A new retention aid for the production of SC printing grades: pilot paper machine results

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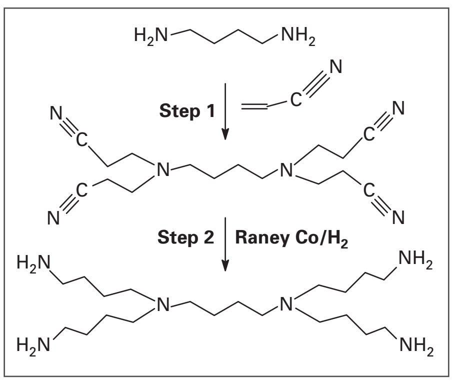
ABSTRACT: A pilot paper machine trial has demonstrated the efficiency of a new dendrimeric retention aid in the production of supercalendered (SC-A) paper. The new additive was particularly effective in retaining fines and clay particles in the sheet. The first-pass retention increased by 6%, even at the addition rate of just 0.5 kg/metric ton . The highest gains in first-pass ash retention resulted in tests of the new additive with a flocculant. We found that the new retention additive did not impair sheet formation and that the sheet's physical properties were improved. We attributed the high efficiency of polymers at the low dosage rate to the high cationic charge available for charge neutralization of anionic dissolved and colloidal materials. Because of its high cationic charge, the dendrimer additive can significantly improve runnability in closed system applications.

Application: Mills may soon benefit from a new retention aid that demonstrated excellent results in pilot trials.

Recent research at Paprican has focused on system closure and methods of improving retention and drainage in closed systems [1–4]. Increased interest in water closure is motivated by both economic and legislative reasons. An increasing number of mills are planning to close their water systems. Recent legislation by provincial and federal governments has resulted in increased costs of water use and discharge. As a result, closing up a water system is an attractive economic choice for many mills.

Closing up mill water systems creates many new problems for papermakers [2–4]. Closed systems concentrate colloidal and dissolved detrimental substances and, as a result, retention, drainage, and paper strength usually decrease. At high concentrations, the detrimental substances interfere with the functioning of wet-end additives including retention aids, wet strength agents, cationic starch, size, and cationic dyes. These factors, taken together, could affect paper machine runnability.

The performance of retention and drainage aids in increasingly closed systems is a concern to the paper industry. In recent papers [2–4], we investigated the performance of retention aid systems at three levels of usage of fresh process water for hydrosulfite and peroxide-bleached thermomechanical pulp printing grades. This led to a better understanding of the chemistry that is most effective in closing up these TMP systems. In the present study, the research was extended with the development of a new polymer retention aid for system closure. It was reported that amine-terminated dendrimeric polymers could be extremely efficient at improving retention and drainage [5–7]. This paper presents the results of a pilot paper machine trial with this new polymer retention aid to verify at pilot scale results that were obtained in laboratory testing.



1. Synthesis pathway and structure of 1,4-diaminobutane-propylamine, DAB(PA)4, beginning with 1,4-diaminobutane.

The new polymer chemistry

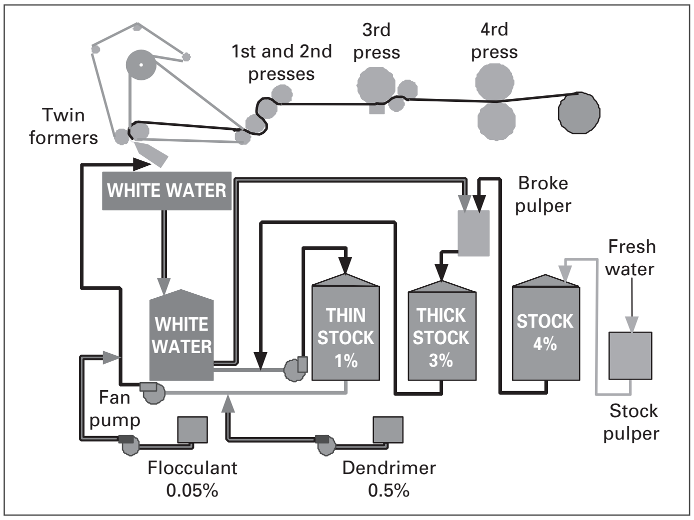
Dendrimers are a new class of macromolecules with a hyperbranched structure. The term dendrimer or branched star polymer is understood to embrace highly-branched macromolecules that emanate from a central core and are synthesized through a stepwise, repetitive reaction sequence. Dendrimeric macromolecules are often referred to as "starburst" polymers. Their structure is well defined in terms of chemical composition and three-dimensional configuration. They are synthesized in a stepwise manner, which provides unique control over chemical and physical properties. This control allows for the development of products tailored to specific applications. For example, the end groups of the dendrimers are accessible for numerous types of modification reactions. (See references [7–9] for further information about dendrimers.)

The hyperbranched dendrimeric structure of amine-based dendrimers, such as DAB(PA)$_4$, contains primary and tertiary amines (at various ratios ranging from 0% to 100%). In aqueous acidic solution, dendrimers behave like polyelectrolytes. The primary, secondary, and tertiary amines become protonated, thereby developing a positive charge [9–11].

The dendrimer used in this study—1,4-diaminobutane-propylamine, DAB(PA)$_4$—has a molecular weight of 300. Its cationic charge density at pH 5 was 18.2 meq/g. **Figure 1** shows the structure of the dendrimer. For comparative purposes, the charges of a typical poly(DADMAC) or branched polyethyleneimine at pH 5 are approximately 5.5 meq/g net and 5.9 meq/g net.

EXPERIMENTAL

Pilot paper machine. The pilot machine had a trim of 330 mm and consisted of a twin-former, a three roll inclined press followed by an extended nip press, a fourth press, and a reel for collection of pressed wet paper (**Fig. 2**). Its operating speed



2. Diagram of Paprican's pilot paper machine showing chemical addition points.

was 600 m/min. The first two press nips were loaded to 45 kN/m and 90 kN/m, while the third and fourth press nips were operated at 300 kN/m and 100 kN/m, respectively. The mass flow rate of fiber through the headbox was 748 kg/h for a targeted sheet dry basis weight of 45 g/m^2. The paper machine had no dryers; we cut the wet paper samples from the reel and either used them to determine the wet-web properties or to dry between blotters on a rotary photographic dryer for subsequent evaluation of dry paper.

We used a peroxide-bleached super calendered (SC-A) grade paper for the pilot machine trial. It was composed of virgin fiber [60% peroxide brightened thermomechanical pulp (TMP), 7% hydrosulfite brightened TMP, 8% semi-bleached kraft] and broke (25%).

At the beginning of the trial, we reslushed 1 metric ton of paper and diluted it to about 3% consistency. To build-up white water rich in anionic dissolved and colloidal materials and fines, paper was made on the paper machine from all the stock. We discarded the formed paper, but stored the whitewater. We reslushed and stored 1 metric ton of new paper in the thick stock tank at a consistency of 2.8%. The ash level in the clay-filled thick stock was 11.7%. We produced headbox stock for the pilot paper machine trial by diluting the reslushed thick stock with the white water produced earlier. The headbox stock freeness was 55 mL CSF. It had a consistency of 0.85% and a pH of 5.1.

Polymers. Figure 2 shows the pilot machine stock supply and dosing points. We ran the pilot machine trial in two modes: by dosing the dendrimer only or by dosing a cationic flocculant and the dendrimer as a dual polymer system. A 0.5% dendrimer solution was metered into the pulp suspension at the fan pump inlet to obtain good mixing. A polyacrylamide solution was metered into the furnish after the fan pump. We maintained a headbox stock temperature of 50°C. The time for the pulp to travel from the polyacrylamide or dendrimer injection points to the headbox was estimated to be 5 and 7 seconds, respectively. We monitored the stock pH at 4 min. intervals and kept it constant at 5.1 by slow addition of 10% sulfuric acid into the returning white water flow.

The polyacrylamide flocculant (Polyplus 713) was supplied in powder form by BetzDearborn of Jacksonville, Florida, USA.

PROPERTY	TEST METHOD	UNIT
Breaking length	CPPA→PAPTAC Standard D.34	km
Burst index	CPPA→PAPTAC Standard D.8	kPa m^2/g
Caliper	CPPA→PAPTAC Standard D.5H	µm
Cationic demand	reference [2]	meq/L
Scott bond	TAPPI UM 403	J/m^2
Consistency	CPPA→PAPTAC D.16	%
Formation Index	reference (12,13)	—
FPR	TAPPI T-269	%
Grammage	CPPA→PAPTAC Standard D.3	g/m^2
Gurley air	CPPA→PAPTAC Standard D.14	s/100 mL
Kajaani fiber length	TAPPI T-271 om-98	%
Sheet ash and FPAR	CPPA→PAPTAC G.11	%
Sheet consistency	CPPA→PAPTAC Standard D.12	%
Stretch	CPPA→PAPTAC Standard D.7	%
TEA index	CPPA→PAPTAC Standard D.34	mJ/g
Tear index	CPPA→PAPTAC Standard D.9	mN m^2/g
Tensile index	CPPA→PAPTAC Standard D.6	Nm/g
Turbidity	TAPPI T-620	NTU

I. Standard Test Methods.

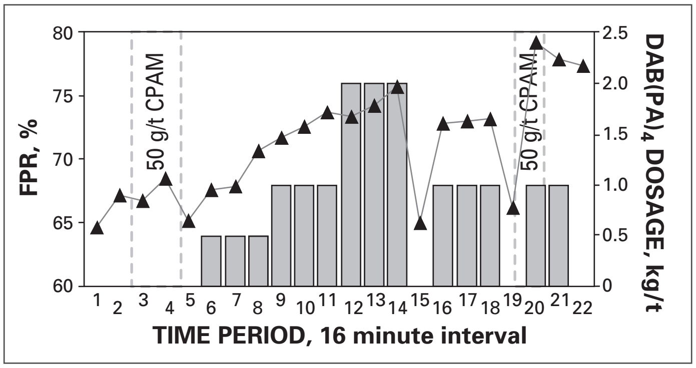
We prepared 200 L of 0.05% flocculant solution by dispersing the polymer in water at room temperature and agitating the solution until full dilution. Polyplus 713 served as the dual retention aid polymer flocculant with the dendrimer because it was very responsive to dendrimer addition in a pulp suspension in a previous study [7].

The dendrimer polymer, DAB(PA)$_4$, was obtained in liquid form from DSM (The Netherlands). We diluted the 100% liquid with tap water, under constant agitation, to a concentration of 0.5%, and prepared 750 L of solution at room temperature. The final pH of the polymer solution was 9.

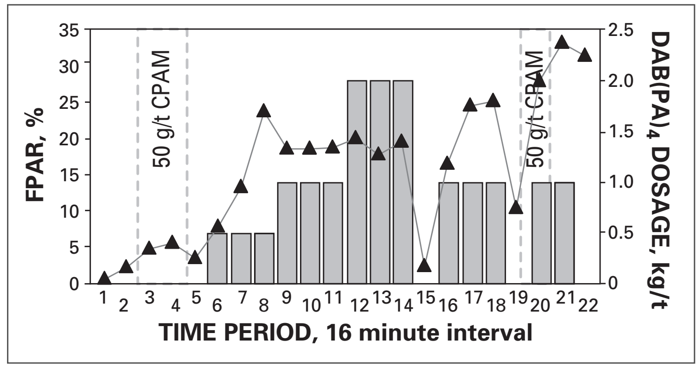
Experimental procedure. The pilot plant trial consisted of 22 intervals of 16 min each. During each period, polymers were dosed as shown in **Figs. 3 and 4**. Over the course of the trial, the flow of pulp to the headbox was constant and there were no adjustments made to give constant basis weight. Machine headbox and white water were sampled at 4 min. intervals to monitor pH, first pass retention (FPR), first pass ash retention (FPAR), white water and headbox consistencies, cationic demand, turbidity, and fines content as a function of polymer dosage. Wet paper samples were collected after the couch roll, after the second press, and from the reel every 15 min. to measure sheet consistencies, sheet ash level, and dry sheet properties such as formation index, grammage, caliper, burst index, tear index, tensile index, TEA index, breaking length, stretch, elastic modulus, Scott bond, and Gurley air resistance. **Table I** lists the test methods used to measure the stock and sheet properties. Sampling began at t = 0 min and the trial lasted 6 h. For clarity the polymer dosage schemes are shown only in Figs. 3 and 4.

RESULTS AND DISCUSSION

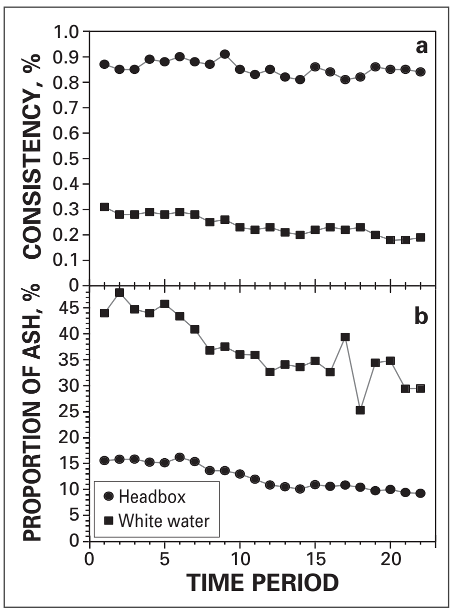
Wet-End Results. Figures 3 and 4 show that the addition of the new retention aid increased the first pass retention (FPR) from 65% to 80% and the first pass ash retention (FPAR) from 0.5% to more than 33%. Comparison of retention to the dendrimer dosing scheme indicates that the downward spikes coincided with



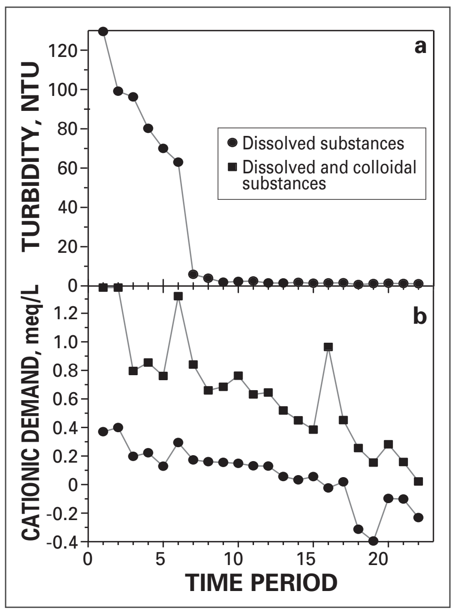
3. Machine first - pass retention (FPR) vs. time period and dosage scheme for the dendrimer and flocculant . Dark columns indicate the addition levels of dendrimer in periods 6 to 21. CPAM (50 g/t) was added in periods 3,4,19 and 20.



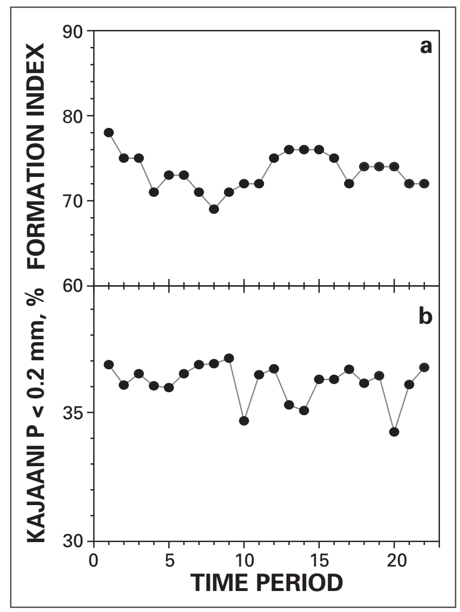
4. Machine first-pass ash retention (FPAR) vs. time period and dosage scheme for the dendrimer and flocculant. Dark columns indicate the addition levels of dendrimer in periods 6 to 21. CPAM (50 g/t) was added in periods 3,4,19 and 20.



5. Headbox and white water consistency and ash content vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



6. Machine white water turbidity and cationic demand vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



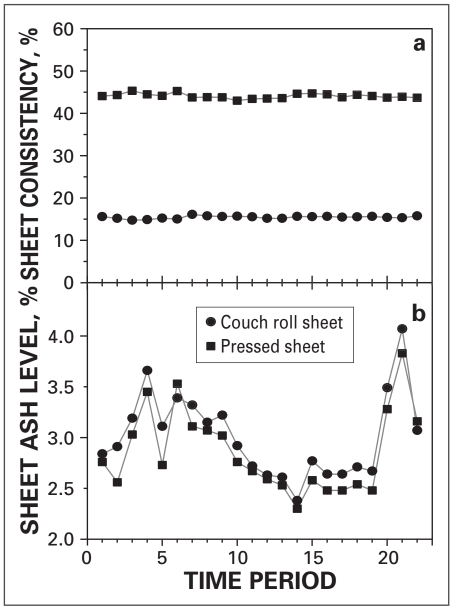
7. Sheet formation index and headbox Kajaani fines fraction vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).

shutting off the dendrimer flow. Closer inspection also indicates that the best results occur when the new retention aid is added with the polyacrylamide flocculant.

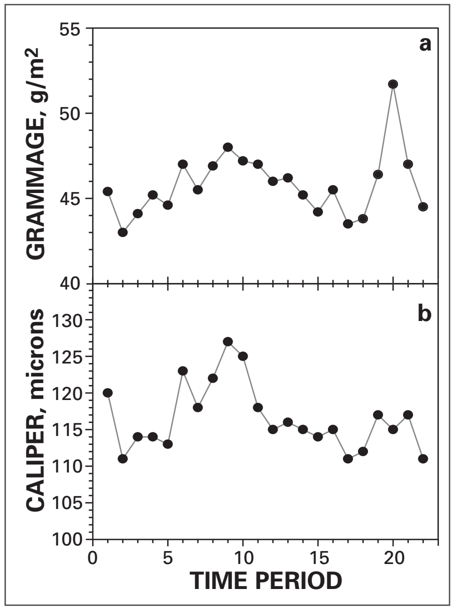
In **Fig. 5**, the consistencies and proportion of ash of the headbox and whitewater are plotted as functions of the trial period. Throughout the pilot trial, there were small random variations in the consistencies of both the whitewater and the headbox samples. However, these variations were too small to influence retention or sheet properties. The data suggest that the new retention aid had a significant effect on fines and clay retention; its introduction reduced the white-water ash from 47% to 30% and the headbox ash from 16% to 9%.

Figure 6 plots the turbidity and cationic demand of the headbox stock. The results show that the turbidity decreased rapidly from 130 NTU to less than 2 NTU. Similarly, the cationic demand of the dissolved and colloidal substances (DCS) and the dissolved substances (DS) also decreased rapidly as a function of polymer dosage. Data show that for the DCS, the cationic demand approached neutrality, while actual charge reversal occurred for the DS.

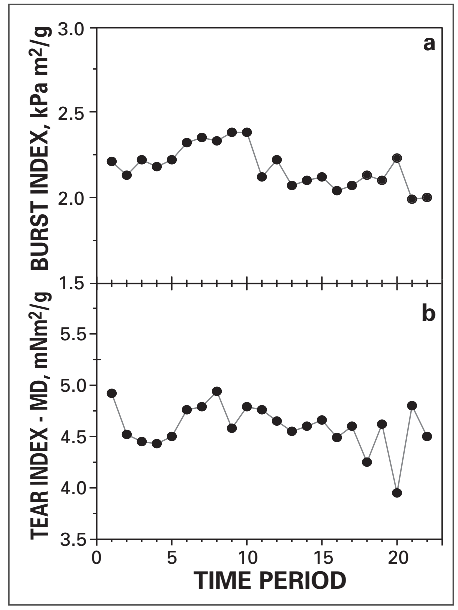
Some doubt had existed during the trial that the increase in retention may have been due to the consumption of the fines and colloidal matter in the headbox stock, because the pilot machine operated as a closed loop circuit. **Figure 7** shows the formation index of a dry sheet and the fraction of fiber shorter than 0.2 mm in the headbox, as determined by Kajaani analysis, plotted as functions of time. Formation index is a sensitive measure of fines content; decreases in formation index are indicative of loss of fines content. The data suggest that the additive did not greatly affect the formation index. The amount of fines did not significantly change during the trial. Therefore, the improvement in retention was not caused by a change in stock composition.



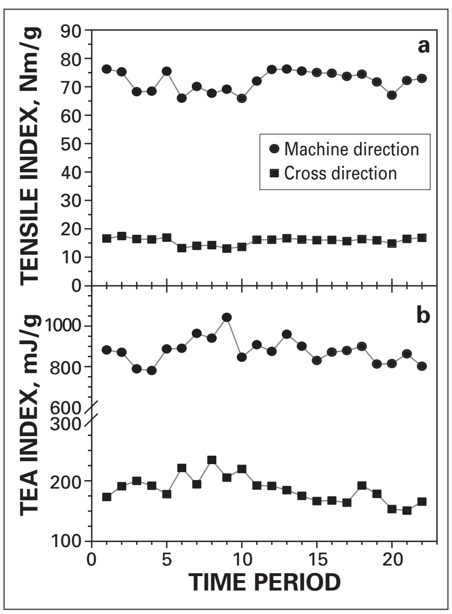
8. Sheet consistency and sheet ash for couched sheet and pressed sheet vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



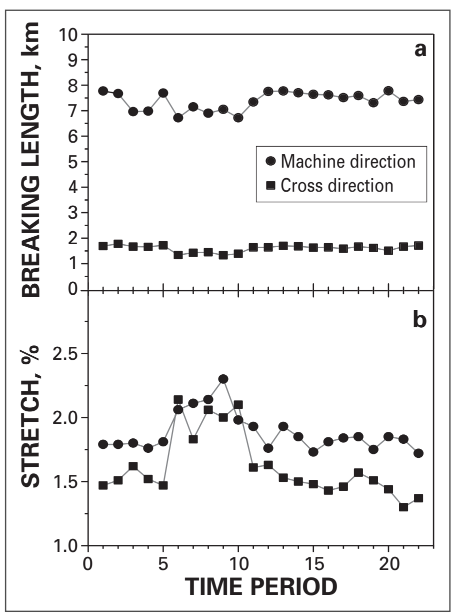
9. Dry sheet grammage and caliper vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



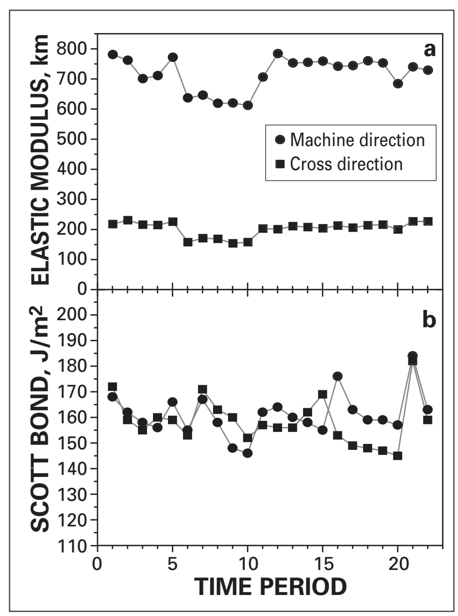
10. Dry sheet burst index and tear index vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



11. Dry sheet tensile index and tensile energy adsorption (TEA) index for machine direction and cross direction vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



12. Dry sheet breaking length and sheet stretch in machine direction and cross direction vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).



13. Dry sheet elastic modulus and Scott bond in machine direction and cross direction vs. time. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).

Figure 8a plots the solids content of the sheet collected after the couch roll and after the press section as functions of time. The results clearly indicate that the addition of retention aid did not affect sheet consistencies. Data in Fig. 8b show that sheet ash retention was good when either the flocculant only was used or when the dendrimer dosage was low. However, the best results occurred when we used the cationic polyacrylamide (CPAM) flocculant and the dendrimer simultaneously.

Dry sheet properties. **Figures 9-14** plot the dry sheet properties against time. The data indicate that the improved filler retention, induced by the addition of the dendrimer retention aid, resulted in increased grammage and caliper (Fig. 9). This will, of course, have a small effect on the strength properties of the sheet. In general, the physical test data show that the new retention aid caused no adverse effect on dry sheet properties. However, differences were clearly visible between the flocculant-dendrimer combination and the dendrimer only.

In Fig. 9a, the highest grammage obtained coincided with the highest fine and ash retention obtained (see Fig. 3) when both the flocculant and dendrimer retention aid were used simultaneously. This is not surprising. We expected that the coagulant-flocculant combination would be the most effective retention aid system.

Figures 10a and 10b present the burst index and tear index data. Both properties were inversely proportional to the ash content, but the effect was not great. Higher sheet fines content increases sheet strength, mainly through increased fiber-fiber bonding, while higher sheet ash content is known to reduce sheet strength [14, 15]. Figure 11 shows that the tensile index (the tensile strength divided by grammage) and the TEA index were not affected by the dendrimer nor by the combined addition of dendrimer and flocculant additions.

As expected, the breaking length (Fig. 12a), elastic modulus (Fig. 13a), and Scott bond (Fig. 13b) were little affected by the use of dendrimer. Figure 12b, however, shows an increased stretch. This may indicate decreased inter-fiber bonding (due to increased ash retention), because increased fiber-fiber bonding would reduce stretch, but increase tensile strength and modulus. However, more data would be required to confirm this finding. Figure 14 shows the plot for Gurley air resistance vs. time. The data clearly show that the air resistance is higher at shorter periods, when only the dendrimer was used. Gurley air resistance is a good indication of the internal structure of a paper sheet. Although the measurement is dependent on a number of properties, Gurley air resistance is most affected by the fines content and fiber length: the higher the fines content or the lower the fiber length, the more compact the sheet and thus the higher the resistance to air flow [14, 15].

CONCLUSIONS

The results obtained in the pilot plant trial indicate that the dendrimer improves the filler retention and total retention when used in an SC-A furnish. Even the lowest polymer dosage tested in this trial (0.5 kg/metric ton) increased the first-pass retention by 6%. The highest gains in first-pass retention and first-pass ash retention occurred when we used the new polymer in combination with a flocculant. The new retention aid did not appear to affect the sheet physical properties.

These promising results were obtained in a pilot plant. A mill trial is required to determine the true effectiveness on a commercial paper machine. Unfortunately, DAB(PA)$_4$ is at present several times too expensive for commercial use, but this may change as production is scaled up. The toxicity of the polymer (LD50 [oral rat] = 977 mg/kg) is an additional consideration. **TJ**

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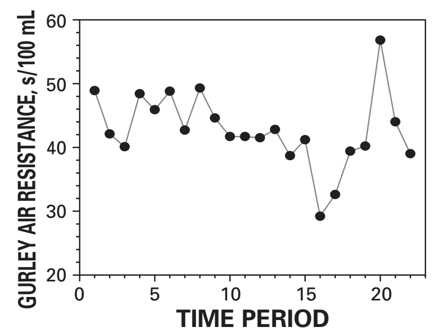

14. Dry sheet Gurley air resistance. Figures 3 and 4 show the dosage scheme for the dendrimer polymer and flocculant (CPAM).

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INSIGHTS FROM THE AUTHORS

During the course of Paprican's search for new, more efficient retention-aid systems, researchers discovered that dendrimers are remarkably effective coagulants (fixatives) for mechanical printing grades of paper. This discovery has been patented (U.S. Patent No. 6, 468, 396; Oct. 22, 2002). The original laboratory work leading to the discovery has been published in Nordic Pulp and Paper Research Journal [(15)5: 407-415 (2000)]. Following the lab work and before a possible mill trial, it was appropriate to conduct a pilot paper machine trial.

When used in combination with a flocculent, dendrimers gave their highest ever observed gains in first-pass retention. For example, a first-pass ash retention of 33% was obtained. The pilot plant trial complemented and supported the previous laboratory research in that it was successful. Even at an addition rate of just 0.5 kg/t, the first-pass retention of fines was increased by 6%. The highest gains in first-pass retention were obtained when the new additive was tested with a flocculent.

Our paper describes the unique structure of dendrimers. Whereas most coagulants presently used by the paper industry are larger polymers, with molecular weights often in the 0.5 - 1.5 million g/mol, the amine-terminated dendrimer used in this work has a molecular weight of 300 g/mol. Most coagulants have cationic change densities much lower than the 18.2 meq./g (at pH 5) found on the dendrimer. Hence, dendrimers are unique coagulants and their low molecular weight coupled with their very high charge density points the way to a new approach in formulating coagulants.

The most challenging aspect of this research was the experimental design of the pilot plant trial. The trial consisted of twenty-two 16-minute time periods. Some were control periods without polymer; others were periods when polymers were dosed, alone and in combination, at various feed rates. Prior to the trial, the pilot plant machine was run for hours without retention aids to produce the kind of white water, enriched in dissolved and colloidal materials, that is found on a modern paper machine. After the trial, one of the reviewers of the work commented that the design of the trial could be used as a model for future trials in pilot plants around the world.

One of the most interesting things about our research is that we observed very high increases in first-pass retention, both of fines and of ash. It was surprising that such a small molecule could be so effective in a furnish that often challenges conventional retention aid systems, especially for ash retention.

This work points the way for development of a new generation of coagulants for paper manufacture. The very high charge densities of dendrimers suggest that molecules of this nature will be especially useful as coagulants in paper mills with tightly closed white water systems. Unfortunately, at present, dendrimers are several times too expensive to compete with conventional coagulants. This situation may change, however, with the advent of improved, more efficient manufacturing technologies.

Based on this work, it would make sense for researchers pursuing the development of highly efficient cationic retention aids to explore the effectiveness and manufacture of coagulants with very high charge density and low molecular weight.

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