Effects of retention aids on retention and dewatering of wheat-straw pulp

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ABSTRACT *Four different retention-aid systems were investigated in relation to wheat-straw pulp: one single-component cationic polyacrylamide and three dual-component systems (cationic polyacrylamide and bentonite clay; cationic starch and anionic silica sol; cationic starch and precipitated aluminum hydroxide). The dual-component systems were found to be more effective as retention aids than the single-component system. The two starch-based systems also enhanced the dewatering of the wheat-straw furnish. The dryness of the sheets after pressing was evaluated by means of a laboratory press simulator. It was found that, despite the increased fines retention achieved by adding retention aids, there is no great change in the dryness of the sheets. Experiments involving the use of highly charged, cationic polyelectrolytes to deswell the wheat-straw pulp indicated that these polymers significantly reduced water-retention values.*

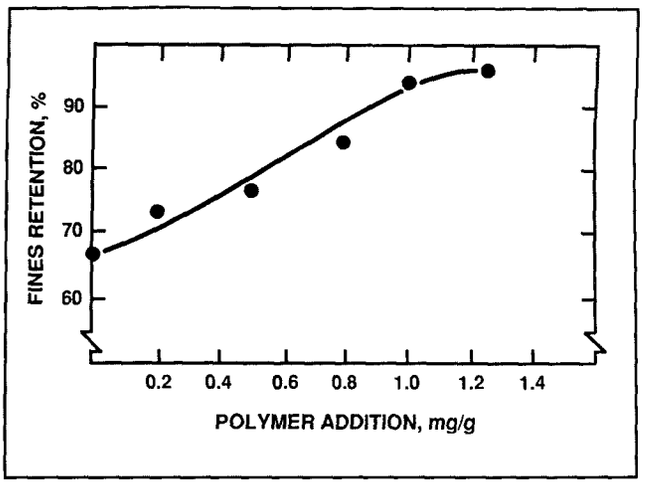
KEYWORDS
Additives
Plant residues
Pressing
Retention aids
Swelling
Water removal
Wheat straw

Until 140 years ago, papermaking fibers were derived exclusively from nonwood plants. Today, more than 93% of the fiber used in the manufacture of pulp and paper is from wood. Nevertheless there are still large areas in the world—predominantly the Middle East, North Africa, and Central Asia—that do not possess large indigenous supplies of wood but have an abundance of agricultural residues such as straw, bamboo, and bagasse. Although the pulp and paper industries in these developing regions are heavily dependent on nonwood fibers, they are expanding rapidly at an annual rate of 5.1%. This compares with an annual rate of 3% in the developed nations (*1*).

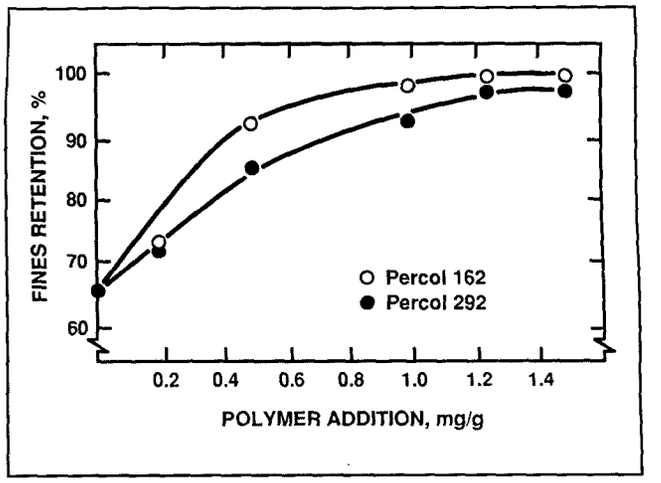
Straw is one of the most widely used nonwood plants for pulp and papermaking. Straw pulp has short and slender fibers, which produce a paper with good formation, a smooth and closed surface, and good printability. However, certain basic properties associated with this kind of pulp cause problems in the papermaking process. Straw pulp contains a lot of hemicellulose and fines. Consequently, the pulp is highly swollen and is difficult to dewater, and picking on press rolls and wet web breaks are therefore often severe problems. Most paper machines using straw pulp are run quite open with only a short circulation. High retention with good dewatering is thus crucial for (a) conserving raw materials, (b) minimizing pollution caused by excessive discharge of fibers, and (c) increasing machine efficiency by decreasing the frequency of web breaks.

Chemical retention and dewatering aids are widely used to enhance wood-pulp-based papermaking operations. However, there is little information about the use of chemical additives in

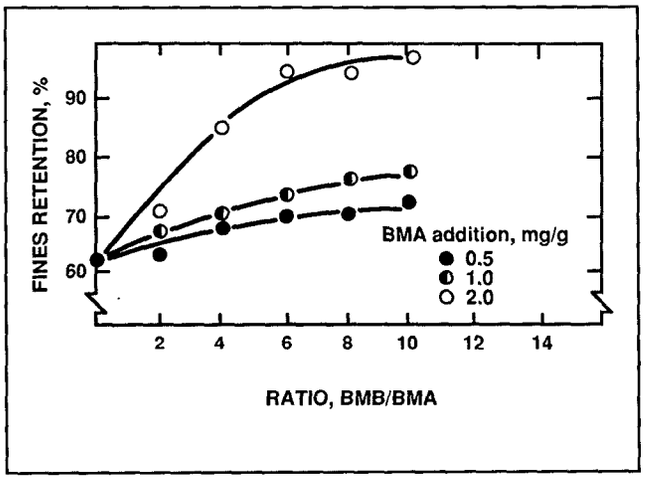
1. Fines retention as a function of polymer addition for Percol 162 (cationic polyacrylamide)



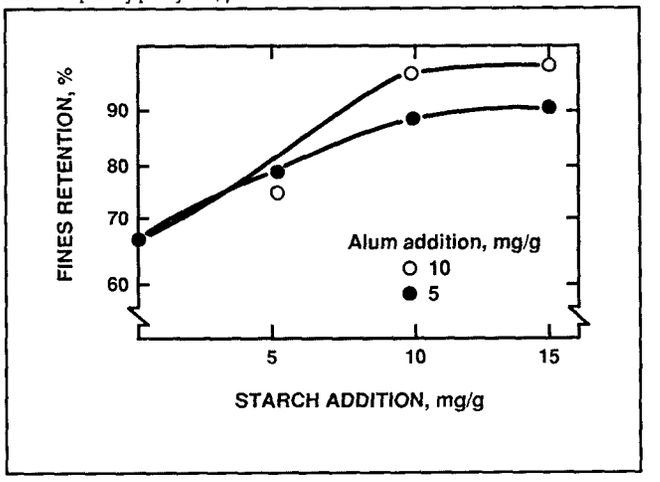
2. Fines retention for the Hydrocol system—a mixture of polyacrylamide (Percol 162 or 292) and bentonite—as a function of polymer addition. Bentonite addition was maintained at a constant level of 2.5 mg/g.



3. Fines retention for the Compozil system as a function of the ratio of BMB (cationic potato starch) to BMA (colloidal silicic acid) at three levels of BMA addition



4. Fines retention for the Hydrozil system—a mixture of cationic potato starch and alum—as a function of starch addition at two levels of alum addition. $[OH^-]/[Al^{3+}] = 3$; pH = 8.0 ± 0.1.



nonwood pulp. This paper examines the use of chemical additives to increase retention and dewatering of wheat straw pulp. Several recently developed microparticle dual-retention-aid systems (*2–8*) have characteristics that agree well with the demands listed. It was considered interesting to perform retention and dewatering experiments with these different systems. For comparison, a retention aid consisting of a single-component, cationic polyacrylamide was chosen.

Results and discussions

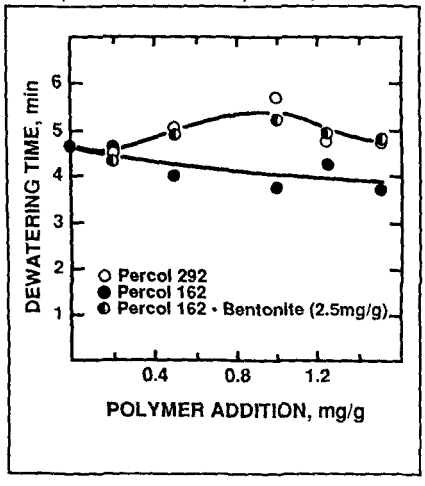
Retention

The results of experiments with the cationic polyacrylamide are presented in **Fig. 1**, which shows that a large amount of polymer must be added before there is any significant increase in retention. This is probably because of the high concentration of dissolved anionic wood polymers and hemicelluloses in furnishes containing wheat-straw pulp and because of the comparatively high electrostatic charges on fibers of wheat-straw pulps. Under these conditions, much of the cationic polymer would be consumed before it could function as a retention aid.

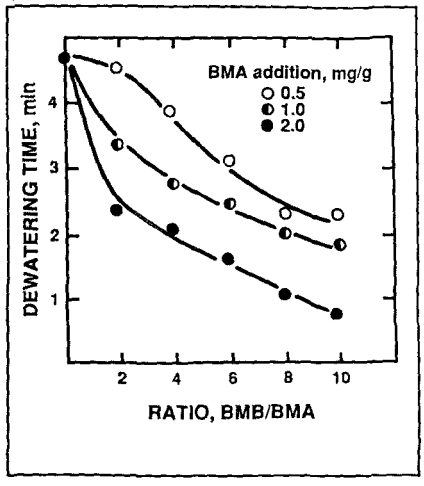
The effect of the bentonite in the Hydrocol system—a mixture of cationic polyacrylamide and bentonite—is shown in **Fig. 2**. Comparison with Fig. 1 shows that the amount of polymer needed to reach a given retention level is approximately halved when bentonite is added. While there are several possible explanations for this response, it is likely that the bentonite acts as a crosslink between polymers adsorbed on the fibers and fines, thereby increasing the efficiency of the polymer. It is also possible that the bentonite acts as a crosslink between soluble complexes of polyacrylamide and anionic wood polymers, since bentonites are known to adsorb both types of polymers. This latter mechanism could be referred to as a network type of flocculation. Figure 2 also shows that the more highly charged polymer, Percol 162, is more efficient, presumably because it reduces the anionic contamination more effectively.

The effect of the dissolved anionic wood polymers is evident in **Fig. 3**, where the results of the experiments with the Compozil system are shown. At the two lowest levels of

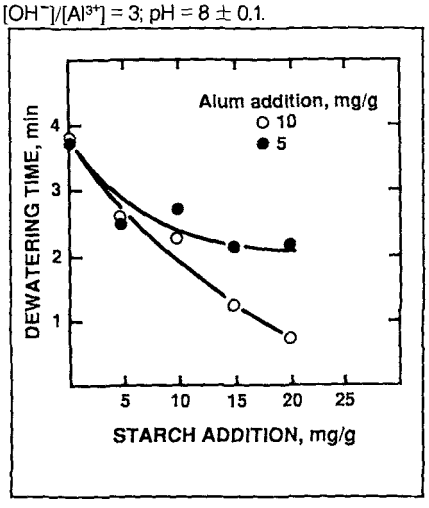
5. Dewatering time as a function of polymer addition for single-component cationic polymers (Percol 162 and 292) and Hydrocol



6. Dewatering time as a function of BMB/BMA ratio for Compozil at three levels of BMA addition



7. Dewatering time for Hydrozil as a function of starch addition at two levels of alum addition. $[OH^-]/[Al^{3+}] = 3$; pH = 8 ± 0.1.



addition the added chemicals have hardly any effect at all, whereas at the highest addition level they lead to a large increase of retention. The most probable explanation of the lack of response at the lower levels of addition is that the polymer is consumed both by the comparatively high anionic charge on the fiber surface and by the dissolved anionic wood polymers. There are hence no free segments available from the starch to permit contact with the anionic silica sol. Instead of increasing the level of addition of the starch, a starch with a higher charge density could be added. It should be stressed, however, that the anionic silica sol is necessary to give the high retention levels achieved, since starch alone cannot exert a comparable efficiency.

The results obtained with the Hydrozil system are depicted in **Fig. 4**. Hydrozil is similar to Compozil except that anionic aluminum hydroxide is used as a microparticle instead of the anionic silica sol. This particle is formed *in situ* in the suspension by adding 3 moles of NaOH to each mole of aluminum. Comparison of Figs. 3 and 4 shows that the Compozil and Hydrozil systems provide similar levels of high retention. In the case of Hydrozil, Fig. 4 shows that retention is increased by increasing the addition of aluminum sulfate. The explanation for this response is that a larger number of crosslinking anionic particles are formed between the cationic starch on fibers and fines.

Dewatering

Because dewatering of wheat-straw furnishes is as important as retention, we also conducted experiments to determine the dewatering capability of the various retention-aid systems. **Figures 5-7** depict dewatering time as a function of polymer addition for the Hydrocol, Compozil, and Hydrozil systems, respectively. It is clear that neither the cationic polyacrylamide nor the Hydrocol system (Fig. 5) can improve dewatering, whereas considerable improvements can be obtained with both of the cationic-starch systems (Figs. 6 and 7). As in the retention experiments, the addition of starch must be increased considerably before large effects can be detected.

There are several possible explanations for the differences between Hydrocol and the other two dual-component systems. One significant factor is the difference in the concentrations of anionic particles. Since the anionic silica particles are only 5 nm in size, their number concentration will be high. This is also believed to be the case for the anionic aluminum hydroxide particles, whereas the anionic bentonite particles have a size of approximately 1 μm, according to the manufacturer, and hence also a low number concentration. At high concentration, the average distance between the particles is low, which would facilitate formation of bridges between the various starch molecules on the fibers and fines. Visual observation confirms that such crosslinking decreases the size of formed flocs, and it is suggested that this "deswelling" of the flocs is responsible for the increase in dewatering. Because the concentration of the bentonite particles is comparatively low, these particles are not able to deswell the formed flocs.

In discussing the effect of the anionic particles, it should be pointed out that if the data in Fig. 6 are plotted as a function of starch addition, all results fall on the same experimental curve. This indicates that the addition level of anionic silica is not critical in the present experiments, and it may be suggested that the lowest level of BMA addition gives a sufficiently high number concentration of anionic particles.

Pressing

Straw pulp is usually highly swollen and difficult to dewater. Low wet-web strength, caused mainly by high moisture, often causes severe process problems. A good retention and dewatering aid should hence improve retention and dewatering without increasing the moisture of sheets leaving the press. A number of press experiments have thus also been performed in this study. The results in **Table I** show that addition of any of the four retention and dewatering aids has virtually no effect on the maximum dryness reached in the press.

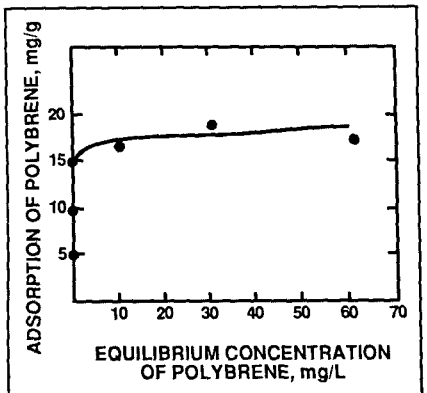
Deswelling

Papers manufactured from wheat-straw pulp show a considerable hy-

I. Increase in dryness on pressing, with and without addition of retention and dewatering aids

	Chemical addition, kg/ton	Starting dryness, T_1, %	Maximum dryness T_2, %	Difference between T_1 and T_2, %	Grammage, g/m²
Without chemicals	...	22	35	13	76
Compozil					
BMA	1.5				
BMB	9	22	34	12	77
Hydrocol					
Percol 162	1				
Bentonite	2.5	22	34	12	76
Hydrozil					
Cato 102	10				
Aluminum sulfate $[OH^-]/[Al^{3+}] = 3$	10	22	35	13	76
Percol 162	1	22	34	12	75

8. Polybrene absorption as a function of equilibrium concentration of polymer in solution



groinstability, which is likely the result of the high swelling of the wheat-straw pulp. This can be a significant problem. Cationic polyelectrolytes are known to deswell cellulosic fibers (*9, 10*), so we conducted experiments to measure the deswelling ability of the cationic polymers on the wheat-straw pulp.

To estimate the cationic demand of the pulp, an adsorption isotherm for Polybrene on the fibers was recorded. The isotherm is presented in **Fig. 8**. By extrapolating the isotherm to zero concentration and taking the amount of polymer charges adsorbed at this level to represent the charge of the material, a cationic demand of 91 μeq/g is obtained. This is fairly high compared with an ordinary softwood pulp, which usually shows a cationic demand of about 30 μeq/g, and is probably due to the high content of hemicellulose in the wheat-straw pulp. It is likely that this high charge also causes the high swelling of the straw pulp.

It is possible to neutralize the charges on the fibers and to decrease the swelling by adding cationic polymer to the fibers. This is shown in **Fig. 9**, where Polybrene—a highly charged cationic polymer—is added to pulps beaten to different Schopper-Riegler (SR) values. The higher the degree of beating, the higher is the deswelling capacity of the polymer. The curves also tend to flatten out at a level of addition comparable with the plateau value in the adsorption isotherm, which is consistent with the deswelling hypothesis.

It is evident in Fig. 9 that fairly large amounts of polymer have to be added before any deswelling is detected. From a cost perspective, this is an obvious drawback. To reduce the consumption of polymer, a highly charged, high-molecular-mass polymer—polydimethyldiallylammonium chloride (poly-DMDAAC)— was therefore used, instead of Polybrene. The level of addition is considerably lower than for Polybrene, but this type of polymer can apparently deswell wheat-straw pulp only at the highest degree of beating, as seen in **Fig. 10**. The lack of deswelling at the lower degrees of beating may be ascribable to the fact that the charges within the cell wall of the fibers are inaccessible to this high-molecular-mass polymer.

Conclusion

It is possible to increase both the retention and the rate of dewatering of wheat-straw pulps by the addition of an effective retention-aid system. The results presented here indicate that Compozil (cationic potato starch and an anionic silica sol) and Hydrozil (cationic potato starch and *in situ*-formed anionic aluminum hydroxide) are effective systems in wheat-straw-pulp applications.

Two other systems—a cationic polyacrylamide used alone and in combination with a bentonite clay—were able to increase the retention but not the rate of dewatering. The addition of the bentonite clay considerably lowered the level of addition of polyacrylamide needed to reach a given retention level.

None of the retention aids had a significant effect on the dryness of the sheets after the pressing in a laboratory press simulator. It is not believed that this will decrease the production capacity of a paper machine.

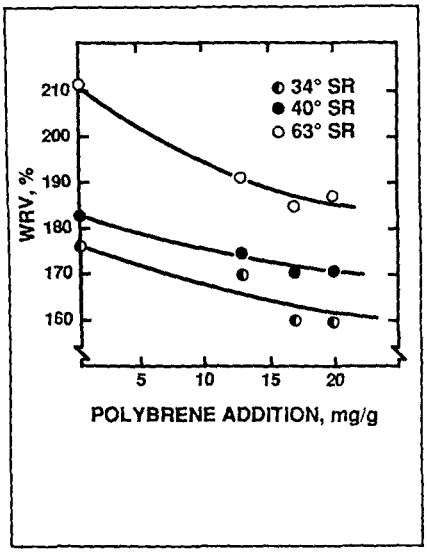
Two different types of highly charged cationic polymers were used to deswell the wheat-straw pulp. The low-molecular-mass polymer, Polybrene, was able to deswell the wheat-straw pulp at all the degrees of beating investigated, whereas the high-molecular-mass polymer, poly-DMDAAC, was able to deswell only the most highly beaten pulp.

Experimental

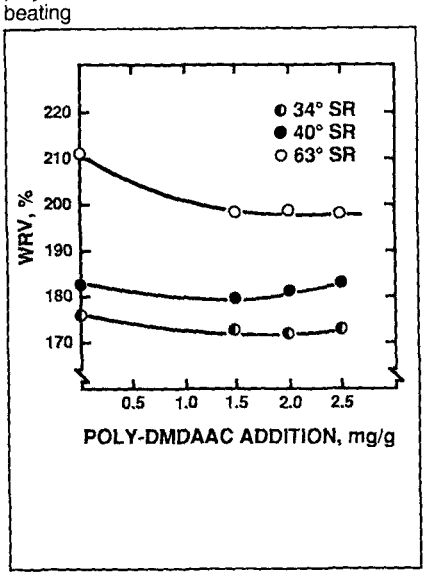
Materials

Pulp. The furnish used in the retention and dewatering experiments consisted of 100% wheat-straw pulp produced by the anthraquinone-soda process. The maximum cooking temperature corresponded to 6-kg vapor pressure and was maintained for 3 h. The yield of unbleached pulp was 43-45%; the yield after single-stage hypochlorite bleaching was 40-41%. Pulp brightness was higher than 72%. The pulp was shipped at about 20% moisture from China to our

9. Water-retention value as a function of Polybrene addition at three levels of beating



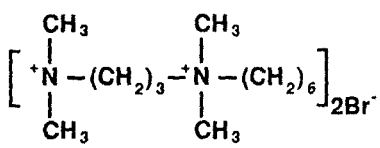
10. Water-retention value as a function of poly-DMDAAC addition at three levels of beating



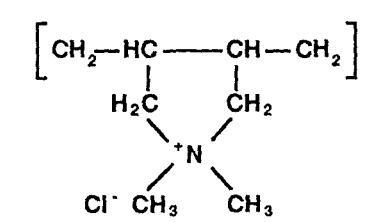
11. Fiber length distribution of wheat-straw pulp (Bauer-McNett)

Screen size, mesh	*Fiber fraction, %*
>30	5
30-50	34.8
50-100	20.6
100-200	24.8
<200	14.8

11. Chemical structure of Polybrene



12. Chemical structure of poly-DMDAAC



laboratory in Sweden, where it was stored in a refrigerator.

The degree of beating of the unbeaten pulp was 25°SR, and unless otherwise stated, the pulp used in all the experiments was beaten in a Valley beater (*11*) to 46°SR. The fiber length distribution results according to the Bauer-McNett method are summarized in **Table II.**

Chemicals. Two kinds of cationic polyacrylamides (Percol 162 and 292, AB CDM, Sweden) with different charge density were used as single-component retention and dewatering systems. All polymer solutions were prepared according to the same procedure: 0.125 g polyacrylamide powder was wetted with 1.5 mL ethanol for 2 min and then thoroughly dissolved on a magnetic stirrer for 2 h. The solutions were allowed to swell overnight without stirring and were then diluted to 250 mL before use.

Hydrocol (AB CDM, Sweden) is a dual-component retention and dewatering system. It consists of a cationic polyacrylamide and a bentonite clay. Two kinds of polyacrylamide were used, Percol 162 and 292. The polymer solutions were prepared according to the previously described procedure, and the bentonite was allowed to swell overnight in deionized water prior to the experiments.

Compozil (EKA Nobel, Sweden) is a dual-component retention and dewatering system consisting of BMA and BMB. BMA is a highly charged negative colloidal silicic acid sol with a particle diameter between 5 nm and 7 nm, and BMB is a cationic potato starch. BMB was gelatinized at 1% concentration in a water bath with continuous gentle magnetic stirring. The temperature was continuously raised to 90°C, and the solution was kept at this temperature for 10 min and then diluted with cold water to the desired concentration. The total time for this procedure was about 50 min. BMB was diluted to 0.3% before use.

Hydrozil (Boliden Kemi AB, Sweden) is a dual-component product that can only be used in alkaline systems. In the present investigation, it consisted of a cationic potato starch (Cato 102) and aluminum sulfate. Sodium hydroxide was used together with aluminum sulfate to form negatively charged aluminum hydroxide. Cato 102 was gelatinized in the same way as BMB.

Polybrene (Jansen Chimica, Belgium) is a highly charged cationic polymer with a molecular mass of 6×10^3 and a charge density of 5.35 meq/g. The chemical structure of this 3.6-ionene is shown in **Fig. 11.**

Poly-DMDAAC (CPS Chemical Co., U.S.A.) is a positively charged polymer with a molecular mass of 1.5×10^5 and a charge density of 6.19 meq/g. The chemical structure of this compound is shown in **Fig. 12.**

All chemicals were used as received without further purification. Tap water was used in the retention and dewatering experiments, but distilled and deionized water with a conductivity of less than 1 μS/cm was used in the adsorption and deswelling experiments. All other chemicals used in the experiments were of analytical grade.

Methods and equipment

The charge density of the fibers was estimated by a procedure using polyelectrolyte adsorption (*12*). The polyelectrolyte was Polybrene, with an adsorption time of 30 min. Prior to the adsorption experiments, the fibers were washed with 0.01 *M* HCl and then with deionized water to pH 4.5. To convert the carboxyl groups on the fibers to their sodium form, the fibers were treated with 0.001 *M* $NaHCO_3$, and the pH was increased to 9 by addition of NaOH. The fibers were then rewashed with deionized water to remove excess electrolyte to a conductivity of the water of less than 5 μS/cm.

In one set of experiments, the deswelling ability of Polybrene and poly-DMDAAC was tested. After converting the fibers to their sodium form, polymer was added to the fiber suspension. After an equilibration time of 30 min with stirring, the fibers were filtered off and their water-retention value (WRV) determined. The total weight of fibers (1 g), distilled water, and chemicals in these experiments was 200 g.

Fines retention was measured using a dynamic drainage jar according to the procedure described by Britt (*13, 14*). Agitation speed was 750 rpm. When the single-component retention-aid system was used, the polymer was added and 2 min allowed to elapse before the onset of dewatering and sample collection. For the Hydrocol system, bentonite was added 2 min after the polyacrylamide, with dewatering started after another 30 s. A similar procedure was used for the Compozil system, where potato starch was added 3 min before the anionic silica sol, which in turn was followed by 30 s of dewatering. In the case of the Hydrozil system, starch was added first to the wheat-straw pulp suspension followed by immediate addition of NaOH sufficient to maintain an [OH]/[Al] ratio of three. The starch was allowed to adsorb for 3 min, at which point $Al_2(SO_4)_3$ was added. Dewatering was started 30 s later.

The dewatering capacity of the various chemical systems was measured with a Water Release Analyser (*15*). However, the procedure had to be modified slightly in order to realistically simulate the effects of the added chemicals. The measured variable in our experiments was the time needed to dewater 500 mL of a 2-g/L suspension with a constant vacuum of 300 mm Hg. The disappearance of the water mirror from the fiber cake formed was taken as the end point of the measurement.

When dual-component systems were used, the cationic polymer (starch or cationic polyacrylamide) was added at a stirring speed of 750 rpm. The speed then was raised to 1500 rpm for 30 s to disrupt large-scale flocs and then decreased to 750 rpm for either 90 s (cationic polyacrylamide) or 150 s (cationic starch) before adding the second component. The 750-rpm stirring speed was maintained for another 30 s and then stopped. After 5 s, the dewatering was started and the dewatering time recorded.

To evaluate the impact of the chemicals on pressing and dewatering, sheets were manufactured on a dynamic sheet former (Formette Dynamique, CTP, France) and pressed in the press simulator described by Carlsson (*16*). With this equipment, it was possible to generate press pulses with a duration and total impulse comparable with that experienced in a conventional press nip. A 25-ms sinusoidal pressure pulse with a maximum pressure of 3 MPa was used. The sheets had a grammage of 75 g/m^2 and a tensile-strength anisotropy of 3–3.5.□

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