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Effects of Pulp Freezing and Frozen Pulp Storage on Fibre Characteristics

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Summary. A requirement of long-term research on pulp fibres in that the material for study be stored for prolonged periods without deterioration and without changes in properties. In this paper effects of pulp freezing and thawing and of frozen pulp storage on fibre, wet web, and handsheet properties are discussed. A variety of radiata pine kraft pulps, a radiata pine sodium bisulphite pulp, and silver beech and hard beech (*Nothofagus* species) kraft pulps are examined.

The expanded walls and diameters of beaten fibres were contracted by pulp freezing. This behaviour made fibres less flexible and less able to collapse during papermaking operations. The freezing treatment also caused fibre kinks and other fibre configurations which existed in a pulp before freezing to be fixed into position and made somewhat resistant to straightening when in strained wet webs. It was found that extents of fibre kink can be varied depending on the degree to which fibre configurations are forced into a pulp network before freezing. Increasing periods of frozen storage caused the intensity and distribution of bonds redeveloped by the freezing treatment to be progressively modified. Fibre walls were, however, not contracted further by increasing periods of frozen storage.

Introduction

The effects on beaten pulps of storage in the frozen state at about −17°C were investigated when it was observed that the wall thicknesses and diameters of beaten fibres which had been frozen and thawed were similar to those of corresponding unbeaten fibres (Kibblewhite, 1972; Kibblewhite, Brookes, 1977 a). Fibre walls were neither swollen nor delaminated after beaten fibres had been frozen and thawed. These findings contrast with those for unfrozen spruce fibres (McIntosh, 1967; Page, De Grace, 1967) and with general opinion (Spencer et al., 1970; Tasman, 1969) because the walls of beaten fibres are normally swollen and delaminated. The present study

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was designed to show whether separately or together pulp freezing and frozen pulp storage modified the properties of unbeaten and beaten fibres.

Results

Handsheet Properties

Beaten Pulps

The properties (except for stretch) of handsheets prepared from beaten radiata pine kraft pulps stored in the frozen state were found to change with the period of storage (Table 1). Pulp freeness and handsheet scattering coefficient increased, and handsheet tensile index, apparent density, and burst index decreased, with increasing periods of frozen storage. Tear index increased with the period of storage to the point of maximum tearing strength and then decreased at low sheet densities in accordance with reversed beating curves (Kibblewhite, 1973). It was surprising that the stretch of handsheets from beaten pulps was the conventional strength parameter unchanged or only slightly changed by prolonged frozen storage. Except for stretch, handsheet properties almost reverted to those of the unbeaten fibres after the beaten and frozen pulps had been stored for 32 months (Table 1).

Prolonged frozen storage of hard beech kraft pulps produced similar trends in handsheet properties to those obtained with the corresponding radiata pine pulp (Kibblewhite, 1979). The rate of reversion of the beaten hardwood pulp to the unbeaten state was, however, very much more rapid than for the softwood pulp. The stretch or extensibility of handsheets prepared from the beech pulps partly reverted to unbeaten values after prolonged frozen storage (12 months). This behaviour contrasted with that shown by the softwood pulp where handsheet stretch was essentially unchanged after 32 months of frozen storage.

Unbeaten Pulps

The freezing of unbeaten silver beech, hard beech, and radiata pine kraft pulps had generally small effects on handsheet physical properties after subsequent pulp beating, except for elastic modulus which was decreased by the freezing of both the hardwood and softwood pulps (Kibblewhite, 1979). Handsheet burst and tensile indices, scattering coefficients, and apparent densities were only slightly lower for the frozen than for the unfrozen pulps. This difference was found to decrease with increasing degrees of pulp beating after thawing, and became negligible at PFI mill beating levels of between 8 000 and 16 000 revolutions. After subsequent pulp beating the storage of unbeaten radiata pine krafts for prolonged periods in the frozen state also had little effect on handsheet properties, except for stretch and elastic moduli which were respectively slightly higher and slightly lower for the frozen than for the unfrozen pulp (Kibblewhite, 1979).

Table 1. Prolonged storage of beaten and frozen radiata pine Kraft pulps

Pulp	Storage conditions	Storage period after beating months	Beating time[a] min	Free-ness Csf	Tear index mN·m²/g	Burst index kPa·m²/g	Apparent density kg/m³	Scattering coeffi-cient cm²/g	Tensile index N·m/g	Stretch %	Elastic modulus MN/m²
Slabwood	Frozen before beating	–	–	766	16.3	1.0	407	266	22	1.1	1500
	Frozen before beating	–	45	564	17.2	8.2	625	155	93	2.9	5000
	Frozen before and after beating	14	45	584	34.2	4.1	559	214	53	3.5	2200
		32	45	718	21.3	1.7	500	253	29	2.8	1400
Slabwood	Frozen before beating	–	–	738	16.4	1.0	402	281	20	1.0	1300
	Frozen before beating	–	45	642	15.4	7.6	603	164	87	2.5	4900
	Frozen before and after beating	32	45	726	26.1	1.8	510	257	33	2.5	1700

[a] Beaten in Valley beater at 1.6% consistency (Kibblewhite, 1973)

Fibre Properties

Pulp Freezing and Thawing Effects

The freezing and/or thawing of beaten sodium bisulphite pulps (yield 53 per cent) at solids contents of about 20 per cent caused extents of fibre kink to be increased, and fibre wall thicknesses, fibre diameters, and fibre cross-sectional wall areas, but not lumen diameters, to be decreased by statistically significant amounts (Table 2). The incidence and extents of fibre wall delamination (Fig. 1) were markedly decreased by the pulp freezing and thawing treatment (Table 2). The swollen and delaminated walls of the beaten fibres were contracted by the pulp treatment and separated wall lamellae and wall elements were apparently brought back into close contact one to another. This observation was in agreement with the cross-sectional dimension data listed in Table 2.

The pulp freezing and thawing treatment apparently caused the wall organisation of beaten fibres to be modified so that they became less flexible and less able to collapse during papermaking operations (Table 2). The numbers of uncollapsed fibres observed *in situ* in handsheets were more than doubled by pulp freezing and thawing.

Frozen Storage Effects

Fibre dimensions and extents of fibre kink were unchanged by the prolonged frozen storage of the beaten bisulphite pulps at about −17 °C (Table 2). In contrast, handsheet densities and the number of delaminations in fibre walls were decreased, and the number of uncollapsed fibres *in situ* in handsheets was increased, with increasing periods of frozen pulp storage. A linear relationship existed between handsheet density and the number of uncollapsed fibres, as expected (Kibblewhite, 1979). Relationships between numbers of fibre wall delaminations and uncollapsed fibres were, however, probably non-linear (Fig. 2). The two sets of data presented in Fig. 2 show that delamination magnitudes but not overall trends were subject to observer bias. Data for Set II were collected some 2 weeks after the data for Set I.

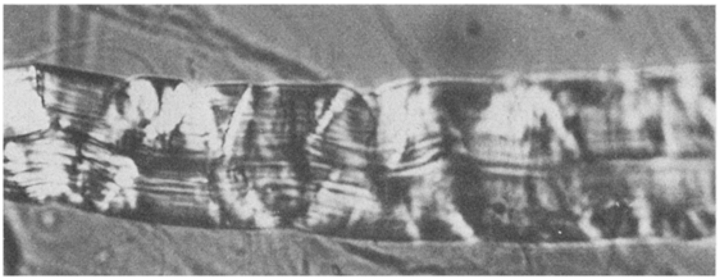

Fig. 1. Longitudinal delaminations in fibre walls

Table 2. Effects of pulp freezing on the fibre properties of radiata pine bisulphite pulps

Pulp freezing conditions	Period of frozen storage	Fibre cross section dimensions				No. of kinks per mm of fibre	Kink index per mm of fibre	No. of wall delaminations per fibre width		No. of un-collapsed fibres	Handsheet apparent density
		Wall thickness	Lumen diameter	Fibre diameter	Cross-sectional wall area						
		μm	μm	μm	μm			Set I	Set II		kg/m^3
Unfrozen control	–	9.3	22.6	41.1	397	2.24	2.86	4.65	3.74	5.3	723
Liquid nitrogen at –196 °C	0.5 hour	7.2	22.5	36.9	213	–	–	–	–	10.3	682
Freezer at –17 °C	20 hours	7.5	23.2	38.2	229	2.83	3.76	3.81	2.57	12.2	663
Freezer at –17 °C	1 month	7.5	22.2	37.2	225	–	–	–	–	13.8	658
Freezer at –17 °C	3 months	7.3	23.2	37.2	218	2.97	4.08	–	–	14.3	648
Freezer at –17 °C	6 months	7.2	23.2	37.6	219	–	–	–	–	15.4	643
Freezer at –17 °C	12 months	7.7	21.2	36.6	225	2.88	3.99	2.29	1.49	16.7	640

Statistical significance:

Mean wall thicknesses different at the 95% level if different by more than	0.64 μm
Mean lumen diameters different at the 95% level if different by more than	2.8 μm
Mean fibre diameters different at the 95% level if different by more than	2.8 μm
Mean wall area different at the 95% level if different by more than	29.3 μm^2
Mean number of kinks different at the 95% level if different by more than	0.52 units
Mean kink index different at the 95% level if different by more than	0.83 units
Mean number of wall delaminations different at the 95% level if different by more than	0.81 units
Mean number of uncollapsed fibres different at the 95% level if different by more than	5.2 units

Table 3. Effects on wet web strengths of freezing heavily kinked Kraft fibres

Pulp storage conditions	Fibre length[a]	Fibre diameter[b]	Fibre kinks per mm of fibre length		Wet web strengths					
					Tensile index		Stetch		Solids	
	mm	μm	Number	Index	N · m/g	σ/Γn	%	σ/Γn	%	σ/Γn
Cold room storage (4 °C)	1.93	29.5	3.4	4.5	1.25	0.038	31.3	0.89	21.3	0.37
Frozen storage (– 17 °C)	1.87	27.6	4.4	6.7	1.15	0.035	34.6	0.57	21.5	0.34

[a] Fibre lengths different at the 95% level if different by more than 0.12 mm

[b] Fibre diameters different at the 95% level if different by more than 2.00 μm

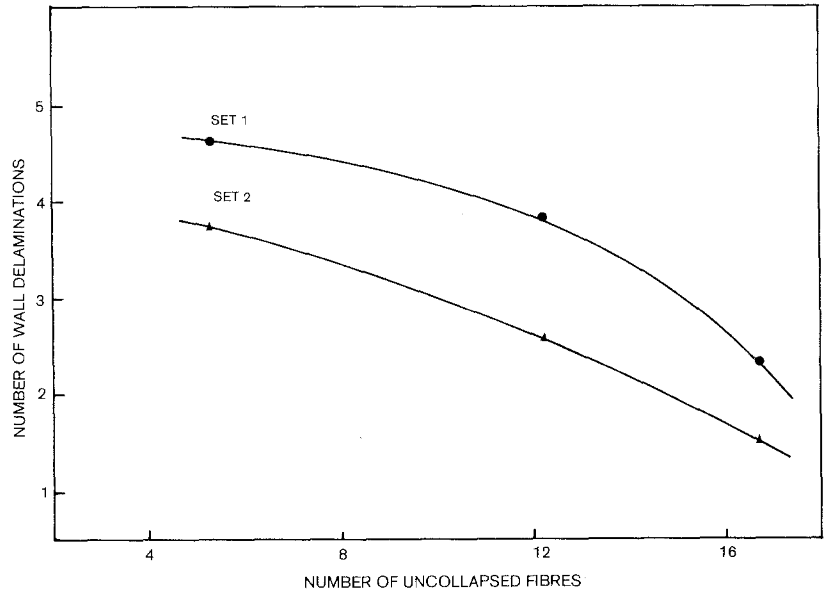

Fig. 2. Numbers of delaminations in fibre walls and numbers of uncollapsed fibres in handsheets

Wet Web Properties

Frozen Storage Effects

The freezing and thawing of a radiata pine kraft pulp caused wet web tensile strength to be decreased and wet web extensibility to be increased (Figs. 3, 4) (Kibblewhite, 1979). The effects of pulp freezing on wet web properties were unchanged by periods of frozen storage of up to 3 months. Wet web tensile strengths were, however, further decreased after 6 months of frozen pulp storage (Fig. 3). Wet tensile strengths were also strongly influenced by small changes in web solids contents. Wet web extensibilities were in contrast very variable and essentially independent of solids contents for the range examined (Fig. 4). Very slight negative correlations between wet stretch and web solids content may exist, as expected (Robertson, 1963).

Corresponding handsheet properties were found to have partly reverted to those of the unbeaten pulp after 6 months of frozen pulp storage (Kibblewhite, 1979) in agreement with the more extensive data listed in Table 1. Fibres in the unfrozen pulp were only lightly kinked when compared with those in the frozen and thawed pulp (Fig. 5).

Heavily Kinked Fibres

The effects of freezing heavily kinked radiata pine kraft fibres at −17 °C for 48 hours at a pulp stock consistency of about 20 per cent were to indirectly increase the extent of kink (Table 3) and to fix the kinks into position so that they were able to partly

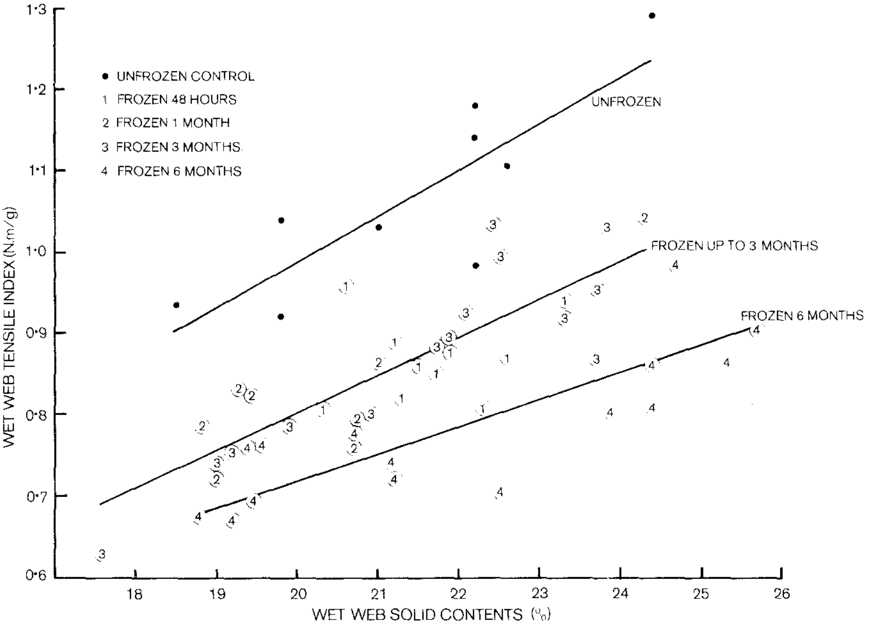

Fig 3. Effects of pulp freezing on wet web tensile strength

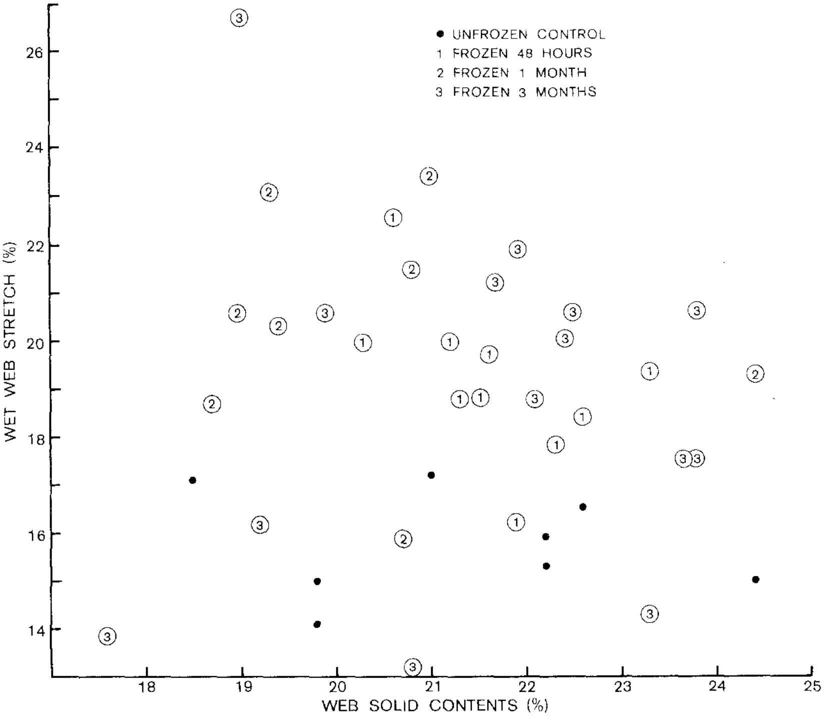

Fig. 4. Effects of pulp freezing on wet web extensibility

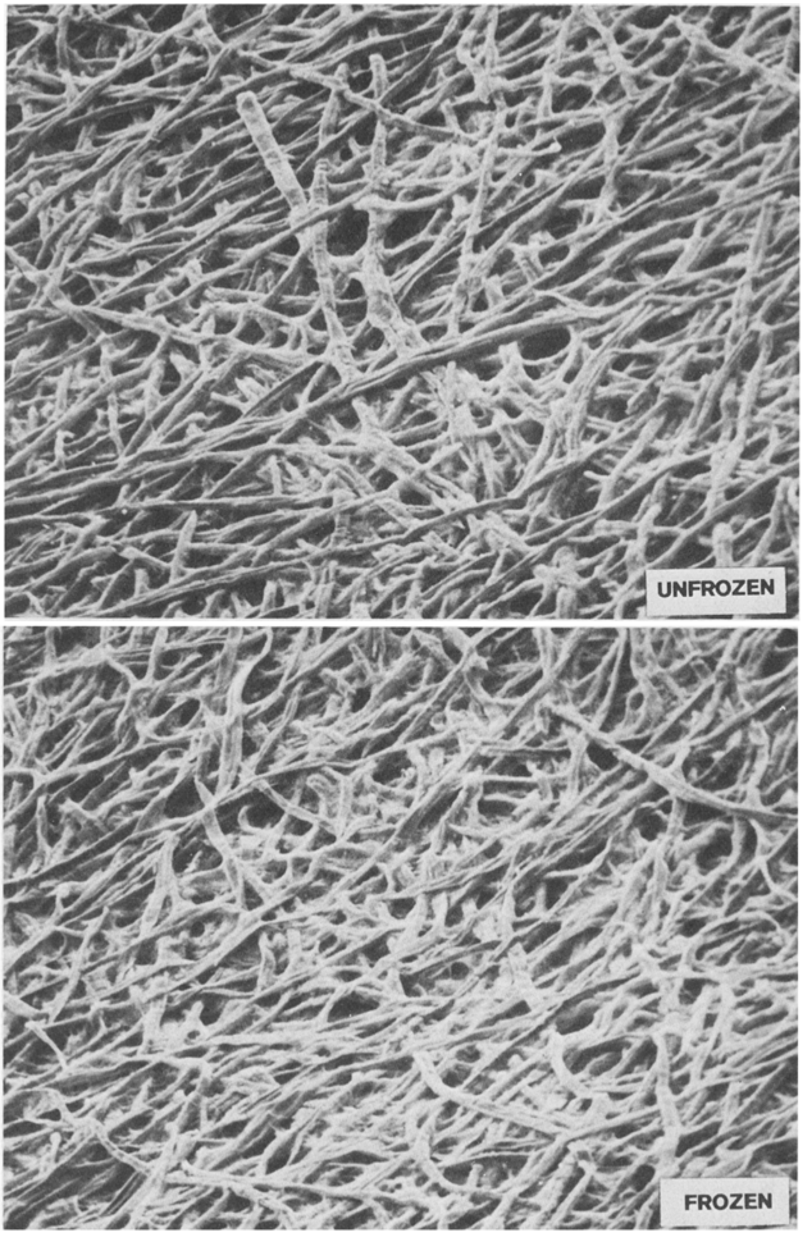

Fig 5. Surface views of wet webs prepared from lightly kinked kraft fibres which had been either frozen and thawed, or left unfrozen. Web solids contents were about 21.5 per cent. Fibres in the mat prepared from the frozen and thawed pulp appear twisted and kinked compared with those in the mat prepared from the unfrozen material

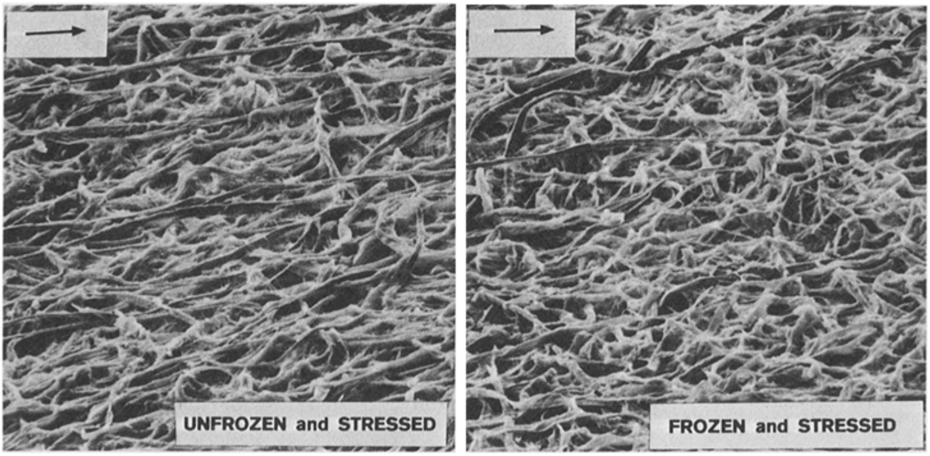

Fig. 6. Surface views of wet webs strained to 80 per cent of their rupture stress value. The webs were prepared from either unfrozen, or frozen and thawed kraft fibres as noted on the micrographs. Web solids contents were about 21.4 per cent. Fibres which had not been frozen and thawed appear to be the most readily straightened when in a strained web. The direction of strain is arrowed

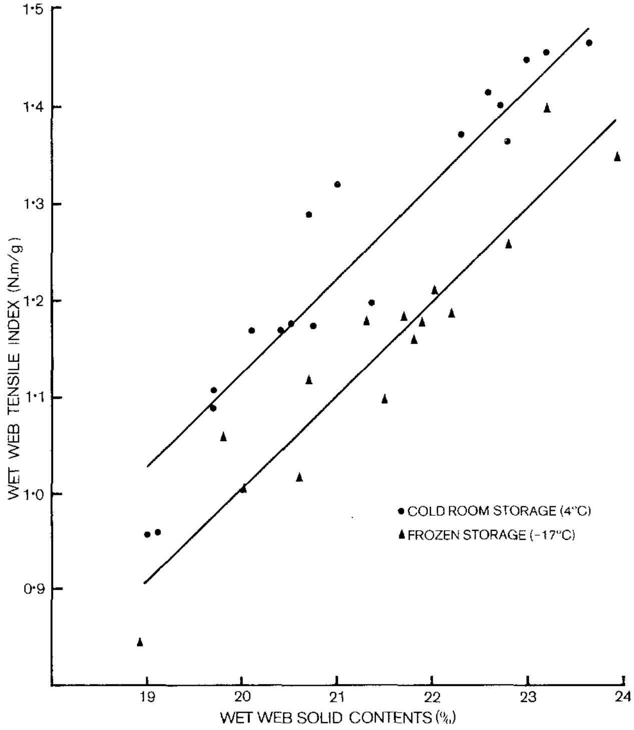

Fig 7. Effects of freezing kinked fibres on wet web tensile strengths

Table 4. Effects on handsheet properties of freezing pulps in which fibre kinks were previously set into position

Pulp storage conditions	Pulp dis-integration period min	Freeness Csf	Tear index $mN \cdot m^2/g$	Burst index $kPa \cdot m^2/g$	Apparent density kg/m^3	Air resistance $s/100\,cm^3$	Tensile index $N \cdot m/g$	Stretch %	Elastic modulus MN/m^2	Scattering coefficient cm^2/g
Cold-room storage at 4 °C	25	694	25	2.2	474	< 2	27	3.6	1400	384
Frozen storage at −17 °C	25	690	27	2.3	484	< 2	28	3.8	1600	374

resist straightening in strained wet webs (Fig. 6). Fibre lengths and fibre diameters were unchanged by the pulp freezing and thawing treatment as expected (Table 3).

Pulp freezing and thawing caused wet web and handsheet properties to be modified (Table 3, Fig. 7). In the frozen and thawed pulps wet tensile strength was slightly decreased and wet stretch was slightly increased, while handsheet properties showed a partial reversion to the unbeaten state. The wet web extensibilities of this pulp were exceptionally high compared with data obtained for the kraft pulp which contained only lightly kinked fibres (Fig. 4). Handsheet properties were found to have been partly reverted to the unbeaten state by the pulp freezing treatment in accordance with the data listed in Table 1 (Kibblewhite, 1979). The handsheet properties of a heavily kinked, chlorinated, and caustic-extracted Howe Sound pulp known to have had its fibre kinks set into position (Kibblewhite, Brookes, 1975) were unchanged by the pulp freezing and thawing treatment (Table 4).

Discussion and Conclusions

Fibre Properties

The freezing and/or thawing of pulps at solids contents of about 20 per cent caused the swollen walls of beaten fibres to be contracted and the extents of fibre kinking and fibre stiffness to be increased (Table 2).

Fibre Stiffness

Fibre stiffness as measured by the number of uncollapsed fibres and handsheet densities (Table 2), was apparently increased by the rebonding of delaminated wall element surfaces which were brought back into contact with one another during pulp freezing and/or thawing. Rebonding probably occurred through the re-formation of hydrogen bonds (Kibblewhite, Kerr, 1980). The measured contraction of fibre walls which occurs with pulp freezing and/or thawing is apparently related to a build-up and/or a fall-off of surface tension stresses and capillarity phenomena as water in its liquid state is withdrawn from between adjacent wall elements during pulp freezing and returned to these positions (when possible) during pulp thawing. The fact that extended periods of frozen storage caused the number of visible wall delaminations to continue to decrease without further measurable changes in wall thicknesses suggests a redistribution of bonds as well as increased numbers of bonds formed within the walls of fibres which had been previously contracted by the pulp freezing treatment. Such a redistribution and increase in the number of bonds is probably related to moisture sublimation and resolidification throughout the freezing period at the very extensive air-to-ice interfaces in the open pulp network stored in sealed bags at stock concentrations of about 20 per cent. The above is considered to be one of the more likely explanations for the measured effects of pulp freezing and/or thawing on fibre stiffness.

Fibre Kinking

Extents of fibre kink are increased by pulp freezing and/or thawing but not by extended periods of frozen storage (Table 2). This increase in the extent of fibre kink is probably brought about by pretreatment pulp preparative procedures rather than by pulp freezing and thawing. Pulps were de-watered to solids contents of about 20% and crumbed using a mechanical pulp fluffer before being sealed in plastic bags and frozen. Under these conditions mechanical changes in fibre configurations are forced into the pulps as water is squeezed from them and fibres are forced against and entangled with one another. These enforced changes in fibre configurations exist in the pulp during freezing and thawing when fibre kinks are apparently set into position by rebonding as fibre walls are contracted and the surfaces of adjacent wall elements are brought into contact with one another. The small increases in volume which occur when water is converted into ice probably have an insignificant effect on fibre configurations. In the unfrozen pulp most of the enforced changes in fibre configurations are reversed when the restraining forces are released as the pulp is redispersed in water. Thus, extents of fibre kink are lower in the unfrozen than in the frozen and thawed pulps.

It can be expected that bond intensities at points of kink will increase with increasing periods of frozen storage in accordance with the effects of this treatment on fibre stiffness (Table 2).

Wet Web Properties

The decrease in wet web tensile and the increase in wet web extensibility obtained with pulp freezing and thawing treatments can be correlated (Kibblewhite, Kerr, 1980) with increased extents of fibre kink (Tables 2, 3). The absence of an effect of frozen storage periods of up to 3 months on wet web strength and extensibility was further evidence of the influence of fibre kink on wet web properties (Fig. 3). Extents of fibre kink were unchanged by increasing periods of frozen storage, whereas handsheet densities and fibre stiffness values were progressively increased (Table 2). The marked decrease in wet web tensile strength which occurred after 6 months frozen storage (Fig. 3) suggests that fibre properties such as bond intensity and stiffness had begun to influence wet web strength to a greater extent than fibre kinking.

Handsheet Properties

Pulp freezing and thawing modified the properties of the unbeaten pulps although the effect was small and essentially eliminated by subsequent pulp beating treatments (Kibblewhite, 1979). Effects of freezing beaten pulps were in contrast strongly marked and caused handsheet properties to partly revert to those obtained with unbeaten pulps (Table 1) (Kibblewhite, 1979). Extended periods of frozen storage (up to 32 months) caused handsheet properties other than stretch to revert to those of the unbeaten pulps. Explanations for this reversion of properties must relate to the increased stiffness of fibres brought about by the contraction and rebonding of fibre walls during pulp freezing and frozen pulp storage, as well as to the related decrease in the areas available for interfibre bonding in handsheets prepared from such pulps.

The slow reversion of handsheet stretch with increasing periods of frozen storage is probably related to the retention of both the increased extents of fibre kink indirectly brought about by pulp freezing and some of the modifications in fibre intrawall organisation caused by the pulp beating pretreatments. Changes in fibre intrawall structure have been shown to have very significant effects on handsheet stretch properties as they often allow the extents of fibre elongation in strained pulps to be increased (Kibblewhite, 1976).

Experimental

Pulping

A range of kraft pulps from radiata pine wood was prepared using conventional procedures. The only kraft pulp requiring further comment was that used in the study of the effect of freezing heavily kinked fibres (Table 3). This pulp was prepared from a dried and reconstituted commercial kraft obtained from the Tasman Pulp and Paper Company. The reconstituted pulp was refined in a 12-inch single-disc Sprout Waldron laboratory refiner Model 105-A powered by a 30-kW motor at a stock concentration of about 16 per cent using plate pattern C-2976. This high-consistency Sprout Waldron treatment was used to improve the papermaking properties as well as to retain the extents of fibre kink pre-existing in the reconsituted pulp.

The kraft pulps from silver beech (*Nothofagus menziesii*) and hard beech (*N. truncata*), and the sodium bisulphite pulp from radiata pine wood at 53 per cent yield were prepared by conventional procedures detailed elsewhere (Kibblewhite, Brookes, 1975; Kerr et al., 1979; for descriptions of both the fibre and papermaking properties of these pulps).

Pulp Freezing and Thawing

Pulps were de-watered to solids contents of about 20 per cent, crumbed and sealed in plastic bags which were stored in a freezer at about −17°C. The unfrozen control pulps were stored at about 4°C. Pulp freezing in liquid nitrogen was carried out by immersing the crumbed pulp directly in this medium at −196°C. All pulps were allowed to thaw at an ambient temperature of about 20°C.

Measurement of Fibre Properties

Fibre Cross-Section Dimensions

Estimates of fibre wall cross-sectional dimensions were obtained using cross-sections of Epon-embedded fibres in accordance with procedures detailed elsewhere (Kibblewhite, Brookes, 1977a).

Fibre Kink

Estimates of fibre kink were made by microscopic and numerical analyses. For each pulp projected fibre images were examined and the number and angle of kinks and bends in each fibre noted. Angles of kink were classified into the following groups: 10–20°, 21–45°, 46–90°, and 91–180°. Kinks in each group were allocated the respective values of 1, 2, 3, and 4. Kink indices comprised the summation of values obtained for 100 fibres in each pulp. Twenty-five fibres on each of four microscope slides were measured for each pulp (Kibblewhite, Brookes, 1975).

Fibre Length

Estimates of mean pulp fibre length were made by tracing projected fibre images and recording their length with a measuring wheel. For each pulp, 50 fibres on each of six microscope slides were measured. Samples were coded and examined in a randomised order to eliminate observer bias.

Fibre Collapse

Extents of fibre collapse in handsheets were estimated through the examination of section faces cut at angles of 45° to the plane of the sheet (Kibblewhite, Brookes, 1977a). Uncollapsed fibres were defined as not having lumen walls in contact. The number of uncollapsed fibres was counted in each of 11 scanning electron micrographs of each of the sectioned handsheet surfaces. Each micrograph was coded and examined in a randomised order to eliminate observer bias. The actual values noted represented the mean number of collapsed fibres in the 11 micrographs examined for each sample. Between-sample variation in handsheet basis weights was taken into consideration in the statistical analysis.

Wall Delaminations

Fibres were mounted on microscope slides and examined using partly polarised illumination. Fibres were oriented vertically in the field of view and the number of delaminations visible in the pairs of fibre walls was counted along a line perpendicular to fibre axes. Each set of microscope slides, containing one slide from each sample, was studied in a single examination period. The slides in each set were coded and examined in a randomised order to minimise observer bias. To further minimise day-to-day variations in this somewhat subjective analysis, microscope settings such as light intensities and polariser positions were noted and reset daily. For each pulp 120 fibres were examined, 30 fibres on each of four microscope slides.

Wet Web Properties

Wet web tensile indices and extensibilities for webs of solids contents of about 21 per cent were determined following procedures outlined by Stephens and Pearson (1970). The rate of strain was 5 cm/min and 16 replicate strips were normally tested for each evaluation.

Procedures used in the preparation of unstrained and strained wet webs for scanning electron microscopy have been outlined in a publication describing the effects of fibre and fibre network behaviour in strained wet webs (Kibblewhite, 1974).

Handsheet Properties

Handsheet preparation and testing procedures were in accordance with Appita standard methods. Pulps were beaten in a PFI mill at 10 per cent stock concentration with an applied load of 1.8 kg/cm and a relative roll and housing speed of 6 m/s.

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