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ABSTRACT

Inorganic cationic microparticles were used in the development of a novel retention aid system based on synthetic water-based colloidal alumina. Filler flocculation was effective when the cationic microparticles were used in conjunction with an anionic polyacrylamide of high molecular weight and low charge density. Moreover, these retention systems of cationic microparticles and anionic polymer are insensitive to shear stress and pH. The results obtained from pilot machine trials showed good agreement with the laboratory findings.

Application:

These retention systems could be used to improve mineral filler retention and achieve good formation in papermaking.

Retention aid systems of cationic microparticles and anionic polymer: experiments and pilot machine trials

CHERIE OVENDEN, HUINING XIAO, AND NICHOLAS WISEMAN

OVER THE LAST TWO DECADES, researchers have developed microparticulate retention aids that improve retention, drainage, and formation. When these retention aids are added to a pulp slurry, small, tight flocs form and adsorb to the furnish components. The resulting sheet has a uniform structure.

The microparticles effectively lock the suspended and dissolved solids in the sheet with the fibers and filler. The whitewater loop is kept clean if the system is used correctly (*1*, *2*). The key parameters for flocculation in microparticulate systems are the polymer charge density, the shape and surface chemistry of the microparticles, and the mode of microparticle interaction (*3–5*).

In this work, we focused on the use of cationic microparticles as a retention aid for clay filler. This retention aid was used either by itself or with a suitable polymer. The cationic microparticle system we used was a synthetic, water-based, colloidal alumina product. Unlike most other microparticles used in the papermaking industry, colloidal alumina is highly cationic and is "fibrous" in shape. With its highly positive charge and controllable particle size, it has the potential to be a wet-end additive for the retention of fine particulates.

BACKGROUND

Much of the literature on microparticle applications in the papermaking industry pertains to anionic microparticles used in conjunction with a cationic polymer of high molecular weight (*6*). In fact, the first two commercial systems (*7*) were based on (a) cationic starch with anionic colloidal silica (*8*) and (b) cationic polyacrylamide with anionic bentonite or montmorillonite (*9*).

Modifications to the original system of cationic starch and anionic colloidal silica have involved coating the surface of the silica with alumina to allow the anionic charge to be retained at a lower pH for acid conditions. Another approach has been to incorporate the alumina into the structure of the silica sol. Bentonite is a natural mineral rock that consists predominantly of smectite clay. The high aspect ratio and the plate-like structure of the bentonite give it ample bridging ability for enhancing retention. The success of the bentonite and cationic polymer system has been largely contingent on the papermaking furnish (*10*, *11*).

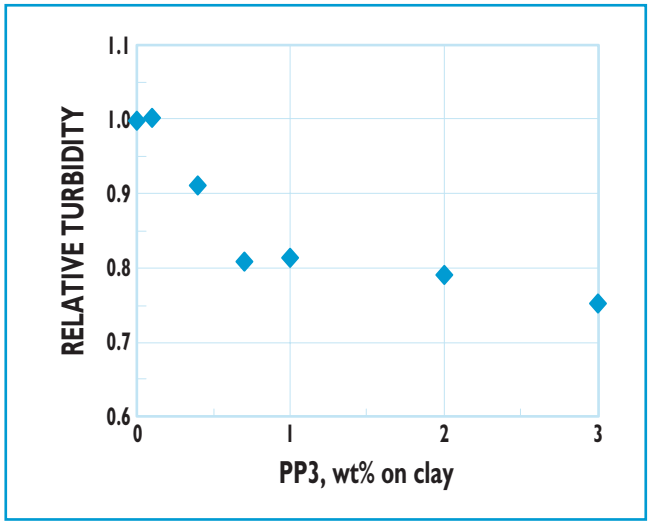
To date, commercial microparticle systems are based on anionic microparticles. Little work has been carried out on the use of cationic microparticles. However, a number of workers have patented cationic colloidal silica microparticles in which aluminium atoms have replaced some of the surface silica. Rushmere describes a system in which anionic polyacrylamide is used with a cationic silica sol (*12*). A patent by Svending describes a similar process for cationic colloidal silica (*13*), but Svending's system uses a cationic polymer such as CPAM (cationic polyacrylamide).

Ono and Deng studied synthetic cationic polymeric microparticles over a range of particle sizes and charge densities (*14*). They studied these particles as retention aids for negatively charged fibers and positively charged precipitated calcium carbonate (PCC) particles, both as a single-component system and with various charged polymers. However, systematic research on cationic microparticles appears to be limited (*15*).

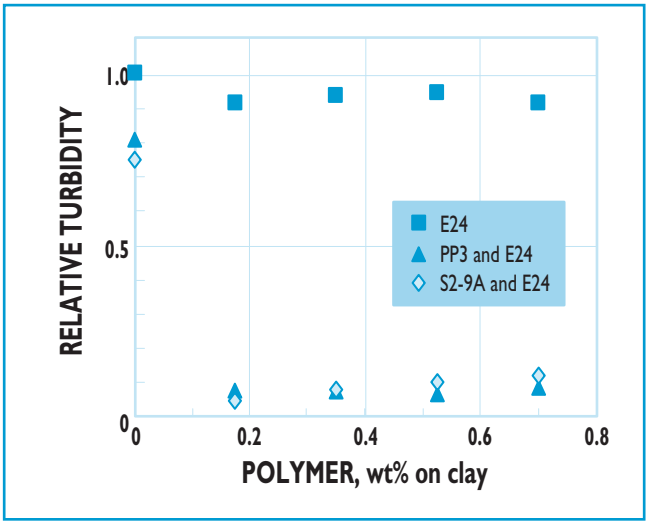
OBJECTIVES

Our objectives in this research were:

- To determine the performance of inorganic cationic microparticle samples as flocculants or retention aids for filler clay, alone and with anionic polymers
- To determine the factors that have an influence on the system, such as the ratio of polymer to cationic microparticles and the component dosages, pH, and shear stress
- To scale up laboratory findings and examine the performance of



1. Relative turbidity of the clay suspension (without fiber) at various dosages of PP3.



2. Clay relative turbidity for Percol E24 and for E24 with PP3 and with S2-9A.

cationic microparticles under more realistic conditions on a pilot paper machine and to establish the correlation between the laboratory findings and pilot plant results.

EXPERIMENTAL RESULTS AND DISCUSSION

Characterization of cationic microparticles

Table I shows the electrophoretic mobilities and particle sizes for two cationic microparticle samples, PP3 and S2-9A. During mobility measurements, we held the pH at approximately pH 3 with 6% acetic acid to obtain consistent results for the sake of making comparisons. The electrophoretic mobilities, or particle surface charge densities, proved to be similar for both samples, but the mean particle size of S2-9A is nearly ten times smaller than that of PP3.

Clay flocculation induced by cationic microparticles alone

Sample PP3 was used alone to flocculate clay in the absence of fibers, at dosages of 0.1–3.0 wt% on clay (clay suspension of 5 wt%). Figure 1 illustrates the effects of varying the dosage. A lower relative turbidity indicates better flocculation, where the relative turbidity is the final turbidity divided by the initial turbidity.

The relative turbidity decreases rapidly as the cationic microparticle dosage increases at the lower end. At around 0.7–1.0 wt% on clay, the relative turbidity levels off. Above 1.0 wt%, there is little further change. This high level of relative clay turbidity obtained with cationic microparticles alone indicates that only a small degree of flocculation is induced. A similar pattern of results was obtained with Sample S2-9A.

Clay flocculation induced by cationic microparticles and anionic polymers

The flocculation efficiency achieved by cationic microparticles alone appeared to be rather limited. In an effort to further improve the flocculation, we added an anionic polymer, Percol E24, to the clay suspension after PP3 was added.

	DELSA mobility, μ·cm/(V·s)	Zeta potential, mV	LS130 number mean, μm
Sample PP3	6.16	79.0	1.490
Sample S2-9A	6.64	85.2	0.167

pH = 3. Conductivity = 1.2 mS/cm.

1. Mobility and particle size of cationic microparticles

The cationic microparticles and anionic polymer each augmented the potential of the other component, creating a substantial synergy. The dual component systems gave greatly reduced turbidity, as Fig. 2 shows. The relative turbidity was reduced remarkably at a total dosage of flocculants of 0.875 wt% on clay (ratio of cationic microparticles to anionic polymer = 4:1). However, no further improvement of flocculation was achieved as the total dosage increased.

Clay flocculation in the presence of fibers

The clay and fibers were first mixed, and the cationic microparticle samples were used in conjunction with an anionic polymer. The cationic microparticle retention aid was added to the clay and fiber suspension as the first component, followed by the addition of the anionic polymer.

The results are shown in Table II. As in the case of clay without fibers, synergy was created between the components of the two-component system. Sample S2-9A appears to give better flocculation with the anionic polymer than does PP3.

Component	Relative turbidity
Percol E24	0.60
Percol E24 with PP3	0.31
Percol E24 with S2-9A	0.11

Cationic microparticles = 0.7 wt% on clay, and Percol E24 = 0.175 wt% on clay. Clay suspension = 5 wt%, pulp slurry = 0.5 wt%, and clay on fiber = 20%.

II. Comparison of clay flocculation (with fibers) as induced by cationic microparticle and anionic polymer

Anionic polymer property effect

We assessed anionic polymers of various molecular weights and charge densities, and the results are shown in **Table III**. The polymer with very high molecular weight (Percol 338) performed well both as a single-component flocculant and as part of a two-component system of polymer and cationic microparticles.

When used alone, the polymers with the "low" and "medium" charge densities gave better flocculation than did the more highly charged polymers. The synergy between cationic microparticles and these low-charge-density polymers was also further enhanced above that of the more highly charged polymers.

This synergistic enhancement is particularly striking for the case of Sample S2-9A. This case shows a large increase in flocculation for the dual system with anionic polymer (Percol 173) over the use of the polymer alone (0.01 vs. 0.30 relative turbidity). This result suggests that a polymer of low charge density and high molecular weight tends to interact via a bridging mechanism, where the polymer's tails and loops extend far into solution to connect with other particles and flocs.

Effect of pH on clay flocculation in a clay and fiber slurry

Figure 3 shows the results of varying the pH. When the cationic microparticle sample PP3 is used alone above about pH 6, there is little effect on the flocculation of the clay and fiber suspension.

At very low pH, the performance is greatly enhanced compared to performances over the rest of the experimental range. However, only one data point is available below pH 5, so its validity may be questionable.

Nevertheless, over the pH range commonly employed in papermaking, pH 6–9, spanning both acidic and alkaline processes, there is little pH dependence when cationic microparticles are used alone. When used alone, the anionic polymer appears to be much more dependent on pH, with its performance being impaired as the pH rises.

The dual component system has some dependence on pH, probably as a result of the sensitivity of the polymer to pH. However, even at the high pH of 10, the relative turbidity of the clay and fiber suspension filtrate is much lower than that of either of the single-component filtrates. Over the range of pH 6–9, the relative turbidity of the dual component system is quite favorable. Thus, it can be deduced that similar results in terms of flocculation may be achieved in both acidic and alkaline papermaking processes.

Effect of shear on flocculation

We examined the effect of shear on the filler flocculation in the presence of fibers by varying the propeller stirring speed of the dynamic drainage jar from 500 rpm to 1500 rpm. This range covers the shear rates experienced on most commercial paper machines (*16*). The results are presented in **Fig. 4**.

For PP3 alone, as the graph shows, the shear rate has little effect on the relative turbidity of the suspension. This outcome suggests that the clay flocs formed by cationic microparticles alone are resilient to the effects of shear. The causes may be the small size of the microparticles and the strong binding between the cationic microparticles and the clay. By contrast, the anionic polymer used alone appears to form flocs that degrade in size as shear increases. This outcome is likely to be a result of larger flocs being formed by bridging.

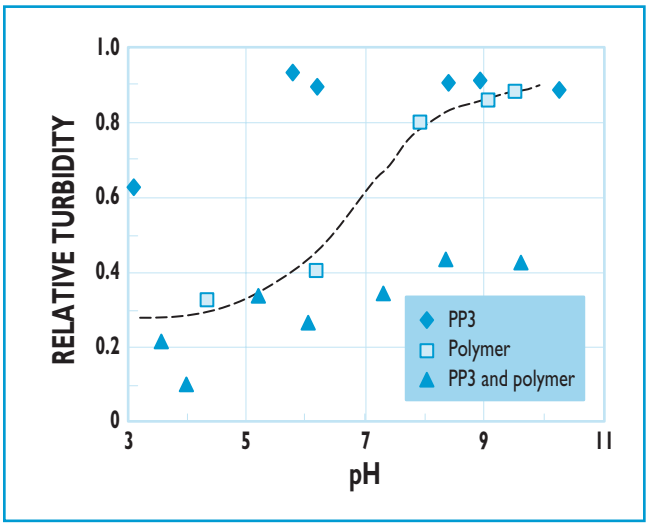
With the dual component systems, the relative turbidity increases as the shear rate rises until it rises above about 1000 rpm, where the relative turbidity tends to level off. This result has practical implications. If the flocs are resilient to shear, then retention will not drop off as a result of turbulence in the headbox or vibrations of the wire.

To study further the effects of addition order and shear on the size of clay flocs, we carried out tests with the cationic microparticle sample PP3 and anionic polymer Percol 173 under various shear conditions. The first component was added to the clay suspension with the stirring rate of the dynamic drainage jar set at 500 rpm. A sample of flocculated clay was withdrawn from the dynamic drainage jar for size analysis. The stirring rate was then increased to 1500 rpm for 60 s, and a second sample was withdrawn. Finally, the second

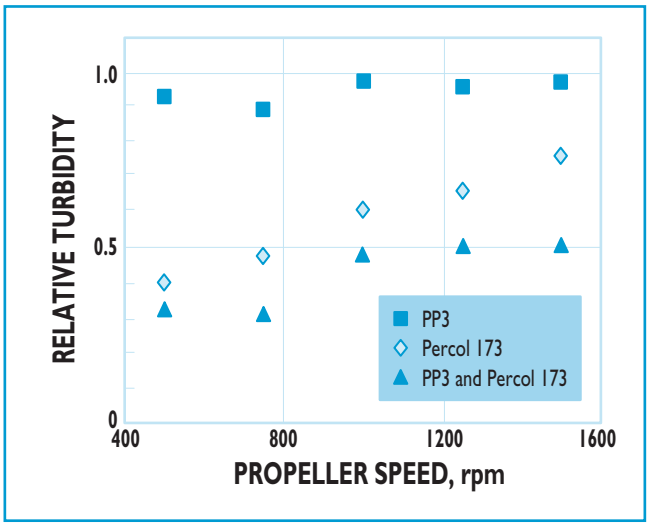
Polymer	Polymer charge density	Polymer molecular weight	Relative turbidity		
			Polymer alone	PP3 + polymer	S2-9A + polymer
Percol 173	low	high	0.30	0.12	0.01
Percol 338	medium	very high	0.19	0.07	…
Percol E24	high	high	0.60	0.31	0.11
Prcol 156	very high	very high	0.51	0.27	0.05

Cationic microparticles = 0.7 wt% on clay (0.7 wt% o.d. fiber), and Percol E24 = 0.175 wt% on clay. Clay suspension = 5 wt%, pulp slurry = 0.5 wt%, and clay on fiber = 20%.

III. Anionic polymer property effects



3. Effect of pH variations on flocculation for a clay and fiber suspension. (Clay suspension = 5 wt%, pulp slurrry = 0.5 wt%, and clay on fiber = 20%.)



4. Effect of variations in propeller speed on flocculation for a suspension of clay and fiber. (Clay suspension = 5 wt%, pulp slurry = 0.5 wt%, and clay on fiber = 20%.)

retention component was added with the stirring rate set at 500 rpm again, and a third sample was taken. The results for the LS130 size analysis are shown in **Table IV** both for PP3 added first and for Percol 173 added first.

Adding cationic microparticles after the anionic polymer results in large clay flocs, which may be detrimental to the finished sheet formation. However, when cationic microparticles are added as the first component, the results are more favorable. When cationic microparticles are added as the first component, high shear does not change the sizes of the flocs appreciably, which indicates that small, shear-resistant flocs form when the cationic microparticles are added first.

The rigid nature of the microparticles is such that they cannot flatten against the surface of the clay particles but must retain a discrete positive charge for interaction with the anionic polymer. Thus, when anionic polymer is added, the floc size grows, probably as a result of polymer bridging between the small flocs by the cationic component of the floc.

MACHINE TRIALS

Trial runs were carried out on the pilot paper machine at UMIST. The aim was to scale up the system of cationic microparticles and anionic polymer studied in the laboratory with the photometric dispersion analyzer (PDA) and the dynamic drainage jar. The cationic microparticle samples PP3 and S2-9A were used in conjunction with anionic polymer Percol 173.

Figure 5 shows the time variation of the backwater solids content for both the laboratory samples and the on-line data from the BTG consistency meter. The numbers represent each change in retention aid conditions. The pattern from the samples manually filtered in the lab follows a trend similar to that for the data from the consistency meter, for both total solids content and ash content. The backwater pH in the machine trials ranged from 5.2 to 6.2.

Table V compares the performances of cationic microparticles or polymer alone in both laboratory and machine trials. The relative turbidity data were obtained from lab-scale PDA experiments. Other data, including values for first-pass retention (FPR), first-pass ash retention (FPAR), and formation index were based on the machine trial and machine paper samples.

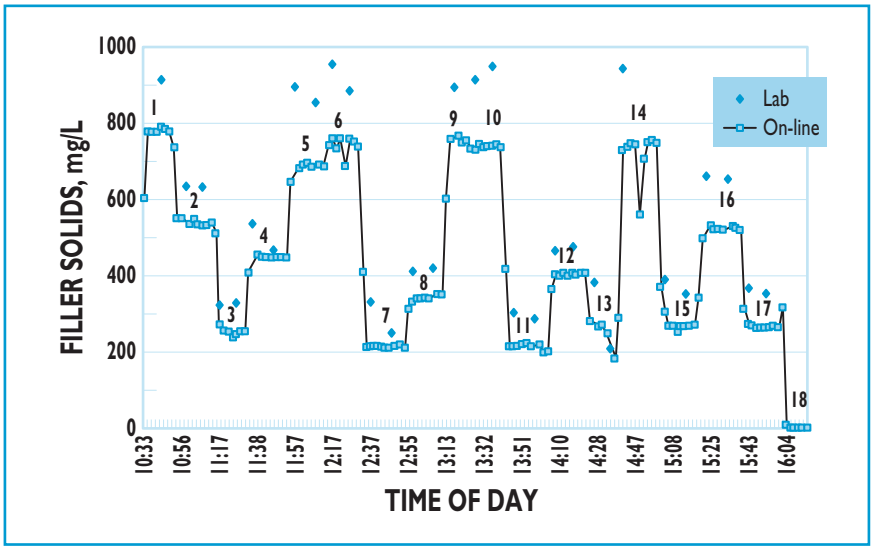
As the results show, the use of cationic microparticles alone at a reasonably high dosage has no effect on either the retention of the furnish components or the final sheet formation. However, the use of the anionic polymer alone gives only a slight improvement in retention, with formation being adversely affected. The higher the formation index, the better the sheet formation.

Sample	Speed, rpm	Mean size, µm: PP3 first	Mean size, µm: Percol 173 first
1	500	3.821	5.078
2	1500	3.855	4.672
3	500	15.380	20.960

IV. Clay floc sizes with PP3 and Percol 173

Table VI presents results for Runs 3, 4, and 5. For these runs, the actual ratio of anionic polymer to cationic microparticles was kept fixed at 0.16, but the total dosage of the two components was reduced from 0.132 wt% to 0.026 wt% on o.d. fiber. As the table shows, the FPR and FPAR percentages decreased.

At the low dosage of 0.026 wt% on o.d. fiber, there is little benefit in using the retention aid system in terms of improved retention, and the formation is also slightly impaired. The highest dosage of 0.132 wt% on o.d. fiber shows a dramatic increase in retention above the control situation of no retention aid added. However, this high dosage also has a dra-



5. Total solids content of the backwater in the machine trial.

Run	Retention aid	Total dosage	Relative turbidity*	FPR, %	FPAR, %	Formation index
control	none	n.a.	1.00	84.1	13.2	66.6
2	Percol 173	0.025	0.41	87.7	40.0	60.1
6	PP3	0.114	0.95	83.5	13.8	65.3
10	S2-9A	0.130	0.58	82.7	10.3	68.6

*Total component dosage for PDA, in weight percent on o.d. fiber: Run 2 = 0.026 wt%, Run 6 = 0.104 wt%, Run 10 = 0.14 wt%.

V. Machine trial performance for CM and anionic polymer alone

matic negative effect on sheet formation, whereas a moderate total dosage of 0.072 wt% on o.d. fiber gives good retention without taking a toll on formation.

One can discern the correlation between the laboratory experiments and machine trials by comparing the relative turbidity results and FPR values in Tables V and VI. Higher first-pass retention, corresponding to lower PDA relative turbidity, was recorded for most runs except for Run 10. In Run 10, Sample S2-9A by itself should have produced better first-pass retention. Overall, the retention values from the machine trial are in agreement with the relative turbidity results from laboratory PDA testing.

CONCLUSIONS

Inorganic cationic microparticles show limited effectiveness in inducing clay flocculation. However, a synergy develops between anionic polymers and cationic microparticles. An anionic polyacrylamide of high molecular weight and low charge density used in conjunction with cationic microparticles produced the best results for clay retention in the presence of fibers.

As a single-component flocculant used with clay and fibers, a cationic microparticle retention aid is insensitive to pH increases above pH 6. Over the normal process conditions of pH 6–8, the dual component system of anionic polymer and cationic microparticles is relatively insensitive to pH.

As a single-component flocculant, the cationic microparticle retention aid is relatively insensitive to the range of shear rates commonly encountered on a commercial machine. The dual component systems are also relatively resistant to shear.

Good agreement with the laboratory PDA results was obtained in a pilot plant trial. The system of cationic microparticles and anionic polymer improved both retention and formation at low dosages.

EXPERIMENTAL PROCEDURES

Materials

As the source of inorganic cationic microparticles, Octasol was supplied by Associated Octel Ltd. and was freshly diluted to 0.2-wt% solutions. Alphatex clay was supplied by English China Clays International, and a fiber suspension of 50:50 Lapponia pine and birch was used. Anionic polymers were supplied by Allied Colloids UK and were used without further purification.

Characterization of flocculation

We determined the efficiency of flocculation by passing the outlet of the laboratory dynamic drainage jar through the photometric dispersion analyzer (PDA 2000, Rank Brothers, UK) in a continuous loop back to the dynamic drainage jar. The outlet of the dynamic drainage jar was fitted with a 70-mesh screen.

To compare the flocculation induced, we used the relative turbidity, which was the turbidity of the final suspension divided by the turbidity of the unflocculated filler suspension. Turbidity was calculated by the intensity of the PDA signal, which follows the Beer–Lambert Law.

Characterization of cationic microparticles

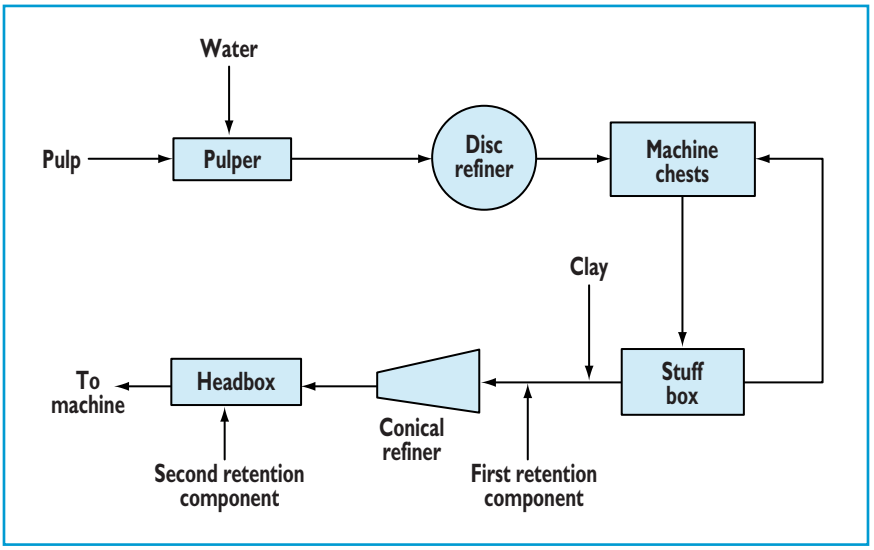
The particle sizes of the various cationic microparticles samples were measured with a Coulter LS130 Laser Sizer. We determined the density of the cationic surface charge of the microparticles by measuring the electrophoretic mobility and zeta potential with Coulter DELSA 440 equipment.

Pilot paper machine trial

In the pilot machine trial, we used a 50% mixture of hardwood and soft-

wood—birch and Lapponia pine. The thickstock was refined continuously with the in-line disc refiner. Alphatex clay (20 wt% on dry fibers) was dosed into the thickstock as a 25 wt% slurry after the disc refiner but prior to the high-shear conical refiner. The purpose of the conical refiner was simply to act as a mixer, providing no additional refining to the stock. As shown in **Fig. 1**, the first retention aid component was added to the clay and thickstock prior to the conical refiner, and the second component was dosed into the headbox.

For the cationic microparticles systems, the microparticles were always added as the first component. The backwater, headbox, and thickstock samples were collected and analyzed for total solids content and ash content for the determination of first pass retention (FPR) and first pass ash retention (FPAR). We also used an on-line consistency meter, a BTG PSA5000 Portable Suspension Analyzer. The formation of each final sheet was analyzed with a Valmet Kajaani Formation Analyzer. The formation index range was 20–122.4. **TJ**



6. Simplified flow chart of the wet-end process for the machine trial.

Run	Retention aids	Total dosage	Relative turbidity*	FPR, %	FPAR, %	Formation index
3	Percol 173 + PP3	0.132	0.34	93.9	70.5	55.2
4	Percol 173 + PP3	0.072	0.50	90.1	54.7	66.8
5	Percol 173 + PP3	0.026	0.78	84.2	18.3	62.0

The ratio of anionic polymer to cationic microparticles was 0.16 for all three runs. For PDA, the actual ratio of anionic polymer to cationic microparticles was 0.25 for all three runs.
*Total component dosage for PDA, in weight percent on o.d. fiber: Run 3 = 0.13 wt%, Run 4 = 0.07 wt%, Run 5 = 0.025 wt%.

VI. Machine trial performance for CM and anionic polymer at fixed ratio

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