanding about microcompressions, and I do not think the misunderstanding exists in my mind or Peter Tydeman's. The point is that we did not expect that you would get microcompressions in fibres in a plate dried sheet. It is under that circumstance when the sheet is dried under restraint that the necking mechanism occurs because there is a strong axial resistance of the fibre coming from the restraint of the sheet. The fibre that is shrinking can only microcompress to the extent that it is capable of taking up any slack in the fibre elsewhere. However, in the case of a freely dried sheet one expects to see extensive microcompression. Now I understand at the moment that you have not looked at freely dried sheets so it is understandable that you have not seen microcompressions. I hope that you will.

**H. Nanko**

Thank you very much. I agree with that. When the fibres are dried under restraint conditions they cannot shrink freely so microcompressions cannot be seen. This is quite natural.
Sometimes there are misunderstandings in that people think they see microcompressions on the fibre surface which are not microcompressions at all, perhaps you agree that they are just at the bonded surface? The microcompressions will never appear in the case of restraint drying but maybe they will appear in the case of free drying.

**Dr. D.H. Page**

The best way to look at microcompressions is using polarized light in the light microscope because there you see the deviations of the cellulose fibrils from the axial direction as they zig-zag backwards and forwards in the S2 layer. That may not come out clearly from your electron micrographs which only clearly show the S1 layer. The fibril direction in the S2 layer does not come out too clearly from your micrographs.

**Ms. P. Moss UMIST UK**

How much fibre shrinkage is due to T.E.M. preparation and embedding techniques?

**H. Nanko**

I do not think there is an effect from these treatments. I use a crosslinking technique with Formaldehyde and the structure is totally fixed. I do not think such treatments change the morphology very much.

**Ms. P. Moss**

Are you quite sure? These effects are well known in processing biological specimens for T.E.M.

**H. Nanko**

If you are talking about cross sections of wet webs, fibres shrink to some extent during embedding treatments. But, if you are referring to dry sheets, there is certainly no significant shrinkage.