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THE EFFECT OF MOISTURE AND MOISTURE GRADIENTS ON THE CALENDERING OF PAPER

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Synopsis Machine calendering at conventional temperatures and line pressures has been compared with calendering at elevated temperatures, and calendering with an induced z-directional gradient in web moisture content. Print uniformity and web strengths are considerably improved by the latter calendering method, while rub off, set off, and print through remain at normal levels.

A moisture gradient is established by calendering the paper web before applied moisture has time to wet the paper's surface. Study of the wetting time shows that newsprint from thermomechanical pulp wets faster than stone groundwood newsprint, that wetting time is decreased when web moisture content is increased, and that pulp drying history is particularly important—papers from bale pulps exhibiting wetting times orders of magnitude greater than those from slush pulps.

The absorption of mineral oil has been measured for papers calendered under different conditions. The studies show that calendering, and moisture gradient calendering in particular, slows the rate of oil absorption—while increasing web moisture content increases the absorption rate.

Introduction

CALENDERING is one of the final process steps in the manufacture of paper and represents the papermaker's last chance at altering the properties of paper before it is passed to the consumer. The closely ground rolls of a machine calender are expected to correct thickness variations in the paper web and impart an aesthetically pleasing finish while leaving the surface and internal structures of the paper web in a state suitable for printing.

Superficially, calendering appears to be a simple process with limited possibilities for optimisation. Alteration of the number of calender nips and the pressures applied was often observed to result in a fixed relationship between the reduction of thickness and of roughness for each grade of paper.⁽¹⁻³⁾ This appeared to be another classic balance in papermaking—there

Under the chairmanship of B. W. Attwood

was a predetermined degree to which the bulk of the paper web had to be permanently compressed in order to achieve an acceptable level of surface roughness.

However, Jackson and Gavelin,⁽⁴⁾ and others since⁽⁵⁻⁹⁾ have shown that machine calendering with sufficiently hot rolls, or with higher paper web moisture contents results in a markedly superior bulk-roughness relationship. Kerekes and Pye⁽⁷⁾ have reported that newsprint calendered with hot rolls (up to 150° C) also shows less reduction in tensile, burst, tear, and stretch at rupture when compared with conventionally calendered newsprint at the same bulk. Further, the author⁽⁹⁾ has shown that heating the calender to 85° C is sufficient to cause a gradient in permanent compression favouring a reduction in the size of surface pores in newsprint and thermomechanical printing paper. This allows the use of lower calendering pressures and results in a combination of a compressive interior structure and a conformable surface of benefit to printability and strength.

Similar manipulation of the bulk/roughness relationship through an increase in moisture content is possible, but limited in practice. It is difficult to produce paper with a high *and* uniform moisture content by conventional methods. The plastic flow of paper in the calender nip is extremely sensitive to moisture content and thus, local areas, or streaks of excessive moisture tend to be crushed (blackened) as the result of calendering.

This limitation is overcome by manufacturing paper at a lower, but uniform moisture content and then applying extra moisture via sweat driers, spray dampeners, or water boxes on the calender. However, penetration of the moisture into the bulk of the paper web as with steam moisturisation has been observed to increase calendering compression and opacity loss.⁽⁴⁾

It may be concluded from the literature that calendering at lower pressures, but with a greater plasticity of the surface of the paper web will result in the optimum balance between bulk and roughness reduction. The increase in plasticity may be confined to the surface by creating a gradient in temperature and/or moisture content which decreases steeply from the surface towards the interior of the paper web at the moment of calendering. For example, such a temperature gradient is produced when calendering with heated rolls at industrial speeds.⁽⁷⁾

The present investigation is devoted to optimising surface plasticity by creating concomitant z-direction gradients in moisture content and temperature at the moment of calendering. A strong moisture gradient has been created by positioning a spray of atomised water close enough to the calender nip that the moisture film created does not have time to wet the surface of the paper web before it is calendered. By heating the calender to 130° C the

moisture film is converted to steam at the moment of calendering thus providing the desired temperature and moisture gradients. The wetting times of the paper and board samples have therefore been measured in order to govern the placement of the spray.

Changes in the surface and interior pore structures of the paper web as the result of gradient calendering can be expected to affect the depth, rate, and uniformity of the absorption of printing ink. Hence, print uniformity, print through, set off, rub off, and ink demand have been measured and are discussed in terms of the pore structures anticipated with conventional, higher temperature, and moisture gradient calendering.

Theory

Influence of temperature and moisture on calendering compression

PLASTIC flow is promoted in response to the stresses applied in the calender nip by increasing the moisture content and temperature of the ingoing paper web. The stress relaxation that results from this plastic flow should tend to offset strength decreases due to the build up of internal stress concentrations or local ruptures of the loadbearing elements in the fibre network. This will be especially the case if the papers are compared at the same thickness or the same contact fraction since lower calendering line loads are required to reach these targets if the deformation of the web is more plastic. Naturally, surface smoothing is also improved by increased plastic flow.

Colley and Peel,⁽⁵⁾ and Jackson and Ekström⁽¹⁰⁾ have shown that the compression of groundwood papers varies similarly, but nonlinearly, with moisture content and temperature. In particular there appears to be a softening temperature in compression⁽¹⁰⁾ which corresponds to the softening temperatures of lignin and hemicelluloses extracted from wood fibres.⁽¹¹⁾ Fig. 1 shows the decrease in softening temperature of dioxane lignin as a function of increasing moisture content.

Since the glass transition temperatures of polymers increase with strain rate (typically 5° C/decade) lignin may soften at a markedly higher temperature at the loading rates imposed during calendering (which are normally several orders of magnitude higher than in the experiments of Jackson and Ekström).

The relaxation time τ for stress in polymers⁽¹³⁾ may be described by:

$$\tau = \tau_0 \exp\left(\frac{U}{K\theta}\right), \qquad . \qquad . \qquad . \qquad (1)$$

where U = activation energy

- K = Boltzmann's constant
- θ = absolute temperature.



Thus, in a general sense moisture may be assumed to decrease the energy of activation and thereby exert a similar effect to temperature on plastic flow.

Indeed, Colley and Peel⁽⁵⁾ have suggested, and Robertson and Haglund,⁽¹⁴⁾ and Baumgarten and Göttsching⁽¹⁵⁾ have confirmed that the following form of master creep relationship is suitable for the description of the permanent compression of paper as the result of calendering:

$$\frac{\Delta t}{t_0} = A(1 + \tanh \mu) \qquad . \qquad . \qquad (2)$$

and

 $\mu = \alpha \log P_{\max} + \beta \log T + \gamma M + \sigma \theta + \varepsilon,$

where $\frac{\Delta t}{t_0}$ = permanent web compression

A, α , β , γ , σ , ε are empirically derived parameters for the type of paper P_{\max} = maximum effective pressure applied in the calender nip

T = dwell time, or time under maximum pressure

M = moisture content of paper

 θ = temperature of paper.

The master creep curve is illustrated in Fig. 2. The permanent compression $\Delta t_r/t_0$ is asymptotic to zero (no compression because the argument μ is too small) and to 2A (no further compression upon increasing μ as the paper has been compressed to its limiting density). The equivalence for creep compression of altering temperature, moisture content, or the logarithm of the time under stress is explicitly expressed in the argument μ .

Colley and Peel⁽⁵⁾ found that for groundwood paper a 1 per cent increase in moisture content was equivalent to an increase of 3° C in increasing per-



Fig. 2—Master creep relationship for the compression of paper

manent compression. Therefore, creating a z-direction moisture gradient by the application of moisture to the surface of paper just before it enters the calender nip should provide a strong gradient in permanent compression.

In summary, plastic flow may be promoted by the application of heat and moisture. The calendering process should therefore be arranged to take advantage of this mechanism for controlling compression. Specifically, confining moisture and heating to the surface of the paper web at the moment of stress application in the calender nip should result in a z-direction gradient in permanent compression and thus surface smoothing without gross structural collapse.

Pore structure and the absorption of printing ink

The board and newsprint samples examined in this study have been printed by the letterpress process using inks which essentially set by the penetration of an oil vehicle into the porous structure of paper. This process is sketched in Fig. 3, where the pore structure has been simplified to a system of cylindrical capillaries for purposes of illustration.

Letterpress solid prints are typically printed with a line pressure of about 40 kN/m. This translates to an effective impression pressure of approximately 2.5 MPa being exerted on the ink film in the press nip. The compression of the paper web in response to this pressure governs the reduction in pore sizes during printing impression which typically lasts about 2 ms at full press speeds. Calculation of the web compression for the case of a compressible groundwood paper based on the creep equations proposed by Colley and Peel⁽⁵⁾ indicate the reduction in pore volume at impression may be as much as 25 per cent.



Fig. 3-A simplified model of ink impression and absorption

Regardless of this web compression, the rate of penetration of ink into the paper web is extremely high at impression when compared to post-impression rates. Lyne and Madsen⁽¹⁶⁾ have reported penetration rates of between 250 and 525 μ m/s at impression for the simulated letterpress printing of newsprint

samples. This may be compared with a rate of $0.1 \,\mu m/s$ for penetration 10 to 100 seconds after the printing moment.

It follows from Poiseuille's law that the depth of penetration of ink into a capillary in the idealised pore system in Fig. 3 immediately after the impression time should be proportional to the radius of the capillary under compression. Since it has been observed that for papers such as newsprint the pigment particles are carried with the oil vehicle during impression⁽¹⁷⁾ the final depth distribution of pigment is largely determined by the distribution of the compressed capillary radii. It also follows from Poiseuille's law that the volume of ink which has penetrated into the web at the end of the impression time is proportional to the third power of the capillary radii under compression. Therefore, the ink remaining on the surface of the idealised paper web after impression is particularly sensitive to the distribution of capillary radii.

Hsu⁽¹⁸⁾ arrived at the following empirical equation for the depth of penetration of ink into paper during printing impression using the theory of Kozeny:

$$l = M \frac{\sqrt{2Pt}}{k\eta} \cdot \left[\frac{1 - \sqrt{P/P'}}{1 - V\sqrt{P/P'}} \right], \qquad (3)$$

where l = the equivalent depth of penetration of ink into the pore if the web were uncompressed

- M = mean hydraulic radius of the pore before compression
- P = effective impression pressure
- P' = pressure required to compress the paper to a voidless solid
- V = void fraction of the uncompressed paper
- $\eta =$ viscosity of the liquid
- t = time

and

$$k=\lambda^2 k_0,$$

where $\lambda =$ tortuosity factor

- = depth of penetration in the pore perpendicular to the paper surface/actual path length of penetration in the pore
- $k_0 =$ Kozeny constant.

The depth of penetration of ink at time t during impression is not only a function of hydraulic radius, but also of the compressibility of the structure (as described by the bracketed term in equation (3)). Thus, calendering alters the rate and depth of ink penetration by reducing pore radii *and* by reducing web compressibility.

Calendering is also likely to affect the rate of relaxation of the web structure following impression, and hence the aspiration of supernatant ink. It is probable that the convex menisci resulting from the viscous resistance of the ink to impression also revert during the relaxation of the web structure to the low contact angle menisci characteristic of oils. However, it is impossible to state the precise contact angle adopted by the ink. The contact angle tends to be decreased by the rough walls of the pores in paper, but tends to be increased by the dynamics of the ink in response to capillary forces.

In the case of capillary suction of ink from the surface of the web the capillary pressure is given by the Kelvin equation:

where γ_{LV} = surface tension between the liquid oil and its saturated vapour

- θ = dynamic contact angle of the advancing oil with the pore surfaces (unknown)
- r =capillary radius,

and substitution into the Poiseuille equation yields:

Therefore, the rate at which ink remaining on the surface after impression is drawn into the web by capillary suction depends strongly on pore sizes in the surface layer of the paper.

The oil vehicle and the pigment particles separate at some point, typically leaving pigment distributed exponentially through the web thickness.⁽¹⁹⁾ The oil continues to be drawn into finer capillaries in the web by differentials in capillary pressure:

$$\Delta P = 2\gamma \cos \theta \left(\frac{1}{r} - \frac{1}{r'}\right), \qquad . \qquad . \qquad . \qquad (6)$$

where r' = radius of the larger pore

r = radius of a smaller pore connected to it.

This implies that the distribution of capillary sizes through the thickness of the web is important in determining the final oil distribution in the web. When oil moves into pores which would otherwise scatter light the opacity of the web decreases. In this way Levlin and Norman⁽²⁰⁾ have shown that oil continues to fill pores larger than the wavelength of light ($\simeq 0.5 \,\mu$ m) for 5 to 15 minutes after printing. Using radioactive tracers they have also shown that the oil continues to migrate into the web for two to three weeks, finally penetrating to approximately three quarters of the web thickness for the newsprint samples studied. This suggests that the final stage of oil migration is due to spreading.

Experimental

Calendering trials

IN order to duplicate as closely as possible the furnish of commercial newsprint, stone groundwood, Defibrator thermomechanical (TMR) pulp, and normal yield sulphite pulp were tapped at 3 per cent consistency from the appropriate mill chests and transported by tank truck to the experimental Fourdrinier paper machine. The following blends were then run in separate five-hour trials:

- G = 80/20 stone groundwood/sulphite
- T = 90/10 TMR/sulphite
- B = 55/35/10 TMR/groundwood/sulphite.

The sample rolls were produced at a grammage of $52 \text{ g/m}^2 \pm 1 \text{ g/m}^2$ and at a moisture content of 10 per cent ± 0.5 per cent. The paper was calendered at 500 m/min in a three-roll machine calender (400, 400, 500 mm roll diameters) having a centre roll heated by an electric element and an upper roll heated with steam. Each blend was calendered with the centre roll at 65° C (M), 100° C (H), and with the application of an atomised water spray with the middle roll at 130° C (W). In all cases the upper roll was held at 65° C. The temperature of the middle roll was measured with a contact thermometer and allowed to fall to the designated temperature during the course of the trial—at which point the sample region was marked.

The configuration of the pilot calender is shown in Fig. 4(a). The web was led over a rubber spreader roll and made half wraps on all three rolls. The atomised water spray (Schlick model 932 using four atmospheres air pressure) could be moved so that the traverse time of the web from the spray to the first nip was kept within the wetting time. The experiments were limited to wire side moisturisation, which is the test side in the results. The volume flow of water to the spray was



Fig. 4-Set-up for moisture gradient calendering

equivalent to 1.5 per cent moisture content in the paper web, but the moisture content of the paper was found to be the same before and after calendering.

A more suitable moisturisation set up is pictured in Fig. 4(b). The moisture added to the web would not have a chance to penetrate into the web during its course through the calender and moisture could be applied to both sides. The ideal situation (if it can be demonstrated that a single hot nip with two-sided moisturisation gives sufficient dwell time) is pictured in Fig. 4(c).

The same configuration as in Fig. 4(a) was used to calender a 350 g/m^2 starch sized multi-ply carton board, having a fully bleached kraft top ply (which was the test surface). The calendering speed was 400 m/min and the water application was 300 ml per meter width/min. The moisture content of the board was 5 per cent before and after calendering at 20° C (C), 100° C (H), and at 130° C with the water spray (W).

Numbers after the symbols are the line pressures used.

It should be noted that for case (W) the surface temperature of the middle roll was measured to be 130° C at the moment of the sampling, but the surface of the paper web was probably limited to 100° C by the supernatant water film.

Absorption study

Bristow⁽²¹⁾ has described an instrument for the measurement of liquid absorption into paper during short time intervals. This is shown schematically in Fig. 5.

Briefly, the paper strip is drawn past a headbox which is dead-weighted so that the pressure exerted on the paper surface by the four walls of the headbox is approximately 0.1 MPa. The headbox is filled with a known amount of liquid which has a time available for absorption determined by the surface speed V and the width of the headbox L. Since the surface speed may be varied the relationship between the amount of liquid transferred and the time available for absorption may be established as in Fig. 6.



Fig. 5-Schematic drawing of Bristow's instrument



The amount of liquid which transfers to the paper web in time t may be described by:

$$K_r + K_a t^{1/2}$$
 (7)

where K_r is the roughness index, or amount of liquid which theoretically would run into the web surface at time zero, and K_a is the absorption coefficient, or slope of the curve. It is apparent from the units for liquid transferred that K_r is effectively the mean depth to which the fluid may penetrate before capillary forces are initiated (i.e. a mean topographic depth from the plane of the headbox opening).

It is also apparent that the curves for water show a measureable wetting time while those for oil do not. Bristow⁽²¹⁾ concluded that the wetting time was a two stage process involving the time for water to run into the surface topography, and the chemical wetting time of the fibre surfaces.

Results and discussion

Absorption study

THE experimental methods of Bristow (described above) were employed to estimate the wetting times of the newsprint and board. The results, shown in Fig. 7, indicate that:

(1) the wetting time of TMR newsprint is shorter than for groundwood newsprint (ca. 40 and 60 ms, respectively).



Fig. 7—The absorption behaviour of uncalendered newsprint from slush (M) and bale (D) pulps

- (2) the absorption coefficient is higher for the TMR than for groundwood newsprint (ca. 180, and 120 ml/m² s^{1/2}, respectively).
- (3) the wetting times of the papers made from bale pulps are approximately 1 second.

The wetting time of the sized board was found to be about 0.2 seconds. The difference in wetting times between papers made from bale pulps and from slush pulps is probably the result of the drying and storage of the bale pulps since the wood species (Norwegian spruce) and pulping processes were essentially the same. The possibility that this behaviour is the result of the spreading of low surface free energy fatty acids during storage of the bale pulps was investigated by extracting these acids with ether. However, as seen in Fig. 7 the Soxhlet extracted paper DTO has not reached the rate of absorption exhibited by the corresponding paper from slush pulp, MTO. This suggests that structural changes during the drying of the bale pulps may be the primary cause of the slower absorption rates.

The influence of moisture content on the wetting time and absorption coefficient is shown in Fig. 8, where it can be seen that increased moisture content tends to shorten the wetting time and increase the absorption co-



Fig. 8-The effect of moisture content on the absorption behaviour of uncalendered newsprint made with TMR pulp in slush (M) and bale (D) form

efficient for papers made with slush pulps. The reverse was observed for the bale pulps, indicating that drying history plays an important role in determining whether the surface voids will expand and increase the rate of absorption or contract with moisturisation and decrease K_a .

The effect of web moisture content on the absorption of mineral oil by calendered newsprint is shown in Fig. 9. Absorption coefficients and roughness indices measured for the newsprint samples appear in Table 1, where it

OF	CALENDE	RED AND	UNCALEN	DERED NE	WSPRINT	
	20%	RH	<i>50%</i>	RH	80%	RH
	Kr	K_a^*	Kr	Ka	K _r	Ka
MG 0 MG 160 MT 0 MT 160	16·0 6·9 16·0 9·0	56·2 31·7 91·6 40·2	16·8 7·1 17·5 9·4	62·3 32·7 93·7 43·2	17·1 9·0 19·2 13·1	64·3 46·9 91·2 62·9

TABLE 1---THE EFFECT OF MOISTURE ON THE ABSORPTION OF MINERAL OIL (VISCOSITY = 0.024 Pa s, SURFACE TENSION = 0.029 N/m) BY TOP SIDE

 K_r = roughness index, ml/m² K_a = absorption coefficient, ml/m² s^{1/2}



Fig. 9—The effect of moisture content on the absorption of oil TABLE 2—OIL ABSORPTION PROPERTIES OF NEWSPRINT (WIRE SIDE) CALENDERED CONVENTIONALLY (M). CALENDERED AT HIGHER

TEMPERATURE (H),	AND CALENDERI	ED WITH A MOIST	FURE GRADIENT (W
			-

	50%	RH
	K _r	K_a^*
MG 160 HG 120 WG 80 MT 160 HT 120 WT 80	11·3 9·5 8·7 14·6 11·8 10·6	51.8 46.5 34.0 53.2 45.3 45.1

* K_r = roughness index, ml/m² K_a = absorption coefficient, ml/m² s^{1/2}

can be seen that moisturisation also leads to an increased absorption coefficient for oil. The concomitant increase in the roughness index K_r indicates the pores have expanded with moisturisation.



oil

Finally, the effect on oil absorption of reduction in surface void sizes as the result of calendering at increasing line loads is illustrated in Fig. 10. There is a disproportionate decrease in K_r with low line loads (MG 80), but the reduction in absorption rate K_a appears to be proportional to the relative increase in the line load applied.

Printability study

Table 3 summarises the printing results for the newsprint samples and Table 4 contains the printing results for the multi-ply board. The board and newsprint samples were letterpress printed in a GFL-laboratory press according to Scan Standard 35. Prints were made at three print densities so

Sample*	Ink demand g/m ²	Set off $0.7 \ s$	Rub off 24 hr	Print through 24 hr	Print uniformity C.V. (%)
MG 80	2.05	0.16	0.13	0.0645	25.6
MG 120	1.90	0.18	0.13	0.0665	20.5
MG 160	1.82	0.21	0.13	0.067	20.6
HG 80	1.85	0.19	0.145	0.0685	20.3
HG 120	1.70	0.24	0.135	0.010	20.1
WG 40	1.87	0.16	0.125	0.068	25.1
WG 80	1.57	0.21	0.125	0.0705	18.6
MT 80	2.27	0.21	0.20	0.062	21.2
MT 120	2.15	0.22	0.20	0.0595	23.6
MT 160	2.00	0.25	0.23	0.0655	21.1
HT 80	2.17	0.23	0.205	0.0645	22.3
HT 120	2.00	0.26	0.215	0.070	21.4
WT 40	2.27	0.18	0.20	0.059	25.4
WT 80	1.97	0.25	0.20	0.068	21.1
MB 80	2.07	0.20	0.17	0.026	23.1
MB 120	1.95	0.21	0.165	0.0575	19.8
MB 160	1.95	0.23	0.18	0.059	21.6
HB 80	1.93	0.22	0.185	0.0635	20.1
HB 120	1.80	$0.\overline{24}$	0.165	0.0655	15.5
WB 40	2.13	0.22	0.175	0.058	19.4
WB 80	1.85	0.24	0.17	0.063	14.8

TABLE 3-PRINTING PROPERTIES OF NEWSPRINT SAMPLES

G = 80/20 stone groundwood/sulphite T = 90/10 TMR sulphite $M = 65^{\circ} C$ Numbers = Line Pressure, kN/m

 $H = 100^{\circ} C$ B = 55/35/10 TMR/groundwood/sulphite W = water spray

that the printing properties could be interpolated at print densities of 0.85 and 1.15 for the newsprint and board, respectively. The ink used for the board had a viscosity of 15 Pas, a pigment content of 17 per cent and a binder content of 6 per cent; while the viscosity and pigment content of the news ink were 2.9 Pa s and 14 per cent, respectively.

Print density, rub off, set off, and print through were measured with an Elrepho photometer and reported according to proposed Scan Standard P 53:2 X.

Physical properties including optical contact fraction and bulk are listed in Table 4 for the board samples, and are listed in Table 5 for the newsprint samples. Optical contact fraction was measured using a dynamic instrument developed by the author.⁽²²⁾

An evaluation of ink demand, rub off, set off, print through, and print uniformity of samples M 160, H 120, and W 80 follows as these samples are the most representative of optimum conditions for conventional, high temperature, and moisture gradient calendering, respectively.

		TABLE 4PR	INTING ANI	PHYSICAI	PROPERT	IES OF MULTI-F	LY BOARD	
Sample*	Contact fraction	Parker print surf 10 kg (µm)	Hunter gloss 75°	Bulk m ³ /kg 10 ⁻⁵	Set off 0.35 s	Rub off 25 min/6 hr	Ink demand g/m ²	Print uniformity C.V. (%)
						print density =	1.15	\leftarrow print density = 1.05 \rightarrow
Uncal.	0.156	6.88	6-8	141	0-48	0-089/0-078	4.85	•
Mill	0.192	6-04	7-1	131	0.36	0-095/0-053	4.45	8-7
W 40	0.193	6.50	7.6	140	0.56	0-070/0-056	4-40	9.3
W 80	0.263	5.79	9.2	135	0.64	0-081/0-051	4·20	8-4
H 80	0.183	6.87	7.0	139	0-34	0.089/0.044	4.55	10-5
080	0.183	6.62	2.0	139	0.53	0-068/0-056	4.65	13-2
Č 120	0.194	6.04	L·L	134	0-44	0-084/0-063	4.50	11-2
			* 350 g/ W = 1	m ² multi-ply water spray—	carton board 2 nips			
			ECH	, ; ;500 ;500	2 nips 2 nips	,		
			amili = Mumb	Brush calenous = Line provide the line calenous ers = Line provide the l	dering + 4 nip cessure, kN/m	mach. cal.		

SAMPLES	
NEWSPRINT	
OF	
PROPERTIES	
5—PHYSICAL	
TABLE	

Sample*	Contact fraction	Bendsten roughness (ml/min)	Bulk m ^{3/kg} 10 ⁻⁵	Extensional stiffness (N/mm)	In-plane tear (mJ)	Stretch at rupture (%)	Tensile index (Nm/g)	Light Scat. coef. (m ² /kg)	Hunter gloss (75°)
					$\sqrt{MD \times 0}$				
MG 0 MG 80	0·144 0·162	1530 240	249 171	218 190	369 281	1.56 1.41	31-0 27-7	56-5 57-0	4-2 9-2 2-2
MG 120 MG 160	0-181 0-189	165 155	159 154	195 195	242 242	1·20 1·06	25·2 18·1	55-0 54-0	11:0 11:8
HG 80 HG 120	0-200 0-201	150 100	154 140	191 186	277 261	1·41 1·23	27·2 23·5	54·5 52·0	14·3 17·0
WG 40 WG 80	0.189 0.222	280 130	157	190 191	<u>310</u> 307	1.52 1.26	29-3 25-8	54-0 52-0	14-0 19-4
MT 0	0.144	1670	297	197	414	1.66	31.3	52.0	4.7
MT 80	0.159	295	193	177	296	1.44	26.8	52.0	
MT 160	0.167	205	173	0/1	183	86-0	19-7	20-0	10.8 10.8
HT 80 HT 120	0-170 0-178	185 145	177 161	164 159	302 239	1-47 1-27	26-8 23-0	50-0 48-5	13-8 15-9
WT 40	0.168	305	196	<u>6</u>	343	1.67	30-0	49.5	14.0
W1.80	0-189	C71	104	7/1	704	06.1	1.07	6.14	1/-0
MB 0	0.153	1530	269	211	341	1.59	30-1 20-1	55.5	4.8
MB 80 MB 120	0.171	245 185	183	183	258	1.47	21.8	20.2 5.55	8·1 11·3
MB 160	0.187	135	165	178	182	1.22	21.9	55.0	11.9
HB 80	0.182	150	166	169	262	1.36	25.1	53-5	14.4
HB 120	0.199	100	152	1/3	214	1.58	23:3	53-0	1.51
WB 80	0.208	105	155	180	266	1.26	25.8	50.5	18.4
	ייש קרש *	80/20 stone grou 90/10 TMR/sulp 55/35/10 TMR/g	ndwood/sulp hite roundwood/s	hite M ulphite W	= 65° C = 100° C = water spray	Numbers = $Lint$ 0' = Unc	e Pressure, kN/m alendered	_	

Ink demand

THE ink demand to reach 0.85 print density was found to have a -0.89 correlation coefficient with contact fraction for the samples listed in Table 3. This indicates the importance of the surface conformability of paper for uniform ink transfer.

Rub off

THE rubbing medium was cotton cloth in the newsprint case, and gravure paper in the board case. The instruments used were respectively an Andersson and Sörensen, and a GFL rub off tester. Rub off was measured at the time interval after printing shown in the tables.

Calendering adversely affects rub off since the reduction in surface pore sizes results in a lower mean penetration depth for the pigment particles.^(23, 24) Rub off is somewhat improved by moisture gradient calendering, but worsened by higher temperature calendering. This may be attributed to the balance between reduction in ink demand and reduction in surface void sizes.

Set off

SET off on kromekote paper was measured using the same line pressure as during printing and is reported for the time interval after the printing moment shown in the tables.

The set off on board was noticeably worse for the moisture gradient calendering technique. This may be attributed to the considerable reduction in surface void sizes slowing the rate of ink penetration during and after impression. The reduction in ink demand has apparently not compensated for this effect.

Set off was approximately the same for the conventional, moisture gradient, and higher temperature calendered newsprint samples, with a possible trend towards higher values in the latter case. The absorption coefficient K_a for mineral oil (of lower viscosity than the news ink used) is shown for various newsprint samples in Table 2. The ink demand divided by the absorption coefficient appears to be a good indicator for set off—at least for each furnish separately.

Print through

PRINT through is affected by the penetration of pigment on impression, but is mainly a function of the movement of the oil vehicle into pores within the paper web which would otherwise scatter light.^(19, 20) Therefore, it would be expected that paper having finer pores in the surface layer of the web would exhibit lower print through as, according to equation (6), the oil migration would tend to be confined to the surface layer by the higher capillary suction forces.

However, the print through of the higher temperature and moisture gradient calendered samples is slightly greater than for those calendered conventionally. This is in spite of the fact that the ink demand was lower for the former samples. The explanation of this apparent contradiction is that the web is compressed during printing and when the surface void size distribution and contact fraction are measured, but is uncompressed during the long term oil migration which is of importance for print through.

This demonstrates the importance of web compressibility in determining the contact fraction. Paper calendered with a gradient in permanent compression achieves the same contact fraction at lower calendering line pressures, thereby preserving web bulk and compressibility. This is illustrated in Fig. 11, where it is seen that the contact fraction is higher at a given bulk for the higher temperature and moisture gradient calendered samples. Greater web bulk may also reduce print through by effectively placing the pigment layer further from the unprinted side of the web.

Print uniformity

PRINT uniformity has been defined in this context as the coefficient of variation of the diffuse reflectance from the letterpress solid prints. Essentially,



Fig. 11—The relationship between contact fraction and web bulk for newsprint calendered conventionally (M), calendered at 100° C (H), and calendered with a moisture spray (W) print uniformity is a measure of the uniformity of the pigment distribution—a lower coefficient of variation indicating a more uniform print.

It can be seen in Tables 3 and 4 that the coefficient of variation is lower for moisture gradient calendering than for higher temperature calendering, and that both exhibit better print uniformity values than does conventional calendering. This is primarily explained by the higher contact fraction observed with the former methods. However, the correlation coefficient between the contact fractions and the printability values for all of the samples listed in Table 3 was only -0.65.

This suggests that another factor such as uneven ink absorption may play a role in print uniformity. Madsen and Aneliunas⁽²⁵⁾ have observed that light and heavy grammage spots in newsprint webs have different print characteristics after calendering. Thus, the high line loads imposed with conventional calendering may aggravate these differences by severely compressing the heavy spots.

Strength results

Calendering at lower temperatures requires the application of high line pressures in order to achieve satisfactory surface smoothness. On examination



Fig. 12—The balance between in-plane tear strength and ink demand for newsprint calendered conventionally (M), calendered at 100° C (H), and calendered with a moisture spray (W)

of Table 5 it is seen that this results in a considerable decrease in stretch at rupture, in-plane tear and tensile strength. At the same time the extensional stiffness of the web is decreased indicating that local failures or redistribution of loadbearing segments are created in the fibre network as the result of the high line pressures. By comparison, higher temperature and moisture gradient calendering achieves the same degree of surface conformity at lower line pressure thereby retaining web strengths. Plasticisation of the web surface allows the polymer constituents of paper to flow locally which promotes a smoothing without collapse of the network structure.

The in-plane tear strength⁽²⁶⁾ and tensile index of newsprint may be taken as indicators of the potential runnability of newsprint webs in a printing press. Since calendering decreases these strengths while improving printability the balance between these effects is an important criterion for judging calendering methods.

As seen in Fig. 12 the balance between in-plane tear and ink demand is improved in going from conventional to higher temperature calendering, and in going from higher temperature to moisture gradient calendering.

Similarly, in Fig. 13 the balance between tensile index and print uniformity is improved in the same sequence.

General

It is a well-known phenomenon in calender operation that increased roll temperatures result in a greater development of gloss. Further, moisture may be added to the web by spray dampeners, or water boxes in order to increase gloss. The usual explanation given for the temperature/moisture dependence of gloss is that web plasticisation allows a greater orientation of the surface topography to the plane of the paper web. However, it is clear from Table 5 that the gloss increase with higher temperature and moisture gradient calendering is greater than the development of surface contact. This suggests that a component of gloss comes from microscale smoothing of less importance to the overall surface contact.

It is interesting in this regard to consider the effect of heating on the microstructure of wood fibres. Stone and Scallan⁽²⁷⁾ used nitrogen absorption techniques to study the change in surface area of dry wood fibres, dioxane lignin, xylan, and pure cellulose when heated to 80° C or above. It was found that there was a progressive loss of surface area in spruce groundwood as the temperature was increased above 80° C, reaching 90 per cent loss at 240° C (the highest temperature studied). Dioxane lignin experienced an almost vertical drop to 10 per cent of its unheated surface area at its softening



Fig. 13—The balance between tensile index and print uniformity for newsprint calendered conventionally (M), calendered at 100° C (H), and calendered with a moisture spray (W)

temperature ($\simeq 140^{\circ}$ C when dry). The same drop in surface area occurred with xylan, but somewhat more gradually over a range from 80° to 240° C.

Stone and Scallan interpreted this behaviour as the continuous collapse of the aerogel formed by the amorphous polymers in paper. If these effects occur as the result of calendering at higher temperature and moisture contents then the adsorption of printing ink vehicles onto the surfaces of fibres and fibre fragments should be significantly affected and closure of the grosser pores could help to explain the increased gloss and slight drop in scattering coefficient.

Finally, a crude estimation of the compression gradient can be made if equation (2) with parameters for groundwood paper⁽⁵⁾ is used to compare the predicted web compression with the observed compression. The effective penetration depth of the plasticisation is calculated to be between 25 and 35 per cent of the web thickness in the case of the moisture gradient technique. Doubtless, the penetration depth could be substantially reduced if a calendering configuration such as shown in Fig. 4 (c) were used.

It should be remembered when applying the moisture gradient technique that papers having moisture sensitive fillers and coatings are not suited to this method as the calender rolls will tend to coat.

Conclusions

NEWSPRINT and a multi-ply board were calendered in a three-roll pilot calender using:

conventional roll temperatures and line pressures

higher roll temperatures

higher roll temperatures and the application of moisture immediately before the calender nip.

The balance between the printing and strength properties of newsprint was improved in the above order.

Similarly the contact fraction, ink demand, and print uniformity of the multi-ply board were improved with the moisture gradient approach, but set off and rub off were worsened.

The wetting time of mechanical printing papers was measured and found to be very dependent on drying history and to be greater for groundwood than for TMR newsprint.

The rate of absorption of oil by newsprint was measured and found to decrease with calendering, to increase with web moisture content, and to be greater for TMR newsprint than for stone groundwood newsprint.

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664

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Transcription of Discussion

Discussion

Mr J. W. Swanson With regard to the wettability experiments and the solvent extraction, I would like to point out a complication, namely, that the rapid wettability will depend on several factors such as the chain length of the fatty acids that exist on the surface, the length of time they have been there, and the degrees of physical and chemical adsorption. The solvent extraction will remove only the physically adsorbed molecules. Frequently an aged paper that is slowly wettable will become water repellent after it has been solvent extracted. We believe that this is due to the removal of the physically adsorbed molecules, which leave the chemically adsorbed molecules that cannot molecularly overturn.

Lyne That is an interesting point. If the same thing can be said of a never dried, or slush pulp, then there is an interesting implication. If the resin acids cause a great deal of this wetting time then of course they are present in the original pulp and are simply coming out and spreading with time. In other words, I pose the question, what is wetting time? The minimum value should be observed at manufacture of mechanical pulps. But there must also be a component due to cellulose in bleached pulps.

J. E. Luce I would like to comment on the differences between the absorptivity of slush and baled pulp. Some years ago we had occasion to look into these differences for many properties. We did this by comparing papers made from never-dried pulps, pulps which had been dried conventionally and pulps which had been dried by solvent-exchange. Generally we saw exactly the same things you did. We could make absorptivity decrease by drying in a conventional way or we could retain the absorptivity by solvent-exchange drying, then decrease it by subsequent conventional drying. What this means is that we are looking not at fatty acid effect in these bleached pulps, but at some inherent property of the cellulose, probably pore size.

Lyne Thank you. That is the conclusion I reached also.

Under the chairmanship of B. W. Attwood

Discussion

Dr G. Hunger I wish to congratulate Dr Lyne on this very fine paper. His literature references already show some similar work done in the area of moisture and heat application to calendering operations. There have been some activities in these areas during the last 10 to 15 years reported (and maybe even more unreported). Unfortunately the technological translation of these laboratory works into large and continuously running production machines has shown almost unsurmountable hurdles. In practice the hurdles are immense, first of all it is almost impossible to maintain such uniform moisture profiles unless you rewet very uniformly. There are also problems with temperature profiles and finding for example, heat resistant roll materials. As to the time lag of the previously dried pulps to react to water, I suggest that this is exactly the phenomenon described by Jayme many years ago, as the 'hornification of cellulose', which we may describe today as fully hydrogen-bonded cellulosic structures, the unbonding of which takes an appreciable amount of time.

Lyne I definitely want to attack your first point and that is that we are not talking about adding moisture to a sheet of paper in a conventional sense. As it says in the beginning of the preprint it is well appreciated that it is difficult to obtain a uniform and high moisture content in a sheet of paper in practice. What we are talking about is having a conventional sheet of paper at conventional moisture contents and then spraying the moisture on the surface. I don't think that that has been reported in the literature before. I think that the idea of spraying atomised moisture onto a sheet of paper would perhaps get round some of the problems of uniformity in smoothness and gloss. It is conceivable that more moisture could be sprayed on in those areas that need it as a form of regulation technique, so I don't believe that the hurdle is so high.

Mr J. A. Bristow I should like to say one or two words about wetting and wetting times. Dr Lyne, in his presentation, has included a figure from an earlier publication of mine which is now 10 years old where I mentioned and showed the existence of wetting times with water on paper as opposed to the interaction of oils and such liquids. I wasn't the first person to introduce the term 'wetting time' but I was, I think, the first person who found a wetting time directly rather than by extrapolation. I have always myself, been somewhat concerned about the use of the term 'wetting item' and I feel that we must be careful about finding out what it is. If one considers wettability as a thermodynamic type of behaviour one knows that one can talk about the wettability of a surface. When one talks about 'highly' wettable or 'slightly' wettable surfaces, one is not entirely sure what 'highly' or 'slightly' means. If one introduces time and begins to talk of surfaces which are 'rapidly' wettable or 'slowly' wettable, one finds oneself in thermodynamic deep water. It is, however, very important to realise in papermaking terms that when we say wetting time something happens here. The work I did was related to the glueability of corrugated board. The phenomenon has also been shown to be important for calendering, litho offset printing, etc. I think that Dr Hoyland's work is very important here and I hope it can be continued to cover sized papers.

Lyne I think that wetting is really a very important fibre water interaction. Perhaps it is *the* fibre water interaction, so I would like to ask one or two chemists in the audience: What is wetting time?

Mr D. M. Wilkinson I would like to point out that in my experience with mechanical pulp and in particular dry crepe waddings, wetting time can change drastically with age. New wadding has, if you will excuse the crude method, a sinking time in water of a few seconds but in a few months it will float on the water surface for days. This can be correlated with the pH of the extract. The pulp becomes more acid during that time. We can combat it by well-known techniques, such as running with an alkaline backwater, removal of calcium and magnesium ions by the use of EDTA, or by adding some wetting agents.

Dr J. D. Peel Dr Lyne's paper confirms that a moisture content gradient is important, but quantitative information on the effects of moisture content and gradient is quite sparse. There is a paper by Ginman of the Finnish Pulp and Paper Research Institute which was given at UMIST Calendering Symposium in 1975, describing the effects of different methods of wetting and levels of moisturising on the relationship between smoothness and bulk. Dr Tarnawski from Lodz worked with me later, at UMIST, on some experiments in which we deliberately varied the moisture treatment of the surface and the moisture level at the beginning. It is very difficult to present the complicated relations obtained and the results are not yet published.

Lyne If I may add to that, it helps if you can measure and take advantage of the wetting time. The spray should be placed close enough to the nip so that you can guarantee that the water is sitting on the surface of paper when it enters the hot nip—this is the new twist here.

Discussion

Dr O. J. Walker Dr Lyne's work has some very interesting applications in understanding what may be happening with a sweat drier.

Lyne I think I alluded to sweat driers in the beginning of my paper as a way of adding moisture to a sheet of paper.

Walker Not only that, but if I interpreted your absorption rate curves, then a sweat drier will make the paper less uniform in moisture content rather than more, which is contrary to what I have always believed, but I am convinced now.