Behavior of Polyamine Fixing Agents on Agglomeration of Dissolved and Colloidal Substances in Papermaking

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Five polyamine fixing agents with different molecular weights but slightly different charge densities were used to treat a deinked pulp. Their efficacy in controlling colloidal substances (CS) in the pulp was measured using focused beam reflectance measurements (FBRM). The objective was to determine if the colloidal substances were affected by the fixing agents by a “colloidal fixation” mechanism, *i.e.*, colloidal particles being fixed onto pulp fiber in an un-agglomerated, single-particle state, or a “colloidal agglomeration” one, *i.e.*, colloidal particles being coagulated by fixing agents into bigger agglomerates. The results showed that colloidal fixation does take place, especially for the polyamine with the smallest molecular weight. Among the five polyamines, it was found that higher molecular weights tended to result in more extensive colloidal agglomeration, but the effect of charge density was almost insignificant. Because it is efficient in differentiating between these two fixation mechanisms, FBRM is a powerful tool in screening different fixing agents.

Keywords: Polyamine; Fixing agent; Dissolved and colloidal substances; Inter-agglomeration; Colloidal fixation

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INTRODUCTION

During the production of paper, especially when using thermo-mechanical pulp and recovered pulp, dissolved and colloidal substances (DCSs) are released from the raw wood material into process water. These substances accumulate very easily in high concentrations due to the recirculation of white water. As a result, they are deposited in the papermaking system, which greatly deteriorates process runnability and final product quality.

There is a diverse range of treatment options available to combat such problems. Using fixing agents to attach DCSs to wood fibers and subsequently remove them from the system within the sheet has been a popular choice for many pulp and paper manufacturers. Fixing agents are water-soluble cationic polymers characterized by high cationic charge density and relatively low molecular weight; typical ones include polyamines (PAs), polyvinylamines (PVams), polydimethyldiallylammonium chlorides (PDADMACs), polyethyleneimines (PEIs), and specially-made highly cationic starches (also called starch-based fixing agents (SBFs)) (Miao *et al.* 2003). Comparison of the effectiveness of these different fixing agents has been a popular research topic for many years (Neimo 1993; Esser *et al.* 2001; Yu *et al.* 2003; Maher *et al.* 2007; Allen and Filion 1996)

Although still disputable, it is generally agreed that polyamines are relatively cost-effective (Gill 1996). A series of polyamine products with different molecular weights and charge densities can be easily prepared by the condensate copolymerization of epihalohydrin and dialkylamine, and sometimes with diamines or triamines as cross-linking agents to increase the molecular weight (Joo *et al.* 2003). While reports on the application of polyamines as fixing agents or anionic trash-catchers to control the DCS content of the wet end of papermaking systems have not been rare, there is little detailed information on the performance of polyamine fixing agents with different structural characteristics. This situation is unfavorable, not only for enriching effective fixing agents, but also for unearthing deeper mechanisms for DCS control.

In this work, five polyamine fixing agents with different molecular weights but only slightly different charge densities were used to treat a deinked pulp to observe differences in the controlling of DCS. Because traditional evaluation methods such as measurements of turbidity, chemical oxygen demand, cationic demand of the pulp filtrates, as well as measurements of the changes in pulp properties, such as drainage speed and ζ-potential, are very time-consuming and ineffective, new technology using an instrument called a focused beam reflectance meter (FBRM) to measure the particle size change was used (in FBRM, particle sizes are expressed as chord lengths). The purpose of using FBRM was to discover whether the DCSs, especially the CSs (colloidal substances), were fixed to the pulp fibers according to a “colloidal fixation” mechanism or a “colloidal agglomeration” mechanism. Colloidal fixation means that the colloidal substances are attached to wood fibers in an un-agglomerated, single-particle state. On the other hand, colloidal agglomeration means that the colloidal substances are preferentially coagulated into bigger agglomerates. For the latter case, while a part of colloidal agglomerates are big enough to be retained within the fiber mat by mechanical trapping; most of those not big enough will be drained into whitewater. Due to the fact that the CS agglomerates in whitewater tend to cause deposit problems more easily than the well-dispersed colloidal substances, colloidal agglomeration generally is not regarded as being desirable, while colloidal fixation is, when a pulp is treated with a high-charge cationic polymer (Leduc *et al.* 2005; Zabihian *et al.* 2012; Pruszynski 2009).

EXPERIMENTAL

Materials

Five polyamines used in this study as fixing agents were synthesized in a laboratory according to known methods (Joo *et al.* 2003). Their properties are shown in Table 1, where the solids content of the polyamines were determined by drying the samples in a dry oven at 105 °C to constant weight. The charge density of the polyamines was determined according to polyelectrolyte titration with a standard 0.001 N sodium polyethylene sulphonate (PES-Na) using a charge analysis system (CAS) by AFG Analytic GMBH, Germany. The intrinsic viscosity was measured with a 4-0.55/16 Ubbelohde viscometer in a 30 °C water bath, with the polymers being dissolved in a 1 M NaCl solution.

The deinked pulp was sampled from a newsprint line from Zhengda Papermaking Co. Ltd., in the Shangdong Province of China, and its properties are listed in Table 2. The pulp consistency was determined according to TAPPI Standard T240 om-02, and the conductivity was determined with a DDS-307 conductivity meter (Shanghai Instrument and Electronics Scientific Instrument Company, China). The charge demand of the whole pulp suspension was analyzed by the back titration method, *i.e.*, a portion of the pulp was overcharged with 0.001 N PolyDADMAC and the excess cationic charge in the filtrate was titrated back to a zero output of the device using 0.001 N PES-Na standard solutions. To determine the separate contributions of anionicity by colloidal substances (CSs) and dissolved substances (DSs), firstly, the DIP raw suspension stood overnight, and then the supernatant was decanted as DCS water. Then, the DCS water was filtered through a 0.22-μm membrane disc filter, and the filtrate was regarded as DS water. The cationic demands of the DCS and DS water were measured using the CAS instrument mentioned above, and the differential of cationic demands between the DCS and DS was calculated as that contributed by the CSs.

Applying Fixing Agents to DIP

The five polyamines were diluted to 1 g/L solutions. Then, to each 100 mL of DIP slurry, 8 mL of a corresponding polyamine solution was dosed, and quick stirring for 45 s followed. The dosage equaled 0.22% of dry chemical to dry pulp (hereafter expressed as % d/d). The mixtures were then filtered through a 200-mesh filter cloth, and the filtrates were collected for further FBRM analysis.

FBRM Measurements

Measuring the particle sizes of the solids in the above-mentioned pulp filtrates was carried out with a S400 focused beam reflectance meter connected to a computer installed with iC-FBRM^{TM} 4.2 software (Mettler-Toledo, USA). The FBRM method, also known as scanning laser microscopy, is detailed elsewhere (Blanco *et al.* 2002a,b; Lumpe *et al.* 2001; Negro *et al.* 2006) and is briefly summarized here. The methodology of this technique is based on a highly focused laser beam scanning across particles in a suspension at a fixed speed. Light is backscattered into the probe whenever the focused laser beam crosses a particle or particle aggregate. The duration time of this backscattered light pulse is measured, and the chord length (CL) is calculated as the multiple of duration time and the velocity of the focused laser beam. Each measured chord length is considered a count. Each second, thousands of chords are measured. As a result, a measure of the size distribution of the particles in the suspension is obtained.

For the measurement, the FBRM probe was inserted into a 100-mL beaker containing 50 mL of the filtrate. The scanning speed was set at 2 m/s, and the scanning interval was 2 s. Stable data were collected for 2 min while the filtrate was continuously agitated at 250 rpm.

RESULTS AND DISCUSSION

Characterization of the Fixing Agents and the Deinked Pulp

The properties of the five polyamine fixing agents are listed in Table 1. It was known that the molecular weights of the polyamines, indirectly expressed as intrinsic viscosity, followed the order A < B < C < D < E. However, A and B were linear products, while C, D, and E were branched.

For charge density, A was the lowest, B was the highest, and C, D, and E were in the middle. Statistically, the charge densities of C, D, and E were essentially the same.

Table 1. Main Properties of the Fixing Agents

Polyamines	Cross-linking agent* (%)	Solids content (%)	Intrinsic viscosity (mL/g)	Charge density (meq/g)
PA-A	0	52.76	4.52	5.93±0.05
PA-B	0	55.88	11.45	6.67±0.07
PA-C	2.1	52.63	13.00	6.26±0.04
PA-D	3.0	54.52	35.15	6.15±0.06
PA-E	3.8	52.50	49.00	6.21±0.02
* The molar percentage of the cross-linking agent to that of total monomers including dimethyl amine, epichlorohydrin, and the cross-linking agent				

The properties of the deinked pulp are shown in Table 2. It can be seen that the charge demand of the whole pulp suspension (3.60% consistency) was 2.536 meq/L, and that of DCS was 0.759 meq/L. Therefore, only 30% of the total anionicity was contributed by the DCS (the remaining 70% was contributed by fibers and fines). Additionally, because the cationic demand of DS was 0.606 meq/L, it can be deduced that of its 30% contribution, 24% was due to DS, while only 6% was from CS.

Table 2. Main Properties of the Deinked Pulp

Consistency (%)	Conductivity (μs/cm)	Cationic demand (meq/L)			
		Whole pulp suspension	DCS	DS	CS
3.60	2600	2.53	0.759	0.606	0.153

Table 3. Theoretical Neutralization Degree of the Whole Pulp Suspension or DCS Charges

	PA-A	PA-B	PA-C*	PA-D*	PA-E*
Percent of Neutralization for the whole pulp suspension* (%)	18.6	20.9	19.4	19.4	19.4
Percent of Neutralization for all the DCSs** (%)	64.2	72.2	67.2	67.2	67.2
* The charge densities of PA-C, D, and E were averaged to be 6.21 meq/g ** Suppose all of the charge of a fixing agent was consumed on neutralizing the negative charges of DCSs but not those of the fiber.					

As stated above, in this study, the five fixing agents were dosed at the same amount, *i.e.*, 0.22% d/d. This decision was made partly due to the fact that in industrial applications, comparisons are often made on the same weight basis. However, the charge densities of polyamines A, B, and the group C, D, E were different; therefore, the charge neutralization degree for the pulp or the DCS by different fixing agents was also different. The lowest was PA-A, the highest was PA-B, and PA-C, D, and E were in the middle (see Table 3). This should be kept in mind during the following discussion.

Behavior of Polyamines on Agglomerating DCS

As described in the Experimental section, after the pulp was treated with a polyamine fixing agent and the water phase was separated with a 200-mesh wire, the particle numbers and size distributions of the particles in the filtrate were measured by FBRM and recorded by the software iC-FBRM, supplying rich information on chord length trends and distributions using different statistical methods. Starting from the simplest, the change of particle number according to different fixing agent treatments was determined first. The results are shown in Fig. 1, where the X-axis corresponds to the particle size range (chord length ranges) and the Y-axis corresponds to the particle number. However, it should be mentioned that the chord length is not the same as the actual particle size (Mangold 2012; Kempkes *et al.* 2008; Ruf *et al.* 2000; Kail *et al.* 2008). For all of the filtrate samples, including the blank one (the filtrate from the original pulp without treatment by any fixing agent), most of the particles had chord lengths smaller than 10 μm; there were fewer between 10 and 50 μm, and almost none between 50 and 150 μm or higher. Concerning the polyamine treatments, it was seen that all of the five fixing agents reduced the particle numbers sharply, which meant that they were all effective at reducing the DCS content. However, their efficacy varied in the general order of A < B < C < D ≈ E, which can be clearly seen when looking at the change in total counts (chord lengths from 1 to 1000 μm) or the change in the number of particles with chord lengths of less than 10 μm. Differences were seen when looking at the change in the number of particles with chord lengths between 10 and 50 μm, where the effectiveness of B and C was found to be inferior to that of A, D, and E. However, at the present stage, the reason for this phenomenon was not clear. It is possible that B and C were less effective at fixing the original particles with chord lengths of 10 to 50 μm directly onto fibers; on the other hand, it is also possible that B and C may have had a greater ability to agglomerate particles with chord lengths of less than 10 μm into larger particles with chord lengths between 10 and 50 μm.

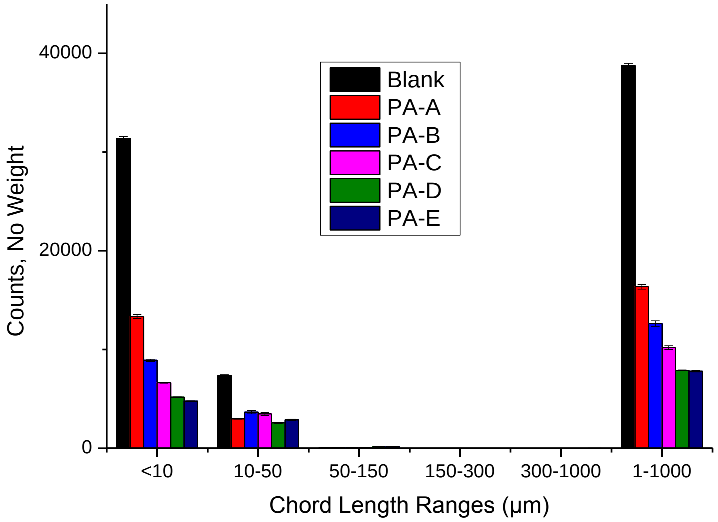

Fig. 1. Change in the number of particles in the filtrates separated from pulps treated with different fixing agents

The second interesting result was the change in particle size due to different fixing agent treatments, which is shown in Fig. 2, where mean chord length (MCL) was used to express the mean particle size (as an example, suppose there are 3 particles with chord length of 10 μm and 4 particles with chord length of 20 μm; in such a case the mean chord length is calculated as (3×10+4×20)/(3+4) = 15.7 μm). Except for PA-A, all of the polyamines increased the MCL of the particles in the filtrates that were separated from the fixing agent-treated pulps. It can be envisioned that when a fixing agent is added to the pulp, the colloidal substances may be fixed onto fiber in a colloidal fixation way, or they may be coagulated together by the fixing agent into bigger agglomerates (colloidal agglomeration). For colloidal fixation, the residual colloidal substances separated into filtrate will remain in their single particle state. But for colloidal agglomeration, the situation might be more complicated: a part of agglomerates are big enough to be retained into the fiber mat by mechanical trapping; for those not big enough to be trapped, while a part of them may still be able to be attracted onto fiber by electrostatic interaction (the CS/fixing agent complexed agglomerates may still have enough residual cationic charges), most of the agglomerates will be drained into filtrate and detected by the FBRM technology. The results in Fig. 2 indicates that polyamine A, with the smallest molecular weight, worked mainly in a “colloidal fixation” manner, but the polyamines B, C, D, and E, with higher molecular weight, caused “colloidal agglomeration”.

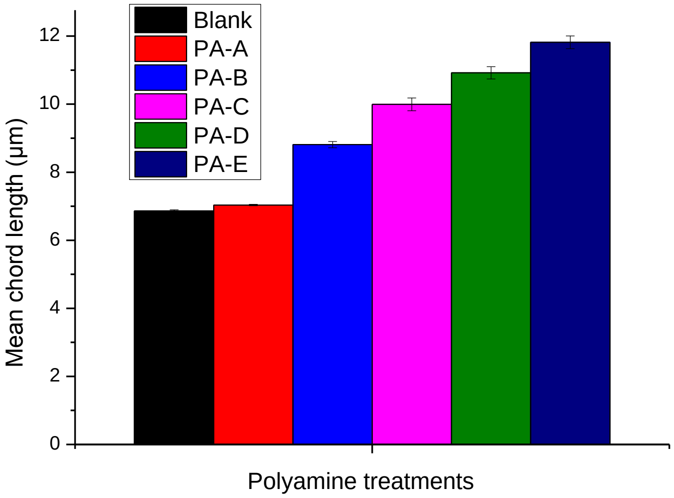

Fig. 2. Change in mean chord length of the particles in the filtrates separated from pulps treated with different fixing agents

To see more clearly what happened as a result of polyamine treatment, the chord length distribution graph given directly by the iC-FBRB software was re-plotted and is shown here as Fig. 3. Compared to the blank one, where no fixing agent was used, all five of the polyamine treatments reduced the particle numbers dramatically, in the order A < B < C < D ≈ E. Another difference was that, when looking at the shape of the distribution peaks, it can be found that the shape of the PA-A curve was very similar to that of the blank curve, but the other four all shifted their peak center to the right. Again, this indicates that PA-A worked according to an almost ideal colloidal fixation mechanism, but the others had some colloidal agglomeration effects.

These differences can be enlarged by a statistical method called square-weighting (also included in the iC-FBRM software), the detail of which are given in Eq. 1,

$$Sqr_i = {(CL_i^2 \times n_i)}\Big/{(CL_{max}^2 \times n_{max})} \tag{1}$$

where *Sqr*i is the square-weighted count of particles *i* which have same chord length, *CL*i is the chord length of particles *i*, un-weighted, *n*i is the counts of particles *i*, un-weighted, *CL*max is the chord length of the particles with the maximal counts, un-weighted, and *n*max is the counts of particles with the maximal counts, un-weighted.

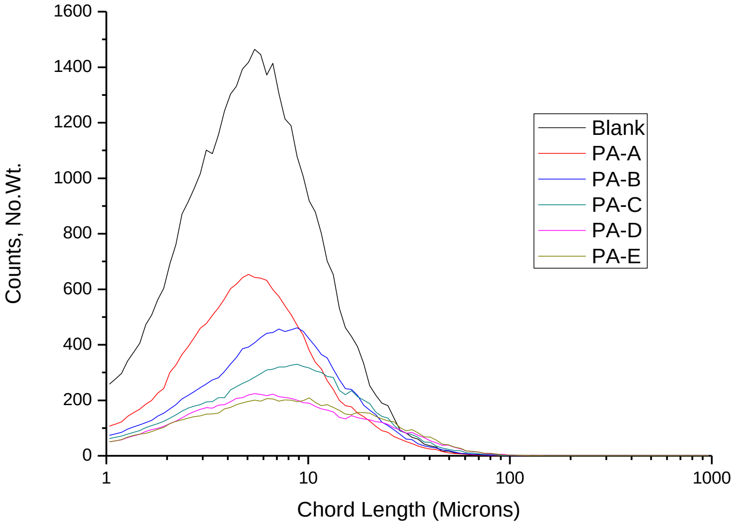

Fig. 3. Change in size distribution of the particles in the filtrates separated from pulps treated with different fixing agents (Note: values of particle counts were not weighted)

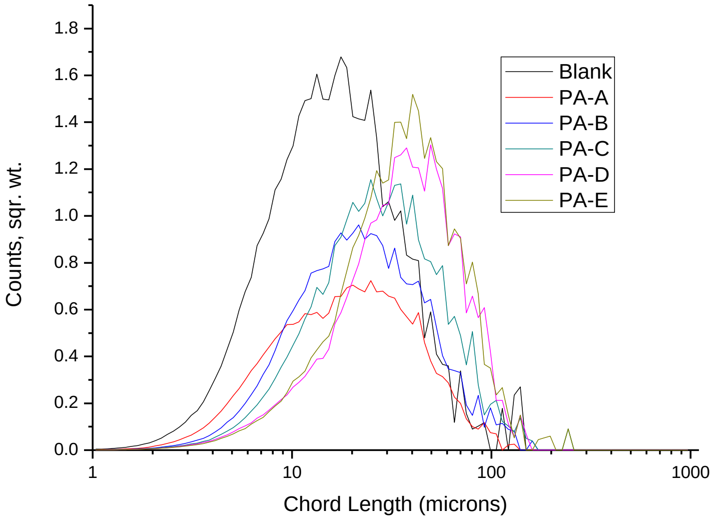

Fig. 4. Change in size distribution of the particles in the filtrates separated from pulps treated with different fixing agents (Note: values of particle counts were square-weighted)

The above method gives more weight to larger particles, and the result is shown in Fig. 4. Compared with Fig. 3, it can be seen more clearly that while the curve shape of PA-A remained almost the same as the blank curve, those for polyamines B, C, D, and E shifted more toward the large particle side, and the overall effectiveness still followed the order A < B < C < D ≈ E.

Overall, it can be seen that when the polyamine fixing agents were used on the pulp, colloidal fixation did occur, especially for polyamines with low molecular weight. It can also be concluded that higher molecular weight polyamines tended to cause more colloidal agglomeration. A comparion of PA-C and D can give strong support for this claim: although PA-D had the same charge density as PA-C, it had a higher molecular weight, and the colloidal agglomerating effect of PA-D was much stronger. However, this effect was also limited to some extent, as PA-D and PA-E had very similar overall performances, despite the fact that PA-E had a higher molecular weight and the same charge density as PA-D. Regarding the removal efficiency of colloidal substances, *i.e.*, the reduction in the amount of colloidal substances, polyamines with higher molecular weight were better, suggesting that some compromise might be taken in selecting a most proper fixing agent. The phenomenon also indicates that polyamines with higher molecular weight may produce larger colloidal aggregates which can be mechanically trapped by the fiber mat during filtration, or some aggregates can still be able to be fixed onto fiber due to residual cationic charges within the CS/fixing agent complexed aggregates. Further evidence to prove such conjectures are being studied by techiniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition, in this study, polyamines were added at the same dosage of 0.22% d/d, whether different dosage also affects the fixition mechanisms are also under studying. The results will be reported separetely.

CONCLUSIONS

1. Colloidal fixation, that is, colloidal substances being fixed onto fibers in their unagglomerated, single-particle state by polyamine fixing agents, did occur, especially after treatment with polyamines having relatively small molecular weights.
2. With higher molecular weights, polyamines tended to cause more colloidal agglomeration; however, their effects in reducing the total amount of colloidal substances were higher, suggesting that some compromise might be taken in selecting a most proper fixing agent.
3. FBRM is a powerful tool to differentiate colloidal fixation and colloidal agglomeration mechanisms in the field of using fixing agents to control the dissolved and colloidal substances in pulps; this can be beneficial in selecting a proper fixing agent.

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REFERENCES CITED

Allen, L. H., and Filion, D. (1996). "A laboratory white pitch deposition test for screening additives," *TAPPI Journal* 79(2), 226-232.

Blanco, A., Fuente, E., Negro, C., Monte, M. C., and Tijero, J. (2002a). "Focused beam reflectance measurement as a tool to measure flocculation," *TAPPI Journal* 1(10), 14-20.

Blanco, A., Negro, C., and Tijero, J. (2002b). "Flocculation monitoring: Focused beam reflectance measurement as a measurement tool," *The Canadian Journal of Chemical Engineering* 80(4), 1-7.

Esser, A., Rübenacker, M., Wirth, T., and Meixner, H. (2001). "Efficient white pitch treatment using tailor made fixing agents based on modified polyethylenimines and polyvinylamines," *Proceedings of 3rd Ecopapertech Conference*, June 4-8, Helsinki, Finland, pp. 245-257.

Gill, R. I. S. (1996). "Chemical control of deposits – Scopes and limitations," *Paper Technology* 37(7), 23-31.

Joo, D., Shin, W., Kim, Y., Kim, J., Choi, J., Choi, S., and Park, L. (2003). "Effect of polyamine flocculant types on dye wastewater treatment," *Separation Science and Technology* 38(3), 661-678.

Kail, N., Briesen, H., and Marquardt, W. (2008). "Analysis of FBRM measurements by means of a 3D optical model," *Powder Technology* 185(3), 211-222.

Kempkes, M., Eggers, J., and Mazzotti, M. (2008). "Measurement of particle size and shape by FBRM and in situ microscopy," *Chemical Engineering Science* 63(19), 4656-4675.

Leduc, M., McAllister, M., Sawicki, J., Todd, C., and Young, S. (2005). "New polymers for the treatment of coated broke in the manufacture of coated fine papers," *PAPTAC 91st Annual Meeting*, pp. D95-D98.

Lumpe, C., Joore, L., Homburg, K., and Verstraeten, E. (2001). "Focused beam reflectance measurement (FBRM) a promising tool for wet-end optimization and web break prediction," *Paper Technology* 42(4), 39-44.

Maher, L. E., Stack, K. R., McLean, D. S., and Richardson, D. E. (2007). "Adsorption behaviour of cationic fixatives and their effect on pitch deposition," *Appita Journal* 60(2), 112-119.

Mangold, M. (2012). "Use of a Kalman filter to reconstruct particle size distributions from FBRM measurements," *Chemical Engineering Science* 70(5), 99-108.

Miao, Q., Huang, L., and Chen, L. (2013). "Advances in control of dissolved and colloidal substances present in papermaking processes: A brief review," *BioResources* 8(1), 1431-1455.

Negro, C., Alonso, A., Blanco, A., and Tijero, J. (2006). "Optimization of the fiber cement composite process," *Industrial & Engineering Chemistry Research* 45(1), 197-205.

Neimo, L. (1993). "Coagulation of anionic fines and colloids originating in LWC broke," *Nordic Pulp and Paper Research Journal* 8(1), 170-175.

Pruszynski, P. (2009). "Understanding and controlling wet end chemistry related to BCTMP introduction to fine paper furnish," *Sino-Canada Workshop of HYP Technologies and Applications*, Ji'nan, China, p. 85.

Ruf, A., Worlitschek, J., and Mazzotti, M. (2000). "Modeling and experimental analysis of PSD measurements through FBRM," *Particle & Particle Systems Characterization* 17(4), 167-179.

Yu, L., Allen, L. H., and Esser, A. (2003). "Evaluation of polymer efficiency in pitch control with a laser-optical resin particle counter," *Journal of Pulp and Paper Science* 29(8), 260-266.

Zabihian, M., Lewis, C., Villanen, H., and Rintala, J. (2012). "The management of hydrophobic particle size for improved paper machine wet-end stability," *TAPPI PaperCon Conference*, New Orleans, LA, USA, p. 4.

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