Retaining raised fibrils and microfibrils on fiber surfaces

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ABSTRACT *I used hexamethyldisilazane treatment to: (a) maintain raised fibrils and microfibrils from fiber surfaces during drying, (b) raise fibrils and microfibrils where they have been dried down on fiber surfaces, and (c) determine if strength properties of sheets produced from HMDS-treated fibers are improved. SEM analysis showed that HMDS-treated fibers retained most fibrils and microfibrils in a raised position, while most fibrils and microfibrils from air-dried and paper-machine-dried fibers were dried down upon the fiber surfaces. Fibers that were air dried or paper machine dried, rewet, and then treated with HMDS raised many dried-down fibrils and microfibrils. The burst, tensile, and compression indices of handsheets made from HMDS-treated and never-dried pulps were greater than handsheets made from pulps dried by air or on the paper machine. This suggests that fibrils and microfibrils that remain in a raised position after drying lead to better contact between fibers.*

KEYWORDS
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Fibrils
Stock preparation
Strength properties
Linerboards
Electron microscopy
Market pulps

The strength of paper products ultimately depends on the strength properties and physical characteristics of the pulp fiber components and their bonding characteristics. Fiber strength properties and physical characteristics are influenced by many factors-type of pulp, species, fiber length, and fiber width, for example. It is also well known that mechanical treatment improves the bonding characteristics of pulp fibers and provides for a stronger paper *(1)*. Fibrils and microfibrils are important because they promote fiber-to-fiber bonding.

During air drying and paper machine drying, many fibrils and microfibrils dry down upon the fiber surface, and fiber bonding potential is greatly reduced. Preserving raised fibrils and microfibrils should help maintain strength properties when pulps are dried. Clark *(2)* concludes that the fibrils and microfibrils on the fiber surface increase the probability of fiber-to-fiber contact. Thus, bonding and consequently sheet strength properties are enhanced. Furthermore, Clark *(3)* extends the concept of Strachan *(4,5)* that the principal bonds between fibers are created by fibrils and by smaller fibrils in the range of microfibrils to nanofibrils.

In previous work *(6)*, I have shown on a small scale that critical-pint drying offers a way to dry fibers without causing fibrils and microfibrils to dry down upon the fiber surface. I also demonstrated that critical-point drying helps in recovering many fibrils from the surface of air-dried pulp fibers that had been rewetted. To determine if strength properties of handsheets prepared from dried pulp with fibrils and microfibrils raised from the fiber surface are maintained in comparison with handsheets prepared from never-dried pulp, an attempt was made to scale-up critical point drying of the pulp. This was not successful because of the difficulty in adequately controlling the conditions of critical-point drying on a larger scale with the equipment on hand. Therefore, the enhancement of strength properties by maintaining raised fibrils and microfibrils could not be evaluated. Consequently, alternative routes needed to be explored.

During SEM studies on the internal structure of insects, Nation *(7)* demonstrated that hexamethyldisilazane treatment gave results as good as those obtained by critical-point drying. The question arises as to whether or not pulp fibers and their ultrastructural components following hexamethyldisilazane treatment would behave similarly. The objectives of this study, using hexamethyldisilazane treatment, are to (a) maintain raised fibrils and microfibrils from fiber surfaces when dried, (b) raise fibrils and microfibrils where they have been dried down on fiber surfaces during the drying process, and (c) determine if strength properties of sheets produced from hexamethyldisilazane-treated fibers are improved.

HMDS treatment air-drying, and paper-machine-drying methods were evaluated by observing the surfaces of softwood kraft pulp fibers, The fiber surfaces of the various dried fibers were compared with those of never-dried fibers using scanning electron microscopy. The pulp fibers were ob served (a) after drying, using the various drying methods, (b) after rewetting, and (c) after rewetting and using

HMDS treatment to raise fibrils and microfibrils. Handsheets were prepared from pulps before and after treatment with each drying procedure, and strength properties were measured.

Results and discussion

Effect of HMDS on preserving and recovering raised fibrils and microfibrils

HMDS treatment of softwood kraft pulps was effective in maintaining raised fibrils and microfibrils from fiber surfaces. SEM micrographs of HMDS-treated pulp and never-dried pulp (Figs. 1 and 2) show the presence of raised fibrils and microfibrils. Air-dried (Fig. 3) and paper-machine-dried fibers showed few fibrils between adjacent fibers or in a raised position from the fiber surface. The effectiveness of fiber bonding should be reduced, and paper strength properties should also be reduced when fibrils and microfibrils are dried down upon fiber surfaces. HMDS treatment of pulp fibers appears to be a satisfactory method for preserving raised fibrils and microfibrils.

Air-dried and papermachinedried fibers, upon rewetting, recover few fibrils (Fig. 4). However, air-dried and paper-machine-dried pulp fibers, rewetted and HMDS-treated, recovered many fibrils and microfibrils from the fiber surface (Fig. 5) and appear similar to the never-dried fiber (Fig. 2).

The manner in which HMDS works on the pulp fibers has not been studied. HMDS is a reagent commonly used in gas chromatography, primarily to prepare silyl ethers of compounds with one os more reactive hydrogen atoms, such as sugars, amino acids, alcohols, and other compounds *(7).* It is not known whether HMDS reacts with some of these components in the pulp fibers.

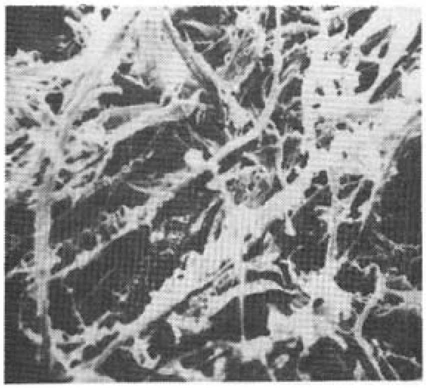
Effect of HMDS treatment on handsheet strength properties

Preserving raised fibrils and microfibrils. Strength properties of handsheets produced from HMDS-treated fiber were closest to those obtained from handsheets prepared from never-dried fiber. Except for tear index, strength properties of handsheets produced from HMDS-treated kraft pulp fibers were well above those of handsheets produced from airdried and paper-machine-dried pulp fibers. Strength properties of handsheets produced from paper-machine-dried kraft pulp were in turn below those of handsheets produced from pulp fibers dried in air.

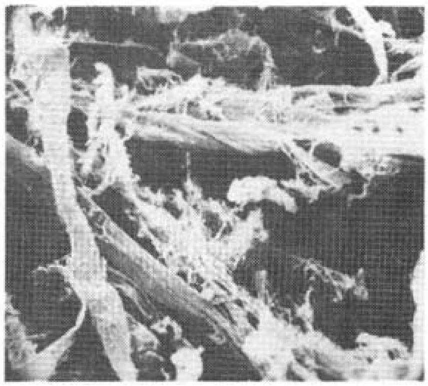
In comparing handsheet strength properties made from pulp at comparable freeness, handsheets prepared from never-dried pulp, as expected, were stronger than those prepared from HMDS-treated pulp (Tables I and II). Burst and tensile indices of handsheets produced from HMDS-treated pulp were higher than those of handsheets prepared from air-dried and paper-machine-dried kraft pulp. Tear strength of handsheets made from airdried and paper-machine-dried kraft pulp fibers were higher than those of handsheets prepared from the never-dried and HMDS-treated kraft pulp fibers.

Compression strength of handsheets prepared from HMDS-treated kraft pulp was higher than that of handsheets produced from air-dried or paper-machine-dried kraft pulp (Table II). This is likely the result of

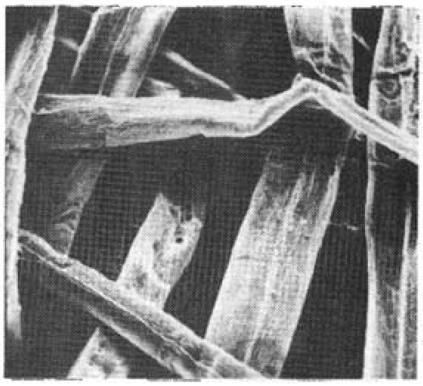
1. HMDS-treated spruce, 100X.



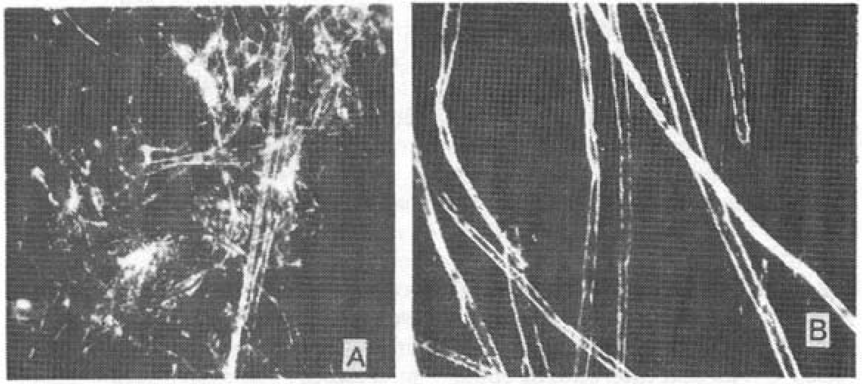
2. Never-dried spruce, 200X.



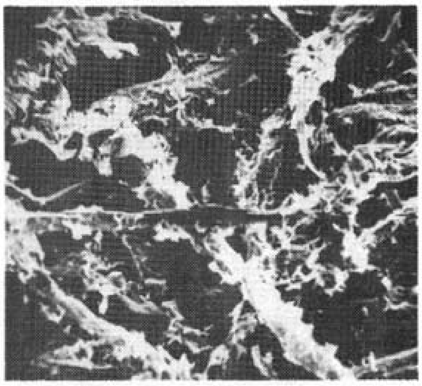
3. Air-dried spruce, 500X.



4. A. Never-dried spruce fibers in water. Note the presence of many fibrils: 310X. B. Air-dried spruce fibers in water. Note the lack of fibrils: 310X.



5. Spruce that was air dried, Wetted. and treated with HMDS, 200X.



better bonding caused by the retention of upright fibrils and microfibrils on the pulp fibers' surfaces after drying.

HMDS appears to hare brought about a fundamental change in pulp and fiber properties. The increase in bonding strength properties may be explained as a consequence of keeping the fibrils and microfibrils raised from the fiber surface so that interfiber bonding may take place.

While pulp freeness did affect individual strength property values, there was no overall trend. Individual burst, tear, tensile, and compressive indices, expressed as percent of the same sheet strength property produced from never-dried fiber, gave no discernible trend with freeness (Table II).

Recovering laid down fibrils and microfibrils. With spruce kraft handsheets prepared from air-dried or paper-machine-dried fibers that were rewet and HMDS treated, burst and tensile indices were higher than for those handsheets prepared from air-dried and paper-machinedried pulp fibers (Table II). Tear indices were about equivalent, but compression indices were not improved with the HMDS treatment.

The differences can also be determined in strength properties between handsheets made from fiber where fibrils and microfibrils have been dried down upon fiber surfaces and then recovered, compared to handsheets made from fibers where raised fibrils and microfibrils were preserved during drying. This is done by comparing handsheets made from air-dried, paper-machine-dried, rewet, HMDS-treated fiber to handsheets made from HMDS-treated fiber. For this case, tear and tensile indices were higher, burst indices were about equivalent, and compression indices were lower.

I. Properties of 205-g/m² handsheets made from never-dried unbleached spruce kraft pulps

CSF, mL	Burst index, kPa–m²/g	Tear index, mN–m²/g	Tensile index, Nm/g	Compression index, kN/m	Density, kg/m³
560	7.89	18.6	98.2	6.26	832
410	7.90	18.5	96.3	6.07	853
275	7.18	16.6	101.1	6.22	886

II. Effect of HMDS treatment, air drying, and paper machine drying on 205-g/m² handsheet properties[a]

Treatment	Freeness, mL	Burst index, %	Tear index, %	Tensile index, %	Compression index, %
	Unbleached spruce kraft				
HMDS	560	79.7	107	81.6	106
	410	86.5	99.5	90.3	130
	275	87.4	96.4	94.0	112
Air dried	560	79.2	119	74.5	80.8
	410	77.0	117	73.9	79.2
	275	62.4	131	67.5	79.3
Paper machine dried	560	55.1	115	58.1	72.8
	410	55.2	119	61.1	70.7
	275	62.9	133	64.1	74.0
Paper machine dried, rewet, HMDS treated	560	79.1	120	102.0	65.2
	410	86.3	139	104.0	75.5
	275	92.5	140	110.0	72.8
Air dried, rewet, HMDS treated	560	76.4	122	81.1	76.4
	410	84.3	124	103.0	76.3
	275	88.2	120	110.0	78.3

[a] Expressed as percent of handsheet property produced from never-dried fibers at the same freeness (Table I).

Conclusions

HMDS treatment offers a way to dry pulp fibers without causing fibrils and microfibrils to dry down upon the fiber surface. Overall handsheet strength properties were greater when made with pulps treated with HMDS than with pulps that were air dried OF paper machine dried. For dried fibers, where fibrils and microfibrils are already dried down upon the fiber surface, rewetting followed by HMDS treatment raises many fibrils and microfibrils.

Experimental

Fiber furnish

Spruce (*Picea glauca* Voss.) unbleached kraft pulp (kappa no. 45) was refined in a PFI mill to nominal CSF of 560, 410, and 275 mL.

Fiber drying

Air-dried fibers were prepared by drying never-dried fiber at 20°C and 27% RH. Paper-machine-dried fibers were prepared by forming never-dried fibers into 205-g/m² pads and drying them on a drum dryer at a temperature of 120°C. With HMDS treatment, never-dried fibers were first dehydrated through a series of ethanol solutions of 70% 85%, 95%, and 100%, with 5 min stirring in each. After the absolute ethanol treatment, the pulp fibers were immersed in HMDS for 5 min. The HMDS was allowed to evaporate overnight from the fiber in a hood at room temperature. (Drying fibers from ethanol by itself in the absence of HMDS does not preserve raised fibrils and microfibrils.)

Handsheet preparation and strength requirements

Tests were made on 205-g/m² handsheets made from the dried pulp samples as well as never-dried pulp. Handsheets of such heavy basis weight were made to minimize fines loss. Preparation of handsheets followed the procedure of TAPPI T-205. For evaluations in which HMDS was used to recover raised fibrils and microfibrils, handsheets were made from paper-machine-dried and air-dried fiber pads that were shredded and rewet by slushing in a British Disintegrator at 500 revolutions. The pulp was dewatered on a Buchner funnel and HMDS treated as described. Any effect on fiber morphology during disintegration would be expected to be small compared to that brought about by initial paper machine or air drying.

Strength tests on handsheets followed the procedures of TAPPI: burst index, T-403; tensile index, T-404; and tear index, T-470. Compression tests were performed according to the method of Jackson, Koning, and Gatz *(8)*. Ten replications were performed for each strength test.

Microscopy

Specimens dried by the various techniques were mounted on aluminum stubs and gold coated to approximately 100A thickness for SEM observation. The gold-coated pulp fibers were studied and photographed using a Cambridge Mark II SEM at an accelerating voltage of 20 kV. Never-dried fibers were also observed in the SEM. Because wet fibers cannot be used in the vacuum environment of the SEM, the never-dried fibers were dried by the critical point technique. Critical point drying is an acceptable method of preserving neverdried fiber morphology and is a commonly used technique in electron microscopy *(6)*. Critical-point-dried fibers were prepared by first dehydrating never-dried fiber in ethanol followed by infiltration with liquid carbon dioxide in a FPL-made bomb *(6)*. The bomb was warmed to 35°C (above its critical point of 31°C), and the carbon dioxide was allowed to escape, slowly, as a gas.

To observe if any fibrils and microfibrils are recovered on air-dried and paper-machine-dried pulp fibers upon rewetting, specimens were immersed in water for 8 h and photographed in the water environment with the aid of a light microscope.

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