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# THE INFLUENCE OF GRAMMAGE, MOISTURE CONTENT, FIBRE FURNISH AND CHEMICAL MODIFICATIONS ON THE HYGRO- AND HYDRO-EXPANSION OF PAPER

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# ABSTRACT

The conventional way to evaluate dimensional stability, regardless of end-use purpose, is to measure the change in dimensions when the moisture content is changed by changing the relative humidity. Sorption of moisture from moist air is a relatively slow process and for the evaluation of printing papers this may not be the most appropriate method.

In the present work, data from conventional hygroexpansion measurements has been compared with data from hydroexpansion measurements, i.e. expansions caused by the sorption of liquid water, sprayed onto papers printed with a random speckle pattern, the expansion being monitored by electronic speckle photography.

Sheets made from different pulps, with different fines contents and different modifications were studied at different grammages and water-transfer levels. The effect of drying-mode, i.e. restrained drying or free drying, was also studied. It was concluded that sheets expand less with a given amount of adsorbed water when it is sorbed in liquid form rather than from moist air. Chemical treatments known to increase both the dry and the wet strength, e.g. polyelectrolyte multilayers and cross-linking through periodate oxidation, did not significantly improve the dimensional stability when the papers were exposed to liquid water.

# INTRODUCTION

Paper is a cheap and very versatile material with many uses. However, most paper products, tissue products excepted, have one severe problem in common; the fibres interact strongly with water and the products are hence very sensitivity to water. With increasing moisture content, not only are the paper's strength properties reduced but the paper also tends to change its dimensions. The latter effect, which is usually known as dimensional instability is one of the greatest problems encountered when wood fibres are used for boxes, printing papers etc. [1]. Changes in moisture content due to changes in relative humidity cause curl and cockle during the storage of paper and also cause accelerated creep, mechano-sorptive creep, in papers under load [2, 3]. During a four colour offset printing operation,  $1-2 \text{ g/m}^2$  of fountain solution is transferred from the printing rolls to the paper (e.g. [4]), causing dimensional changes and thus increasing the risk of register error.

Traditionally, dimensional stability is measured as hygroexpansion (e.g. [5–7]), i.e. the expansion is measured as a function of the change in relative humidity. A recent study [8] has however shown that there can be great differences in the dimensional stability measurements depending on whether the expansion is normalised with respect to the change in relative humidity or with respect to the change in moisture content, because different fibres and differently modified fibres adsorb different amounts of water from moist air. A low water uptake and low expansion is an advantage for boxes and materials exposed to humidity changes, but in a printing press the change in moisture content is expected to be rather constant, since the transferred amount of fountain water is probably constant at constant surface roughness, and hygroexpansion measurements may not be relevant. There is great difference in the dynamics in these different sorption situations, where the change during printing occurs in matter of seconds, whereas the moisture adsorption and subsequent dimensional changes continue for several minutes or even

hours in the event of a large change in relative humidity [9]. When the moisture content increases in paper, dried-in strains associated with drying will be released and this also mean that equilibrium measurements are doubtful as a representative measure of the dimensional stability during printing.

In the literature, there are a couple of reports of attempts to measure the dimensional changes when paper is subjected to liquid water using an electronic speckle technique in combination with contact transfer methods for applying water to the paper [10–12]. However, if a large pressure is applied, the transfer roll mangles the paper and thus compresses it and when this deformation relaxes, the recovery will be measured as a hydroexpansion. For example, the contact technique shows an expansion even when no water is transferred [12, 13]. The speckle technique has earlier been used to measure the hygroexpansion of board [14] and, on a microscopic scale [15, 16], to study how a drop of water alters a one square millimetre area when it is distributed by capillary absorption over the studied area.

Recently, the authors developed a new technique based on electronic speckle photography and water application by spraying [17]. The results from this study indicated a different expansion mechanism when paper is subjected to liquid water than when it is contact with moist air, since the expansion is smaller than during hygroexpansion measurements and the sheets tend to re-shrink while maintaining a more or less constant, and still elevated, moisture content. The proposed mechanism is that the moisture content is initially high enough to loosen the fibre-fibre joints within the top fibre layers in the sheet and that, as the water penetrates further into the sheet, the surface is dried out and the fibres re-conform to a less extended state.

The aim of the present work is to use the new technique to further study these phenomena, and also to compare the hydroexpansion with hygroexpansion data for sheets with the same fibre treatments as those reported by Larsson and Wågberg [18] and Larsson *et al.* [8], i.e. sheets that have different degrees of contact within the fibre joint, sheets that are hydrophobic and sheets with a reduced moisture sorptivity.

## MATERIALS AND METHODS

#### Fibres

As reference pulp, an unbeaten virgin softwood kraft pulp (SCA, Östrand Mill, Sweden) bleached according to a (OO)Q(OP)(ZQ)(PO)-sequence was used. Fines were removed by spray screening through a wire with a 75  $\mu$ m mesh in an equipment developed at Innventia (former STFI-Packforsk), Sweden. The pulp was washed and the carboxyl groups on the fibres were

converted to their sodium form according to an earlier described procedure [19].

A thermo-mechanical pulp (2200 kWh/adt) from spruce with a freeness of about 75 ml (Holmen Paper, Hallstavik, Sweden), both with and without fines, was also used for comparison with the kraft pulp. To avoid microbial growth, the pulp was stored in a freezer and thawed just before use. When necessary, the fines in the mechanical pulp were removed using a BDDJ (Britt. Dynamic Drainage Jar).

# Chemicals

Polyallylamine hydrochloride (PAH, Aldrich) with a molecular weight of 15 kDa and polyacrylic acid (PAA, Aldrich) with a molecular weight of 7 kDa were used to build polyelectrolyte multilayers (PEM) on the fibres. The PAH was received as a powder and the PAA as a 50% aqueous solution. They were dissolved in or diluted with deionised water prior to use. The information regarding the molecular masses of the polymers was provided by the supplier, and the polymers were used as received without further purification.

Sodium metaperiodate from Sigma were used for the oxidation of the fibres.

The hydrochloric acid, sodium hydroxide, sodium chloride and sodium bicarbonate were of analytical grade.

# Fibre modifications

The kraft fibres were modified in three different ways;

- 1) Thermally hornified for 24 hours at 105°C according to an earlier published procedure [18].
- 2) Treated with polyelectrolyte multilayers (PEMs) by sequential adsorption of PAH and PAA [20]. The sheets were tested both with and without further heat treatment at 160°C. A treatment known to induce cross-links in the multilayer structure, and thus increase the tensile strength of the sheets [21].
- 3) Periodate-oxidised to induce cross-links within the final sheet in a 6 g/l fibre suspension with 2.72 g NaIO<sub>4</sub> per gram fibre for two hours according to the procedure described by Larsson *et al.* [8], resulting in an approximate carbonyl content of 0.6 mmol/g.

# Sheet preparation

Restraint-dried sheets with target grammages of 50, 90 and 130 g/m<sup>2</sup> were prepared using tap water in a "Rapid Köthen" equipment (Paper Testing Instruments, Pettenbach, Austria). The sheets were dried at  $93^{\circ}$ C under a reduced pressure of 95 kPa for 15 minutes, except for the 50 g/m<sup>2</sup> sheets which were dried for 10 minutes.

Freely dried sheets were manufactured as described by Larsson and Wågberg [18], by placing a "Rapid Köthen" sheet between two PTFE-wires. After formation, two pairs of holes were made in the sheet to be used to measure the shrinkage when dry [18].

TMP-sheets containing fines were prepared by first building up an equilibrium content of fines in the white water by making and rejecting 10 sheets before making the sheets for use in the study.

All sheets were stored at 23°C and 50% RH until mechanical testing.

# Mechanical testing

After conditioning at 23°C and 50% RH, the sheet grammage was determined and dry tensile tests were performed in accordance with the ISO 1924–3 standard. Sheet thickness and density were evaluated by measuring the structural thickness according to a method developed at Innventia (former STFI-Packforsk) [22].

# Hydroexpansion measurements

The dimensional instability due to hydroexpansion was measured using a newly developed technique better described in [17]. The method measures the change in dimensions with a CCD-camera integrated in a FIBRO DST1210 system (Fibro Systems AB, Stockholm, Sweden) utilizing electronic speckle photography, as a highly atomized, and evenly distributed, water burst is sprayed onto the paper. The spray was generated using an "AutoJet Modular Spraying System" (Spraying Systems Sverige AB, Gävle, Sweden) to control the water and atomization air pressure, in combination with a "SUJ13A" nozzle (Spraying Systems Sverige AB). The amount of water transferred to the paper was controlled by varying the spray time between 0.05 and 0.11 seconds. The measurements were performed in a climate-controlled room (23°C, 60% RH), and the linear in-plane expansion was measured. Since the hand-sheets are isotropic, the expansion was calculated as the arithmetic mean of the expansion in two orthogonal directions.

# Moisture content monitoring

The change in moisture content of the samples upon water transfer was monitored using a FIBRO MCA1410 near-infra-red probe (Fibro Systems AB, Stockholm, Sweden). Since the probe has to be in close proximity to the sample, the moisture content could not be measured simultaneously with the dimensional change and hence the moisture content was determined as a separate measurement. The probe was calibrated by measuring the MCA-signal at different moisture content by changing the relative humidity, followed by dry content determination. The equipment is further described in [17]. The measurements were performed in a climate controlled-room (23°C, 60% RH).

# RESULTS

Table 1 shows the mechanical properties of the sheets used in the study. As shown in earlier studies [8, 18], the different fibre treatments and the two drying modes resulted in very different mechanical properties.

## **Restraint-dried sheets**

Figure 1 shows how sheets with different grammages respond to the same absolute amount of water  $(1.8 \text{ g/m}^2)$ . The figure shows that the sheets with a lower grammage, i.e. subjected to a larger change in moisture content, exhibit not only a greater expansion but also a more rapid expansion. Interestingly, the low grammage sheet also shrinks more rapidly after about 20 seconds. Figure 2 shows the response of sheets of a given grammage (90 g/m<sup>2</sup>) with three different amounts of water. The figure shows the same trend as Figure 1, i.e. a greater change in moisture content leads to a greater expansion and a faster expansion rate.

# Freely dried sheets

The same experiments as in Figure 1 and 2, were performed with freely dried sheets, and the same trend was identified (Figures 3 and 4), but with more pronounced and higher absolute expansion and expansion rate values. The re-shrinkage after 90 seconds was relatively less pronounced when the sheets were dried freely.

	Shrinkage (%)	Grammage (g/m <sup>2</sup> )	Thickness (μm)	Density (kglm <sup>3</sup> )	Tensile strength index (kNmlkg)	Strain at break (%)	Tensile stiffness index (MNmlkg)
Reference $50 \text{ g/m}^2$		50.3 +	89 +	563 +	24.6	1.86 +	4.22
0 0 B.III		0.3	1	2	0.6	0.16	0.07
Reference 90 g/m <sup>2</sup>		89.0 ±	147 ±	604 ±	20.7 ±	1.55 ±	3.81 ±
U		1.4	1	5	0.5	0.16	0.10
Reference $130 \text{ g/m}^2$		131.0 ±	214 ±	612 ±	22.5 ±	2.01 ±	3.90 ±
C		1.6	3	5	0.2	0.11	0.22
Freely dried	5.1	50.2	146	343	6.3	3.56	0.56
50 g/m	0.2	0.3	$\frac{1}{2}$	$\frac{1}{3}$	$0.3^{-1}$	0.44	$0.06^{+$
Freely dried $90 \text{ g/m}^2$	5.4 +	90.0 +	252 +	356 +	6.9 +	4.00	0.69
90 g/m	0.3	2.2	9	$\frac{1}{2}$	0.2	0.20	0.04
Freely dried 130 g/m <sup>2</sup>	5.2 ± 0.2	128.8 ± 2.6	361 ± 5	357 ± 2	6.7 ± 0.3	4.22 ± 0.21	0.58 ± 0.04
TMP 90 g/m <sup>2</sup>		92.3 ± 1.1	170 ± 1	543 ± 4	47.7 ± 1.9	2.25 ± 0.16	4.91 ± 0.36
TMP (no fines) 90 g/m <sup>2</sup>		91.3 ± 1.6	169 ± 2	539 ± 3	42.5 ± 1.8	1.99 ± 0.11	4.81 ± 0.33
Hornified 90 g/m <sup>2</sup>		89.8 ± 1.5	180 ± 2	500 ± 12	9.4 ± 0.5	0.65 ± 0.05	2.69 ± 0.20
Oxidised 90 g/m <sup>2</sup>		93.3 ±	152 ± 2	612 ± 9	41.3 ±	$3.27 \pm 0.09$	4.48 ± 0.27

**Table 1.** Mechanical properties of the studied sheets. All values are given with 95%confidence limits.

	Shrinkage (%)	Grammage (glm <sup>2</sup> )	Thickness (μm)	Density (kglm <sup>3</sup> )	Tensile strength index (kNm/kg)	Strain at break (%)	Tensile stiffness index (MNmlkg)
PEM 90 g/m <sup>2</sup>		89.2 ± 1.6	141 ± 2	634 ± 3	52.1 ± 1.3	5.66 ± 0.13	4.15 ± 0.16
$\frac{\text{PEM} + \text{heat}}{90 \text{ g/m}^2}$		89.4 ± 4.5	141 ± 6	635 ± 8	56.7 ± 0.6	5.73 ± 0.12	4.44 ± 0.22

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#### Table 1. Continued

# Influence of pulp and fines

To study whether the choice of pulp has any significant difference on the hydroexpansion, and to study the influence of fines, 90 g/m<sup>2</sup> sheets were made from both fines-containing TMP and TMP that had been de-crilled. The results are shown in Figure 5 where it is evident that, compared with the TCF-pulp, the expansion of the less hydrophilic [23] mechanical fibres is delayed 0.1-0.2 seconds both with and without fines. With a transferred amount of about 1.8 g/m<sup>2</sup>, there was no significant difference in the maximum expansion in sheets made from any of the pulps, but somewhat surprisingly the TMP-sheets did not expand significantly more when subjected to 30% more water (2.3 g/m<sup>2</sup>), although the expansion of the reference TCF-pulp was considerably increased. The removal of fines resulted in a slight reduction in the maximum expansion, but no significant change in expansion rate.

## Chemically and thermally modified fibres

The reference fibres (TCF) were hornified, treated with PEMs [18] and periodate-oxidised, to induce cross-links, to a carbonyl content of about 0.6 mmol/g [8]. Figure 6 shows that the only treatment that really affected the initial phase of the expansion was a further heat treatment of the PEM-treated fibres, a treatment that made the sheets go from absorbing to non-absorbing when a drop of water was placed on the sheet. These sheets showed a delay in expansion similar to that of the TMP-sheets shown in Figure 5. With regard to the maximum expansion, the hornified fibres, i.e. fibres with a



**Figure 1.** Cumulative hydroexpansion of restraint-dried handsheets of different grammages for a water transfer of 1.8 g/m<sup>2</sup>. (a) Logarithmic time scale up to 90 seconds and (b) linear time scale up to 4.5 seconds. The figures in the plots are the maximum amplitude of change ( $\varepsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half \ e-max}$ ) and the slope ((dɛ/dt)<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are the mean of 12 measurements with 95% confidence limits.



**Figure 2.** Cumulative hydroexpansion of restraint-dried handsheets with a grammage of 90 g/m<sup>2</sup> for different amounts of water. (a) Logarithmic time scale up to 90 seconds and (b) linear time scale up to 4.5 seconds. The figures in the plots are the maximum amplitude of change ( $\varepsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half e-max}$ ) and the slope (( $d\epsilon/dt$ )<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are the mean of 12 measurements with 95% confidence limits.



**Figure 3.** Cumulative hydroexpansion of freely dried handsheets of different grammages for a water transfer of 1.8 g/m<sup>2</sup>. (a) Logarithmic time scale up to 90 seconds and (b) linear time scale up to 4.5 seconds. The figures in the plots are the maximum amplitude of change ( $\varepsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half \ e-max}$ ) and the slope ((dɛ/dt)<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are the mean of 12 measurements with 95% confidence limits.



**Figure 4.** Cumulative hydroexpansion of freely dried handsheets with a grammage of 90 g/m<sup>2</sup> for different amounts of water. (a) Logarithmic time scale up to 90 seconds and (b) linear time scale up to 4.5 seconds. The figures in the plots are the maximum amplitude of change ( $\varepsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half \ \epsilon-max}$ ) and the slope (( $d\epsilon/dt$ )<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are the mean of 12 measurements with 95% confidence limits.



**Figure 5.** Cumulative hydroexpansion of handsheets made of TCF-pulp, TMP and TMP without fines with a grammage of 90 g/m<sup>2</sup> for two different water amounts (a) 1.8 g/m<sup>2</sup> and (b) 2.3 g/m<sup>2</sup>. The figures in the plots are the maximum amplitude of change ( $\varepsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half \ e-max}$ ) and the slope ((dɛ/dt)<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are the mean of 12 measurements with 95% confidence limits.



**Figure 6.** Cumulative hydroexpansion of handsheets made of reference fibres, hornified fibres, fibres treated with 5 layers of PEMs and periodate-oxidised fibres with a grammage of 90 g/m<sup>2</sup> for two different amounts of water (a) 1.8 g/m<sup>2</sup> and (b) 2.3 g/m<sup>2</sup>. The figures in the plots are the maximum amplitude of change ( $\varepsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half \ \epsilon-max}$ ) and the slope (( $d\epsilon/dt$ )<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are the mean of 12 measurements with 95% confidence limits.

reduced degree of fibre-fibre contact, showed a lower expansion than the reference while the PEM-treated sheets, i.e. consisting of fibres with an increased degree of fibre-fibre contact, showed a greater expansion. Interestingly, the PEM-treated sheets that had been subjected to further heat treatment after drying showed an even greater maximum expansion than those that had not been heat-treated, despite having the same amount of adsorbed PEMs.

The parameters indicated in all the figures, i.e. the maximum expansion, the time to reach half maximum expansion and the initial rate of expansion, are summarised in Table 2.

**Table 2.** Summary of all parameters presented in Figures 1–6, i.e. the maximum amplitude of change ( $\epsilon_{max}$ ), the time to reach half the maximum expansion ( $t_{half \epsilon-max}$ ) and the slope (( $d\epsilon/dt$ )<sub>initial</sub>) for the time interval of 0.05–0.55 seconds. All values are given with 95% confidence limits.

	$arepsilon_{max} \ (\%)$			tim	time to half $\varepsilon_{max}$ (s)			$(darepsilon ldt)_{initial} \ (\% ls)$		
	$\frac{1.3}{(glm^2)}$	1.8 (g/m <sup>2</sup> )	2.3 (g/m <sup>2</sup> )	1.3 (g/m <sup>2</sup> )	$\frac{1.8}{(glm^2)}$	2.3 (g/m <sup>2</sup> )	$\frac{1.3}{(glm^2)}$	$\frac{1.8}{(g/m^2)}$	$2.3 \\ (glm^2)$	
Reference 50 g/m <sup>2</sup>	0.044** ± 0.003	0.052 ± 0.004		0.50** ± 0.10	0.50 ± 0.07		0.045** ± 0.005	0.053 ± 0.006		
Reference 90 g/m <sup>2</sup>	± 0.030	$0.035 \\ (0.032^*) \\ \pm \\ 0.002 \\ (0.002^*)$	0.044 ± 0.003	0.43 ± 0.04	$\begin{array}{c} 0.49 \\ (0.58^*) \\ \pm \\ 0.04 \\ (0.09^*) \end{array}$	0.48 ± 0.03	0.034 <u>+</u> 0.005	$\begin{array}{c} 0.037 \\ (0.033^*) \\ \pm \\ 0.003 \\ (0.003^*) \end{array}$	0.050 ± 0.003	
Reference 130 g/m <sup>2</sup>		0.029 ± 0.002	0.034** ± 0.003		0.61 ± 0.04	0.92** ± 0.15		0.029 ± 0.002	0.027** ± 0.004	
Freely dried 50 g/m <sup>2</sup>	0.150** ± 0.009	0.165 ± 0.007		0.74** ± 0.07	0.65 ± 0.05		0.12** ± 0.01	0.150 ± 0.006		
Freely dried 90 g/m <sup>2</sup>	0.090 ± 0.007	0.114 ± 0.007	0.140 ± 0.006	0.88 ± 0.11	0.99 ± 0.11	1.13 ± 0.12	0.07 ± 0.01	0.083 ± 0.010	0.094 ± 0.006	

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	ε <sub>max</sub> (%)			time to half $\varepsilon_{max}$			$(d \epsilon   dt)_{initial} \ (\%   s)$		
	1.3 (glm <sup>2</sup> )	$\frac{1.8}{(glm^2)}$	2.3 (glm <sup>2</sup> )	1.3 (g/m <sup>2</sup> )	1.8 (glm <sup>2</sup> )	2.3 (glm <sup>2</sup> )	1.3 (glm <sup>2</sup> )	$\frac{1.8}{(g/m^2)}$	2.3 (g/m <sup>2</sup> )
Freely dried 130 g/m <sup>2</sup>		0.082 ± 0.005	0.099** ± 0.009		1.04 ± 0.08	1.01** ± 0.08		0.058 ± 0.003	0.072** ± 0.005
TMP 90 g/m <sup>2</sup>		0.034 ± 0.002	0.036 ± 0.002		1.03 ± 0.08	1.04 ± 0.10		0.023 ± 0.003	0.026 ± 0.003
TMP (no fines) 90 g/m <sup>2</sup>		$0.031 \\ \pm \\ 0.001$	$0.032 \pm 0.002$		0.72 ± 0.12	1.00 ± 0.05		$0.026 \pm 0.002$	0.023 ± 0.003
Hornified 90 g/m <sup>2</sup>		0.029 ± 0.001	0.038 ± 0.003		0.46 ± 0.03	0.52 ± 0.05		0.029 ± 0.001	0.042 ± 0.004
Oxidised 90 g/ <sup>2</sup>		0.035 ± 0.003	0.046 ± 0.004		0.46 ± 0.04	0.52 ± 0.04		0.042 ± 0.005	0.052 ± 0.040
PEM 90 g/m <sup>2</sup>		0.042 ± 0.003	$0.056 \pm 0.006$		0.77 ± 0.04	0.87 ± 0.05		$0.033 \\ \pm \\ 0.003$	0.039 ± 0.004
$PEM + heat$ $90 \text{ g/m}^2$		$0.050 \pm 0.004$	$0.076 \pm 0.004$		1.61 ± 0.13	1.59 ± 0.09		0.021 ± 0.002	0.028 ± 0.002

\* second set of measurments, no curve shown

\*\* expansion curve not shown

#### Moisture content analysis

To quantify the amount of absorbed water in the sheets, and to measure how fast the absorbed water evaporates from the paper, a near infra-red (NIR) probe was placed above the paper surface approximately two seconds after the water burst hit the surface. Since the NIR-technique is thickness- and

gradient-dependent, the technique gives accurate absolute values only when the water is evenly distributed. In Figures 7–10 it is of interest to determine the diffusion rate of the water within the sheets during the first few seconds and to identify when equilibrium is reached. For all sheets and water levels studied here, TMP-sheets excepted, equilibrium was reached within 20 seconds. Figures 7, 8, 9 and 10 show the absorption curves that correspond respectively to the expansions shown in Figures 1 and 2, Figures 3 and 4, Figure 5, and Figure 6. In all these figures (Figures 7–10), the moisture content is more or less constant between 15 and 90 seconds, although the corresponding dimensional change curves (Figures 1–6) show a lateral shrinkage of the sheets during this time.

Every sheet type used in the study were calibrated separately to be able to transform the MCA-signal into moisture content, by measuring the signal and sample weight at six different relative humidities, and hence different moisture contents, followed by gravimetric dry matter determination. As shown in Table 3, there were a good linear relationship between the signal and the moisture content during the calibration. The calibration did however seem to overestimate the change in moisture content upon water application, which theoretically is between 1.7 and 1.8 percentage units for a 90 g/m<sup>2</sup> sheet when absorbing a water amount of 1.8 g/m<sup>2</sup>.

# DISCUSSION

## Summary of the earlier hygroexpansion measurements

As mentioned in the introduction, two hygroexpansion studies have recently been carried out in the laboratory of the authors. In the first study [18], handsheets were prepared from untreated, PEM-treated and hornified fibres, since these treatments are known to affect the degree of contact within the fibre-fibre joints [24]. The results of this investigation showed that the degree of contact, as earlier proposed by Uesaka and Qi [25], has no significant influence on the hygroexpansion after the release of dried-in strain when the sheets are dried under restraint, but that it has some effect when the sheets are dried freely. Since the aim of this work is to compare hygro- and hydroexpansion from a printability point of view, it is however more relevant to investigate the hygroexpansion during the first humidity cycle. Figure 11 shows the initial 50-20-45-65-85-change in relative humidity for both restraint-dried and freely dried sheets. No correlation can be seen between the assumed difference in degree of contact between the fibres, achieved with PEM treatment or severe heat treatment, and the hygroexpansion when the sheets were dried under restraint, whereas there was a slight increase in hygroexpansion



**Figure 7.** Estimated moisture content, measured as NIR-probe-voltage, as a function of time for restraint-dried sheets with (a) different grammages and (b) different amounts of water at a constant grammage of 90 g/m<sup>2</sup>. All values are the mean of 12 measurements with 95% confidence limits.



**Figure 8.** Estimated moisture content, measured as NIR-probe-voltage, as a function of time for freely dried sheets with (a) different grammages and (b) different amounts of water at a constant grammage of 90 g/m<sup>2</sup>. All values are the mean of 12 measurements with 95% confidence limits.



Figure 9. Estimated moisture content, measured as NIR-probe-voltage, as a function of time for handsheets made of reference fibres (TCF), TMP both finescontaining and decrilled with a grammage of 90 g/m<sup>2</sup> for two different amounts of water (a)  $1.8 \text{ g/m}^2$  and (b)  $2.3 \text{ g/m}^2$ . All values are the mean of 12 measurements with 95% confidence limits.



**Figure 10.** Estimated moisture content, measured as NIR-probe-voltage, as a function of time for handsheets made of reference fibres, hornified fibres, fibres treated with 5 layers of PEMs and periodate-oxidised fibres with a grammage of 90 g/ m<sup>2</sup> for two different amounts of water (a) 1.8 g/m<sup>2</sup> and (b) 2.3 g/m<sup>2</sup>. All values are the mean of 12 measurements with 95% confidence limits.

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Paper sample	k	т	$r^2$	Start MC	⊿МС	0 – 15 s
	(%lmV)	(%)		(%)	$1.8  g/m^2$	$2.3 \text{ g/m}^2$
Restraint-dried 50 g/m <sup>2</sup>	0.0394	-31.9	0.991	8.5	3.6 ± 0.4	
Restraint-dried 90 g/m <sup>2</sup>	0.0311	-25.1	0.992	8.4	$2.4\pm0.2$	$2.9 \pm 0.2$
Restraint-dried 130 g/m <sup>2</sup>	0.0285	-23.1	0.993	8.3	$1.9 \pm 0.2$	
Freely dried 50 g/m <sup>2</sup>	0.0392	-31.9	0.993	9.2	3.6 ± 0.4	
Freely dried 90 g/m <sup>2</sup>	0.0297	-23.7	0.994	9.2	$2.5\pm0.3$	$3.5 \pm 0.3$
Freely dried 130 g/m <sup>2</sup>	0.0290	-23.5	0.989	9.4	$2.0 \pm 0.2$	
TMP	0.0440	-40.0	0.994	10.2	$3.4 \pm 0.4$	$2.9 \pm 0.2$
TMP (no fines)	0.0408	-36.3	0.992	10.3	$2.7 \pm 0.3$	$4.5 \pm 0.4$
Hornified PEM	0.0307 0.0314	-24.3 -25.4	0.992 0.995	8.6 8.6	$2.3 \pm 0.2$ $2.4 \pm 0.2$	$2.6 \pm 0.3$ $3.0 \pm 0.3$
PEM + heat	0.0314	-25.5	0.993	8.1	$2.5 \pm 0.2$	$3.1 \pm 0.4$
Oxidised	0.0319	-26.0	0.994	8.6	$2.5\pm0.2$	$2.9\pm0.3$

**Table 3.** Linear regression parameters when fitting the moisture content against the MCA-signal (y = kx + m) and the measured change in moisture content 15 seconds after spraying the samples with water at amounts of 1.8 and 2.3 g/m<sup>2</sup>.

coefficient with increasing degree of contact between the fibres when the sheets were dried freely.

In the second study [8], it was shown that both the hygroexpansion and the moisture sorptivity are reduced when the cellulose in the fibre wall is periodate-oxidised into dialdehyde cellulose, which probably forms hemiacetal cross-links during drying. The hygroexpansions showed up to 28% lower amplitude of change when the different papers was subjected to a change in relative humidity from 20 to 85% RH after the dried-in strains had been released. However, the oxidation did not reduce the  $\beta_{MC}$ -value, i.e. the expansion normalised with respect to the actual change in moisture content. On the contrary, for the first cycle between 20 and 85% RH, where there is a



Figure 11. The expansion of the sheets as a function of the moisture content when they were subjected to a 50–20–45–65–85-change in relative humidity for (a) restraint-dried and (b) freely dried sheets. The equations in the figures are the least-mean-square (LMS) fits between 20 and 65% RH for the restraint-dried sheets and all values for the freely dried sheets For the restraint-dried sheets,  $\beta_{MC}$ -values for the change from 65 to 85% RH is given. (Data taken from [18])

simultaneous release of dried-in strain together with the moisture sorption (Figure 12), the hygroexpansion coefficient, measured between 20 and 65% RH, increased steadily with increasing degree of oxidation, showing that the oxidised sheets are even more sensitive to changes in moisture content. It may be that the releasure of dried-in strains is postponed in the case of the oxidised sheets, since the slope is reduced to the same level, a value of 0.040, for the last step from 65 to 85% RH. Nevertheless, there should be a similar or even larger expansion of the sheets from the oxidised fibres when they are subjected to liquid water if the hygroexpansion measurements are to be relevant for evaluating the printability properties of such a paper.

The second study also showed that the oxidation of the fibre wall reduced the sorption rate of water into the sheets during the first adsorption cycle, i.e., as shown in Figure 13, they sorbed less moisture during the same time at the same relative humidity. This is assumed to be an advantage from a storage point of view, where the oxidised sheets are less sensitive to the natural changes in relative humidity, but it is not likely to improve the performance in



**Figure 12.** The expansion as a function of the moisture content when the TCF-pulp and pulps with three different levels of oxidations measured as carbonyl content are subjected to a 50–20–45–65–85-change in relative humidity. The equations in the figures are the LMS-fits between 20 and 65% RH. The beta-value between 65 and 85% RH is 0.040±0.001 for all four curves. (Data taken from [8])



Figure 13. The moisture content of reference TCF-sheets and of sheets of three degrees of periodate-oxidised TCF-pulps on a first exposure to a change in relative humidity from 30 to 90% RH. (Data taken from [8])

a printing press where the amount of water absorbed in the fibre wall probably is constant, unless the water absorption is slower into these sheets due to a denser fibre wall with smaller pores. Such a decrease cannot, however, be seen in Figure 10.

## Hydroexpansion compared with hygroexpansion

# Effect of drying mode

It is a well-known fact that a freely dried sheet has a larger hygroexpansion coefficient than a restraint-dried sheet [26, 27] and, as seen in Figures 1–4, this is also the case for the hydroexpansion. If these figures are compared with Figure 11, it is also, as reported by Larsson *et al.* [17], clearly seen that the hydroexpansion coefficient, here defined as the maximum expansion divided by the change in moisture content (graphically shown in Figure 14a as the slope of the linear fit), is lower by a factor of 2–3 than the hygroexpansion coefficient of a sheet made from the same pulp. There are several possible explanations of this behaviour. Firstly, it could be explained as being due to the lower mobility of liquid water and that the fibre wall is therefore less

delaminated even though the same amount of water is absorbed, i.e. the water is never equally distributed within the whole fibre. Secondly, the absence of expansion could be due to the fact that not all the water is absorbed within the fibre wall, but is instead retained within the capillary structure or at the surface of the fibres. Finally, it could be explained, as proposed by Larsson *et al.* [17], as being due to a re-conformation of the top fibre layers allowing the fibres to take a less extended conformation in the plane of the sheet.

Figure 14a shows that the maximum hydroexpansion increases linearly with increasing change in moisture content for low moisture content changes in freely dried sheets, but that there seems to be a deviation from linearity for higher moisture changes. For restraint-dried sheets, on the other hand, the slope of the linear correlation between maximum hydroexpansion and moisture content was much lower and the linear fit not as good. The time for the expansion to reach half of its maximum shown in Figure 14b, which is a measure of the relative expansion rate, was constant over the studied water application levels. This implies that the maximum expansion and the expansion rate follow the same trend, as is also seen in Figure 14c. The fact that the rate of expansion increases linearly with increasing change in moisture content for the freely dried sheets suggests that there is no accumulation of liquid water between the fibres, i.e. that the water is almost immediately absorbed by the fibres after application, at these low water levels, and that the different local expansions are additive. If the same argument is applicable for restraintdried sheets, the absence of linearity in the expansion rate should be due to the release of dried-in strains, i.e. the same affect as during hygroexpansion measurements. This means that the sorbed water has two effects on sheet properties; a release of dried-in strains and an expansion of the fibre wall when it is adsorbed. Depending on the drying conditions, these different processes will have different relative influences on the overall change in paper dimensions when the paper is exposed to liquid water,

The strongest argument for a fibre rearrangement in the top fibre layers proposed by Larsson *et al.* [17] is the sudden in-plane contraction a short time after water application, following the initial expansion, although the moisture content remains almost constant. Figure 15 shows the dimensional changes in both restraint-dried and freely dried 90 g/m<sup>2</sup> sheets sprayed with 1.8 g/m<sup>2</sup> water and the change in moisture content in a restraint-dried sheet. It is clear that the restraint-dried sheets reach their maximum expansion already after a couple of seconds, whereas the freely dried sheets expand for a somewhat longer time, in this case 10–20 second, while the moisture is evenly distributed within the sheet after 10–20 seconds, as predicted earlier by Ketoja *et al.* [12]. After about 20 seconds, both the restraint-dried and the freely dried sheets start to contract, although the moisture content remain constant up to about



**Figure 14.** The key parameters, i.e. (a) maximum expansion, (b) time to half maximum and (c) initial slope for the TCF handsheets shown in Figures 1–4, as functions of the change in moisture content upon application of water. All values are the mean of 12 measurements with 95% confidence limits. The broken lines indicate LMS-fits forced through the origin.



**Figure 15.** Cumulative hydroexpansion and moisture content as functions of time for restraint-dried and freely dried 90 g/m<sup>2</sup> sheets at a water application level of 1.8 g/ m<sup>2</sup>. The starting MCA-voltage was 1077±3 mV. Up to 90 seconds the expansion values are average values of 18 measurements and moisture content values averages of 12 measurements. After 90 seconds, all the values are averages of 6 measurements. All values are given with 95% confidence limits.

100 seconds. On a microscopic scale however, Sjödahl and Larsson [16] were not able to see this almost immediate shrinkage when a drop of water was allowed to absorb and penetrate in the plane through the studied square millimetre area of a restraint-dried test piece.

During a hygroexpansion measurement, both the expansion and the moisture uptake are rather slow. When subjected to small changes in relative humidity, such as those shown in Figure 16, which lead to a one percentage unit change in moisture content, it takes 20–30 minutes before approaching equilibrium. Liquid water on the other hand is equally distributed after 10–20 seconds, i.e. approximately 50 times faster, in the hydroexpansion cases presented in this study. This, in combination with the one-sided heterogeneous sorption, probably leads to greater stress gradients and steeper moisture gradients within the network [28], which means that the extrapolation of the more homogeneous hygroexpansion measurements is questionable for the evaluation of dimensional stability during printing.



Figure 16. The moisture content and expansion of a restraint-dried sheet as a function of time during step-wise changes in the relative humidity. (Data taken from [8])

## Influence of choice of pulp and the effect of fines

Nanri and Uesaka [29] compared restraint-dried sheets made from different mechanical and chemical pulps and found no major difference in hygroexpansion coefficient between the different pulps. For this reason, the results in Figure 5 are somewhat counter-intuitive due to the absence of further expansion when the moisture content change in the TMP-sheets was increased. One possible explanation is that the stiffer and less collapsed TMP-fibres expand inwards towards the lumen instead of outwards. However, this would mean that the moisture is sorbed differently when it is adsorbed from moist air than when it is absorbed from a liquid phase.

Figure 5 also shows that the onset of absorption of the sprayed water is somewhat slower in the TMP-fibres than in the TCF-fibres. This is due to the fact that the TMP has more lignin and wood extractives, which are relatively hydrophobic on the surface of the fibres. Whether these sheets present the same features in a printing press, where the water is pressed into the structure, must however be further examined in a device more similar to a printing press. However, if the delay is significant even when the water is pressed into the paper, dynamic measurements are the only way to grade printing paper performance, since the expansion measured at equilibrium is probably independent of any initial delay.

Salmén *et al.* [30] showed that the hygorexpansion was higher for finescontaining sheets when the relative humidity was changed from 30 to 60% RH. The effect was seen in both freely dried and restraint-dried sheets, but the effect was less pronounced for restraint-dried sheets. Unfortunately, the moisture content in that study [30] was not monitored to clarify whether this could be explained by a difference in moisture content increase. Nevertheless, the results presented in the present work (Figure 5) show the same trend, i.e. less expansion when using de-crilled TMP-fibres, at both water application levels, even though the expansion values were not significantly different.

## Chemically and thermally modified fibres

Since no improvement in hygroexpansion was achieved in the case of restraint-dried sheets by a chemical change or a combination of chemical and thermal changes in the degree of contact within the fibre joint [18], it is interesting to note that these treatments did have a significant effect on the hydroexpansion of the sheets (Figure 6). By using hornified fibres, which have a reduced degree of contact within the fibre-fibre joint [24], the maximum hydroexpansion was reduced at both levels of water application. At the same time, the adsorption of polyelectrolyte multilayers (PEMs), which is known to increase the molecular contact area in the fibre-fibre joint [24], increased the hydroexpansion. When the PEM-treated fibres were heat-treated after drying, which make the sheet go from absorbing a drop placed on the sheet to a contact angle greater than 90°, the hydroexpansion was even more pronounced. Furthermore, the heat treatment resulted in a delay in the expansion similar to that shown by the TMP-fibres.

Single fibre contact angle measurments on PAH/PAA-treated fibres show a contact angle for water greater than 90° [31], which means that the individual fibres should not adsorb liquid water. Nevertheless, sheets made with PEM-treated fibres absorbed water when water was applied through a highly atomized water spray. Since the individual fibres will ideally not be spontaneously wetted by liquid water, the present result raises the question as to whether capillary water actually influences the dimensions of the sheet. Especially, since the heat-treated sheets, which have higher contact angles for water, have a higher maximum expansion than the non-heat-treated sheets. This also means that the exact mechanism behind the increased hydroexpansion due to the PEM-treatment is not known, and that it is important to clarify this in

future investigations. Based on the earlier discussion, it might be suggested that the applied water leads to two different effects; diffusion and plastization. The water diffuses into the fibre wall causing a sheet expansion while the liquid water also plasticizes the sheet in the surface layers, allowing a movement of the fibres in the external layers. In sheets with an inherent wet strength, caused by an increase in the fibre-fibre joint strength, there will be no plasticization in the surface layers and the fibre movement in the surface layers will be transferred throughout the sheet giving rise to a greater movement compared with the sheet with a lower fibre-fibre joint strength once the water has had time to diffuse into the fibre wall. The spraying of the water onto one side of the sheet means that a relatively larger amount of liquid is applied to the fibres in the external regions of the sheets and that a greater movement of these fibres is provided if the water is able to diffuse into the fibre wall.

No similar difference between hygroexpansion and hydroexpansion was found for sheets made from periodate-oxidised fibres. These sheets showed a reduced sorbtivity, i.e. a reduced adsorption of water when subjected to a given change in relative humidity, and an increased wet-strength [8], but these sheets nevertheless showed the same hydroexpansion behaviour as the nonoxidised reference, i.e. a behaviour anticipated from the high relative humidity region in Figure 12. As was concluded by Larsson *et al.* [8], the reduction in sorption rate is lost when these sheets are exposed to relative humidities close to saturation, i.e. a state where capillary condensation can occur. This is probably due to a partial rupture of the cross-links formed and it is thus possible that this also happens when applying water onto periodate-oxidised paper.

The fact that the oxidised sheets have a much higher wet-strength and that the PEM-treated fibres have much stronger fibre-joints makes it is less likely that the joints would break as proposed by Larsson *et al.* [17]. Nevertheless, all the sheets tested here show the same re-shrinkage after a couple of seconds, and further research is definitely needed to clarify the reason for this behaviour.

# CONCLUSIONS

Measurements with a new hydroexpansion measurement technique, utilizing spray application of water, has been performed on sheets made from kraft fibres treaded in the same way as in two earlier hydroexpansion studies in the authors' laboratory, sheets with different grammage, and sheets made from TMP. The results showed that:

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- Freely dried sheets had, as in hygroexpansion measurements, a significantly greater hydroexpansion than restraint-dried sheets, but the maximum measured hydroexpansion was lower than the hygroexpansion of the corresponding sheet for both drying-modes.
- Sheets made from TCF-pulp and TMP showed the same maximum expansion at a water application level of 1.8 g/m<sup>2</sup>, whereas the TCF-sheets had a greater hydroexpansion at 2.3 g/m<sup>2</sup> indicating that the water is incorporated into the TMP-fibres in a manner that will not increase the outer dimensions of the fibre at higher water uptakes.
- Sheets made from highly hornified fibres, i.e. fibres with a lower degree of fibre-fibre contact, showed a lower maximum hydroexpansion whereas sheets made of fibres with an improved degree of contact showed a greater hydroexpansion. Differences not seen in hydroexpansion measurements.
- Sheets made of fibres that had been cross-linked through periodate oxidation showed an expansion behaviour which was not significantly different from that of the non-oxidised reference, suggesting that this treatment has an effect only when moisture is adsorbed from humid air.
- The earlier proposed hydroexpansion mechanism could not be verified by measurement on sheets with a greater fibre-fibre joint strength or a higher wet-strength.

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# **Transcription of Discussion**

# THE INFLUENCE OF GRAMMAGE, MOISTURE CONTENT, FIBRE FURNISH AND CHEMICAL MODIFICATIONS ON THE HYGRO- AND HYDRO-EXPANSION OF PAPER

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# Jukka Ketoja VTT

Just a couple of short questions about your technique. How do you see that your moistening is even?

## Per Larsson

I used a technique where I added colour to the water before spraying it, and then by image analysis I could see that the water was rather equally distributed. Of course, there are differences from one spraying to another but, if you do several sets of measurements, you will have a rather even distribution. The data is presented in the Nordic Pulp and Paper Research Journal article that will be published in December.

## Jukka Ketoja

Right! How do you keep the paper straight? Do you have some mechanical restraint?

## Discussion

# Per Larsson

Yes, the sample is placed between two Teflon surfaces where there is a hole in the upper one. So you have the sample on one surface, and then you have a second surface with a square hole on top of the first one.

# Jukka Ketoja

Yes. I have found your results very interesting, particularly the long-term behaviour and I am just wondering whether the mechanical stresses could cause it. Concerning the hydro-expansion versus the amount of liquid transferred: I think it is very natural for the hydro-expansion to be a very nonlinear function of the moisture content. As you apply liquid to the surface, the stress in the surface is huge in the beginning, so you will have a lot of inelastic deformations taking place. That is why I think it is quite expected that the hydro-expansion is a very non-linear function of the transferred amount of moisture. This is very different from hygro-expansive behaviour.

# *Kit Dodson* University of Manchester

Could we go back to the slides that you showed of the initial rates of hydroexpansion with the regression lines (figures 14 (c) in the paper in the proceedings, ed.)? If you look at those points, I would say that they go through an initial slope of 0.02 which is perfectly reasonable in a physical sense, you have a shock. But you appear to be forcing the regression to go through zero. Why is that?

# Per Larsson

Yes, it is forced through zero. It is related to the technique, we cannot measure at lower water transfer levels and since it is quite reasonable that we will have a simultaneous release of dried-in strains at higher moisture contents, and since we are working at values up here (i.e. where the dots are), we will sort of reduce the values and make the regression tilt. Also, I would say that intuitively there will be no expansion, if you do not add any water at all.

# Kit Dodson

What you are saying is that the time constant is very high for the initial jump. Either that or the measurement technique is inadequate to detect the moisture expansion of 0.02. But both of those lines go through 0.02 as far as I can see if you are going to do a regression you need to use that.

# Per Larsson

Yes, but if you do not force it though zero you will actually have a really good regression but, for the restraint-dried sheets, you will have a release of driedin strains simultaneously and this will force these points to lower values. Then when you do your regression, you will of course end up with a non-zero intercept. So it is very tricky how to do this.

# Kit Dodson

Do we have another regression, a pair of regression slides for initial rate?

# Per Larsson

Yes, it is the same for them (figure 14(a) in the paper in the proceedings, ed.).

# Kit Dodson

Right! I am just a little worried about bringing statistics into disrepute. Thank you.

# Wolfgang Bauer Graz University of Technology

My first question is regarding the measurement of the moisture content, using an NIR probe. How do you measure the dimensional change and the moisture content at the same time?

# Per Larsson

Actually, they are not measured simultaneously. It is separate measurements: so I do 12 measurements of the expansion, and then I do 12 measurements of the moisture content.

# Discussion

# Wolfgang Bauer

Thank you. My second question refers to your paper. I have seen that in one of the graphs where you showed the hydroexpansion for the different basis weights, the "unexpected drop" in hydro-expansion is largest for the lightest sheet which should have the highest moisture content. Your explanation for this drop was that the water front was wandering down into the sheet, but for the lightest sheet this effect should be most limited. Do you have an explanation for that?

## Per Larsson

Yes, I follow you, but I do not really know. I need to think about it.

# Wolfgang Bauer

Thank you very much for an excellent paper.