Drying

The drying phase on the paper machine starts at about 65-75% moisture content of the paper web. The final moisture in the paper web is around 4-7%. The behaviour of the paper web during drying is a complex combination of processes, many of which occur simultaneously Robertson¹ visualizes water removal during drying in five steps. which may be overlapping : !) Decrease in interfiber capillary water without air intrusion, 2) Emptying of interfiber capillaries, 3) Change in magnitude and action of surface tension forces as water menisci are reduced from fiber dimensions to the dimensions of fibrils or interfiber distances, 4) The disappearance of interfiber water and water held in the lumen, and 5) Shrinkage and collapse of fibers. As a result of water removal and the associated surface tension forces, a significant strength development takes place in the web during the drying phase.

The analysis of the mechanism of drying needs to be done from the point of view of the macrobehaviour of the fiber assemblage, and the processes occuring at a micro-level within the cell wall and in the areas of fiberfiber contacts.

H. P. Didwania

Drying of Paper

The state of art on the theory of drying in paper has been surveyed and critical aspects have been iden ified. At consistencies of paper web during drying (30% or more), a large bulk of the water is expected to be present within fiber. Intrafiber diffusion rates then become critical. Fibers of very different composition, chemical treatment and morphology have been shown to have very similar pore size distribution. Therefore, it is theorized that the first falling rate periods of the different filters will have identical slopes (shown true for viscosegrade pulps). The second falling-rate period depends on other complex factors (chemical composition, surface characteristics of the fibers, method of preparation, etc.) Predrying the samples reduces the average pore size and also slows the drying rate. Beating is reported to increase the "secondary hydrate" which has a slower drying rate than the imbibed water. Based on available data (not complete), the overall drying rate (a weighted average of the different periods) does not secm to be significantly affected with beating.

The drying operation, in general is divisible into a constant rate period and a falling-rate period (Figure 1) After a short initial adjustment period of unpredictable form, there follows a constant drying rate period, in which the surface of the solid is wet with liquid and the rate of evaporation is not a function of the water content; the major factors affecting the rate of drying in this period are the air velocity past the surface, heat conduction from adjoining dry surfaces, and radiation from the surroundings². The rate of drying falls off during the falling rate period either because the wetted surface decreases or because the rate of interdiffusion becomes nal liquid Either of these controlling. mechanisms of drying or each in turn may previl during the fallingrate period. When internal liquid diffusion is controlling, there is a tendency for the evaporation to occur not at the surface, but at points within the solid structure (example thick pulp slabs). In the case of fibrous materials where capillary or imbibed water is present, the falling-rate period may be considered to occur during evaporation of this "bound" water. Upon continued drying, beyond the first falling rate period, however, a second fallingrate period is encountered. This second falling rate period is theorized to be influenced by a water content held by greater attraction than that upon the imbibed water.

A detailed study of the mechanisms of hot surface drying has been carried out by Dreshfield and Han³ and by Han and

Ippta, April, May & June, 1977, Vol. XIV No. 2



> BASIS WEIGHT - 200 lb. TAPPI Hot Surface Temp. - 221°F.



Figure 2. Moisture Profiles During Hot Surface Drying³.

Ulmanen⁴. They used laminated sheets with beta ray absorption to follow the moisture profiles and a soluble dye technique to determine the course of water migration. Figures 2-4 show typical profiles for moisture, temperature, and dye concentration as drying proceeds. Heat is supplied from the hot surface establishing a temperature gradient across the sheet. Evaporation occurs at the air surface, the moisture from the surface being replaced by the action of capillary suction forces. Evaporation also occurs at the hot surface and is likewise replaced. Vapour permeates from the hot towards the air surface under both an actual and a partial pressure gradient. At first, much of this vapor condenses in the body of the sheet, enhancing the thermal conductivity. This moisture movement creates a humped distribution and the concentration of dye at the two evaporation sites. The relative concentration of dye in the center begins to fall as a result of condensation cycle. When the rate of movement to the evaporation sites is too slow, the sites of evaporation move into the sheet. conductivity, Thermal vapor permeability, and surface flow then become rate controlling factors⁵. The correlation of vapor permeability and relative partial pressure has been studied by vollmer⁶. Figure 5 shows a typical relationship. Curve A the represents permeability measured with an inert gas.

Ş,

Ippta, April, May & June, 1977 Vol, XIV No. 2

Curve B is the calculated curve for water vapor. Curve C, is the observed relationship. The difference between the Curves B and C is the measure of moisture movement in the adsorbed layers. This difference varies with the flow-rate, it increases initially with flow rate but eventually reaches a constant value. Rounsley⁷ has derived an equation for multimolecular adsorption which may be used to correlate the amount of water in the adsorbed layer with the relative humidity.

 $A = \frac{B.C.X}{1 + (C-1)X} \begin{bmatrix} 1 - X^n \\ 1 - X \end{bmatrix}$

where A is the amount adsorbed, X is the partial pressure and B. C, n are constants. Eigure 6 shows a good fit of Rounsleys' equation to a typical sorption isotherm for cellulose. Rounsley assumed that the first molecular layer is tightly bonded, with an energy of adsorption greater than that for the subsequent molecular layers which he assumed approximates the energy of condensation. The molecules in the outer layer are free to move over the surface. The number of molecular layers is assumed limited and in the range of four to six. This shows that down to about 7% moisture (the amount of moisture associated with the bound layer), surface flow can be considered to provide a mechanism of the rapid moisture flow⁵.

The removal of intrafiber water is a very important consideration during the drying operation. At the consistencies of the paper web during drying, a large bulk of the water in the paper web is

Ippta, April May & June 1977 Vol. XIV No[•] 2





BASIS WEIGHT - 200 LB, TAPPI







°137

likely to be present in the paper web (Table A). [The hydrodynamic specific volumes of pulp fibers can go up to 4 cm³/gram of fiber, as per literature⁹]. Page et al. 10 and Stone et al. 11 have shown that a substantial portion of the water in a web 40-50 percent dry is in the intrafiber voids, rather than in the interfiber voids. Hence intrafiber diffusion rates become important. The complexities of the intrafiber diffusion are formidable for several reasons: the microgeometry of the fiber is not well established and also the water molecule can exist with celluloseinside the fibril, on the surface of the crystal, and on the totally disordered sites-with different degrees of binding¹².

Using a concept of cell wall structure based on a multiplicity of lamallae coaxial with the cell, Stone and Scallan¹¹ suggest that during, the drying, the lamallae draw together progressively into thicker and thicker aggregates, decreasing the total pore volume, but leaving approximately the same median separation in the spaces that remain(Figure 7.) It is tentatively suggested that a fiber dries radially inwards towards the lumen. Beating of a dried pulp aids in reopening the pores that closed during drying. In the swollen cell wall of spruce sulphite pulp fibers, which contain almost 1 cm⁸ water per gram of dry material, they report that 20 percent of the water is present in spaces





rc.

Table A Possible Hydrodynamic Specific Volume of Cellulose Fibers									
20 40 50			4.6 2.1 1.6						

a. Assumptions: (1) The pycnometric specific volume of cellulose in water == 0.62cc./gm. (8; (2) That the entire water in the slurry is present within the fiber.



UNSWOLLEN

Fig. 7. Simplfied Diagram a Drying/Reswelling Cycle¹¹

Ippta, April May & June 1977, Vol. XIV, No. 2

between lamellae and 80 percent, lamella. spaces within in observed to was This ratio persist throughout the drying cycle. Fibers of very different composition, chemical treatment and morphology possessed a wide range of pore volume, yet were shown to have very similar pore size distribution. It is hypothesized that this distribution is not of biological origin, but is based on a property of the cellulose molecule.

Actual drying curves for the cellulose fibres have been reported by Lauer¹³, Daruwalla et al.¹⁴ and Aver^{15,16}.

Lauer¹³ studied the drying curves of various rayon-grade cellulose fibers. The first falling-rate periods had identical slopes for the viscose-grade wood pulps but the actual rates varied. The second falling rates varied remarkably in slopes as well as in rates depending on the method of preparation (Table B). The amount of solution water found increased in the order cotton, linters, prehydrolyzed sulfate pulps, sulfite pulps, nonoriented oriented rayon, rayon. He hypothesized that in the first fallingrate period vaporized as free water is soon as it reaches the surface of vaporization by diffusion from the interior of the fibers. At a characteristic moisture (Xs), all the free water is removed and solution water begins to diffuse. This water has a lower vapor pressure, as established by freezepoint lowering¹⁷, which would explain the retardation of evapo-

ration. The slopes of the second rate curves indicate the resistance to diffusion. He suggests that the diffusion inside the fiber is the rate-controlling step and is determined by the structure of the intercrystalline region.

Daruwalla et al.¹⁴ made a study of the kinetics of the removal of water from native, alkaliswollen, and regenerated cellulose fibers. In all cases, the rate of evaporation curves appeared to be made up of five distinct and separate portions and there were four points in each curve at which sudden changes of direction took place. These points were different for the different pulps. In his study of kinetics of water removal of six fiber-water samples, Ayer¹⁵ showed that the treatment which a sample has received prior to drying has considerable effect on the amounts of water retained as primary adsorbate.

Ayer¹⁶ also studied the drying

rates of an unbleached sulphate pulp which was beaten for several intervals in a Valley laboratory beater. William freeness and drying rate curves were determined for each beating interval (Table C). The drying curves exhibited three drying rate periods: a constant rate period in which unbound surface water was evaporated; a failing rate period devoted to the removal of capillary or imbibed water, and a second falling rate period in which primary adsorbed hyd-

TABLE-B.

	-			
DRVINC DATA	FUD	AID_DDIFA		MACHINE_DRIED FIRERS ¹³
PRIMO PAIA	TUK	AIK-DAILU	AIND	MACHINE-DRIED FIDENS

Fiber	Species 7	Freatment	D.P.	Log 1st Rate	Xsd	Log 2nd Rate	Bound	water mol
Cotton	Acala 1517	None	3860	-0.743-0.008(100M)	15.0	-1 109-0.0298(10	0-M)	0.56
Linters	••••	K-b ^a	890	-0.732-0.008(100-M)	20.0	-0.538-0.0235(10	0-M)	0.72
Linters	•••	K-b	880	-0.714-0.008(100-1.)	18.7	-0.782-0.0264(10	0-M)	0.71
Wood Pulp	Mixed Hardwood	s psa ^b	965	-0.701-0.008(100-M)	20 5	-0:404-0.0219(10	0-M)	0 70
Wood Pulp	Mixed Hardwood	ls psa	615	-0.700-0.008(100-M)	21.8	-0.519-0 0235(10	0-M)	0.72
Wood Pulp	Loblolly Pine	psa	1075	-0.698 0.008(100-M)	20.4	~0.352-0.0212(10	0-M)	0.68
Wood Pulp	Loblolly Pine	Sic	1655	-0.702-0.008(100-M)	23.2	-0.151-0.0191(10	0-M)	0.77
Wood Pulp	Spruce	Si	1041	-0.701-0.008(100-M)	23.8	- 0.183-0.0196(10	0-M)	0.78
Wood Pulp	Hemlock	Si	635	-0.700-0.008(100-M)	22.5	-0.253-0 0203(10	0-M)	0.71
Wood Pulp	Pinus Sylvestris	Si	745	-0.7(0-0.001(100-M)	22.9	-0.156-0 0191(10	0 <u>-</u> M)	0.76
Paper Pulp	-	Si	1680	-0.790-0.008(100-M)	•••	•••		1.47
Rayon Yarn	Viscose U	nstretched	1 385	-0.283-0.008(100-M)	41 3	-0.322-0.0183(10	0-M)	0.96
Rayon Yarn	Viscose 48%	Stretching	g 385	-0.333-0.008(100-M)	40.0	-0.273-0.0181(10	0-M)	0.97
Rayon Yarn	Viscose 78%	Stretching	g 385	-0.495-0 008(100-M)	33.5	-0.548-0.0237(10)	0-M)	1.16

a. K-b=Kiered and bleached

b psa = prehydrolyzed sulfate

c. Si =Sulfite

d. X_s = Moisture control, % at intercept of 1st and 2nd falling rate curves.

Ippta, April, May & June, Vol. XIV No. 2

Beating time, min.	Canadian Standard Freeness*	Schopper Riegler Freeness*	Percent fiber at bound water intersections			Grams water bound on basis of 100 g. o.d. fiber		
	19. 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19. – 19.		Capillary	Secondary	Primary	Capillary	Secondary	Primary
0 10	cc. 800 85	сс. 880 875	24 21	90 80	90 90	305 351	 13 9	11.1 11.1
20 40 80	725 5:0 140	855 775 400	26 19 14	75 70 60	90 90 90	261 383 547	22.2 31.8 55 6	11.1 11.1 11.1

Table C (16)Fiber-WaterRelationshipWithBeating

*Converted from William's Freeness

rate is driven off Analysis of the drying rate curves (Figure, 8) indicated that as beating is accomplished. new spaces of capillary nature are opened for the imbibition of water. In addition, some type of "secondary hydrate" is exhibited. This water is bound in such a way that its drying rate is at least one-third that of unbound water It appeared that there is not a significant increase in hydroxyl groups available for the adsorption of water in beaten pulp. He postulated that the decreased "freeness" of beaten pulps is due to an increase in a "secondary hydrate" brought about by additional surface exposure and macrocolloidal hydrate formation. An analysis of his data, however, does not indicate any significant difference in the overall drying rates between the beaten and the unbeaten pulps.

Drying consists in the progr. ssive removal of water starting with the larger pores in the sheet and continuing down the spectrum until the water is evaporated from pores of molecular dimen-



g. 8-Drying Rate versus Precent Oven-dry Fiber (southern Pine Kraft Pulp) (16) sions. Usually the drying curves exhibit three drying rate periods: a constant-rate period in which free water is evaporated; a falling rate period devoted to the removal of imbibed water. and a second falling rate period in which primary adsorbed hydrate is driven The rate of evaporation off. during the constant-rate period is not a function of the water-contant; the major factors are the air velocity past the surface, heat conduction from the adjoining dry surfaces, and radiation from the surroundings. The rate of drying falls off during the falling rate period either because the wetted surface decreases or the rate of internal liquid diffusion becomes controlling. In the latter case, there is a tendency for the evaporation to occur at points within the structure. Thermal conductivity, vapour permeability and surface flow become rate controlling.

Literature Cited

- 1. Robertson, A. A., Svensk Paperstid. 66, No. 12: 477 (June 30, 1963).
- Sherwood, T.K., I. & E. C.,
 22, No. 2 : 132 (February, 1930).
- 3. Dreshfied, A. C., and Han, S. T., *Tappi* 39 : 449 (1956).
- 4. Han, S.T. and Ulmanen, T., *Tuppi* 41 : 185 (1958).
- 5. Wrist, P. E., *Tappi* 44, No. 1: 181A (January, 1961).
- 6. Vollmer, W, Chem. Ing. Tech. 26, No. 1 : 90 (1954).
- 7. Rounsley, R. R. Am. Inst. Chem. E., J. 7 (2), 308 (1961).
- 8. Nissan, A. H., Discussions Faraday Soc. No. 11 : 15 (1951).
- Robertson, A.A., Consolidation of the Paper Web, Ed., F. Balam (Technical Section, B.P. & B.M.A., Cambridge, 1965), 105.

- Page, D. H. and Tydeman, P.A. Consolidation of the Paper Webs, Ed. F. Bolam (Technical Section, B.P. & B.M.A., Cambridge, 1965), 371.
- Stone, J.E., and Scallan, A.M. Consolidation of the Paper Web, Ed. F. Bolam (Fechnical Section, B.P. & B.M.A., Cambridge 1965), 145.
- Nissan, A.H., Discussions In Trans. B.P. & B.M.A., Ed. F. Bolam, Cambridge, Sept. 1965, p. 116.
- 13. Lauer, K., *Tappi* 44 : 122 (1961).
- Daruwalla, E.H., and Shet, R.T., J. Polymer Sci., Part A, 2; 943 (1964).
- 15. Ayer, J.A., J. Polymer Sci. 21 : 455 (1956).
- 16. Ayer, J.A., *Tuppi* 41 : 237 (1958).
- Preston, J.M., and Nimkar, M.V., Textile Res. J. 23, 119 (1953).

Ippta April, May & June 1977, Vol. XIV, No. 2