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SHORT COMMUNICATION

W. P. Hsu
M. Kosmulski
E. Matijević

Retention of whiteners in fibrous mats

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W. P. Hsu · M. Kosmulski
E. Matijević (✉)
Center for Advanced Material Processing
Clarkson University, Potsdam
NY 13699-5814, USA

Abstract The retention performance of pigment whiteners was studied in an experimental papermaking process to illustrate the interactions between whitener particles and the cellulose fibers in the presence of retention aids (polyamine and alum). Special emphasis is paid to the effects of the electrokinetic properties of the reactants.

Key words Cellulose fibers · Papermaking · Pigment retention · Retention aids · Whiteners

Introduction

One of the intriguing phenomena of colloid and polymer science is the pigment uptake in a semidilute-to-concentrated cellulose dispersion, containing various papermaking retention aids (alum, polyelectrolytes, etc.) and/or sizing agents [1–19]. The system is complex in its own right, and it is certainly of great interest in the history of papermaking.

Paper is a mat of cellulose fibers, consisting of various degrees of fiber cuttings. To increase the sheet strength and consistency, an adequate mixture of long and short fibers is needed. Short fibers are known to fill between longer ones and are held to each other by hydrogen bonding through the fairly large population of hydroxyl groups; hence, water molecules play an essential role in bridging the latter together. The degree of swelling comes from a combination of fiber flexibility and the ability of fibrils to interact with the solvent components [20, 21].

The mechanisms for wet-end retention of pigments and fine fibers have been analyzed by various methods, including their electrokinetic properties [15–17]. Haslam and Steele [3] postulated three processes to be important, i.e., filtration by the fibrous mat, entrapment in fiber pores, and coagulation. Several studies led to the conclusion that optimum pigment retention occurred at the charge neutralization point of the fiber surface, resulting in the flocculation of the systems [5–8]. A bridging mechanism [9–11] was also proposed, based on the chemical complexation of hydroxyaluminum and sulfate ions with the fiber surface in the presence of a retention-aid polymer.

In this work, three different types of whiteners (rutile, silica-coated rutile, and titania-coated silica) were used with the additions of retention aids (alum and Retaminol-K, Ret-K). It was also shown that electrokinetic potentials of all constituents play an important role in the system studied, but that other properties of the components should also be taken into consideration.

Experimental

Materials

Two pulps, consisting of short and long fibers, were a gift from the CDM Corporation (Drummondville, Quebec). The weight of the dry pulp content in water, containing a small amount of formaldehyde, was around 90%. Before use, the samples were oven-dried at 105 °C until constant weight.

Ret-K (Bayer, Germany) is a cationic polyamine, which has been used in the production of laminated papers, especially for whitener retention in the acid-sized paper.

All chemicals, including alum [$Al_2(SO_4)_3 \cdot 18H_2O$], were of reagent grade and deionized water was used in the sample preparations.

The three whiteners were a commercial titanium oxide rutile (DuP, E.I. DuPont), a silica-coated rutile (RLP, WKP, Stuttgart, Germany), and a titania-coated silica (XWG) powder and they were prepared as described elsewhere [22].

Sampling of papers

To make a sheet of the experimental paper, a 200 cm^3 aqueous suspension, containing 210 mg of short and 70 mg of long fibers (a 3:1 pulp), 100 mg of the whitener, and additives, was stirred in a blender for 2 min at the highest speed. The suspension was then poured into a vertical drainage jar (6.7 cm in diameter) with a standard nylon screen (40–50-μm mesh size), fixed to its bottom. After the suspension had settled for 2 min, the white water was removed and the paper was dried at 60 °C until constant weight. The sheets of paper, 35 cm^2 in size, weighed around 85–100 g/m^2, depending on the retention of the pulp.

Analyses

The retention of the pigment whiteners in the paper was determined by thermogravimetric analysis in air. The amount of the whitener remaining in the filtrate ("white water") was measured by light scattering using a predetermined calibration curve. The sum of the pigment content in the paper and the normalized values obtained from the white water was 100 ± 2%.

The electrophoretic mobilities of the whitener particles at different pH values were determined only in KCl (10^{-3} mol dm^{-3}) solutions and in the white water media with a DELSA 440 SX instrument (Coulter Electronics). In the latter case, the measurements were made with pigments after the pulp had been removed. The electroosmosis measurements with cellulose short fibers in the presence of additives were carried out in an apparatus described previously [23]. The technique consists in following the flow of the dispersion liquid caused by an electric field applied across a stationary porous plug made up of cellulose (around 1 g), under conditions of equal pressure at both electrodes. The actual flow was measured by the motion of an air bubble in a capillary tube, connected to the main cell compartments on each side of the plug.

Results

Characterizations of whiteners

The average particle sizes of the three whiteners, as determined by the Coulter N4 particle analyzer, as well as the specific surface area (Brunauer–Emmett–Teller), density, and conductivity (1 wt% dispersions) data, are given in Table 1. The electrophoretic mobilities of the whiteners as a function of the pH in 1×10^{-3} mol dm^{-3} KNO_3 are plotted in Fig. 1. The rutile particles are positively charged up to pH ~ 6, while the isoelectric point (IEP) of titania-coated silica (XWG) is at pH ~ 4.5. As expected, the silica-coated RLP sample is negatively charged at pH > 4.

Cellulose fibers in white water

The cellulose fibers at low ionic strength are negatively charged, as measured by electroosmosis, while in the presence of 10 mg dm^{-3} Ret-K, a reversal of charge of the fibers from negative to positive was observed over the entire pH range studied (Fig. 2).

Table 1 Physical properties of whiteners used in this study

Whiteners	DuP	XWG	RLP
Composition	Rutile	Titania-coated silica	Silica-coated rutile
Average particle size (μm)	0.4	0.9	0.3
Specific surface area (m^2/g)	9.1	5.3	12.1
Density (g/cm^3)	4.2	2.8	4.1
Conductivity 1% concentration (μS/cm)	23	3.4	16

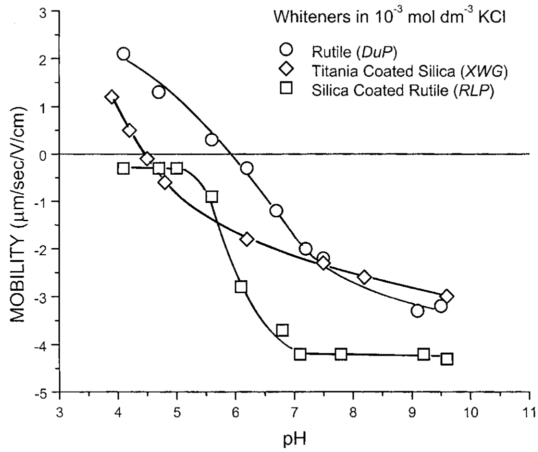

Fig. 1 Electrophoretic mobilities of whiteners, rutile (*DuPont*), silica-coated rutile (*RLP2*), and titania-coated silica (*XWG*), as a function of the pH in 1×10^{-3} mol dm^{-3} KCl

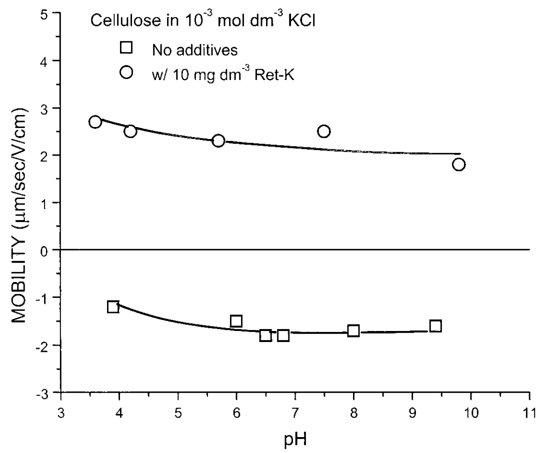

Fig. 2 Electro-osmotic mobilities of cellulose fibers in 1×10^{-3} mol dm^{-3} KCl in the absence and in the presence of 10 mg dm^{-3} Retaminol−K (*Ret*−K)

Whitener retention

Figure 3 shows that the uptake of the whitener XWG in the presence of 0.075 mmol dm^{-3} alum increases with the addition of Ret-K until a saturation limit is reached at ~10 mg dm^{-3}. In another series of experiments, the retention of XWG in the presence of 10 mg dm^{-3} Ret-K was measured as a function of the alum concentration, and a maximum was found at 0.08 mmol dm^{-3} alum (Fig. 4). The pH of the dispersions was not adjusted in these experiments.

The retention of the three whiteners was also studied in two mixed systems as a function of the pH. Thus, Fig. 5 shows that the uptake of pigments in mixture A (0.1 wt% Ret-K, 0.2 wt% alum, 15 wt% whiteners, 45 wt% 3:1 pulp) is the highest over the acidic pH and decreases abruptly at pH > 7.5. In mixture B (0.8 wt% Ret-K, 0.4 wt% alum, 15 wt% whiteners, 45 wt% 3:1 pulp) the concentration of polyamine is significantly higher, and a shift of the retention maxima is observed for the three systems to the alkaline pH values (Fig. 6).

The corresponding electrokinetic data, displayed in Fig. 7, clearly show distinct shifts of the IEP values with the increasing amount of Ret-K for all three whiteners.

Pulp settling

The rate of the pulp settling, as affected by the presence of the retention aid, is displayed in Fig. 8, which shows that the cellulose fibers settle faster in the absence of additives, except for alum.

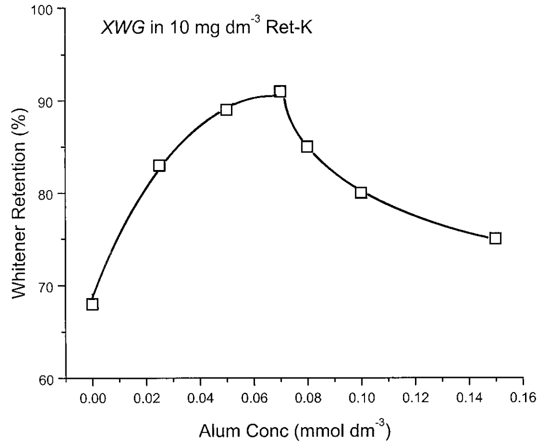

Fig. 4 Retention of the XWG whitener as a function of the alum concentration in the presence of 10.0 mg dm^{-3} Ret-K

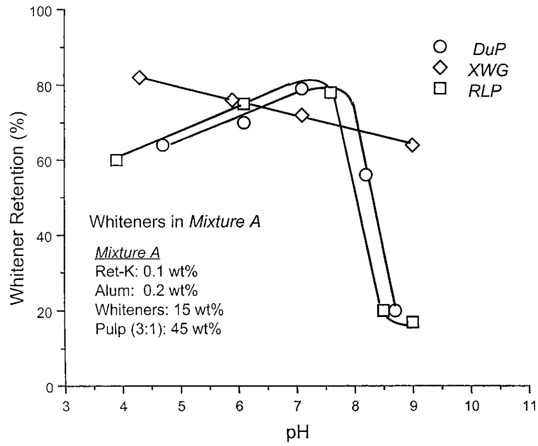

Fig. 5 Retention of whiteners DuP, XWG, and RLP as a function of the pH in mixture A

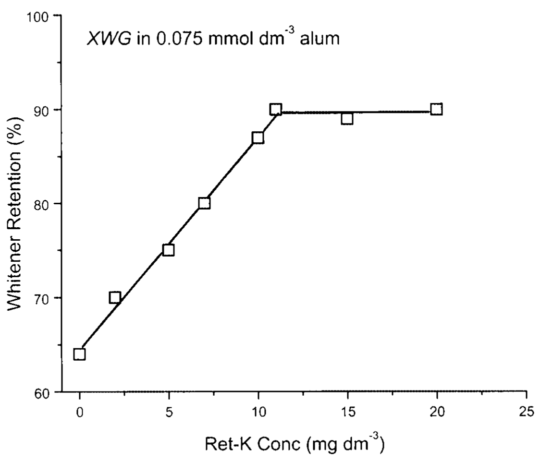

Fig. 3 Retention of the XWG whitener as a function of the Ret-K concentration in the presence of 0.075 mmol dm^{-3} alum

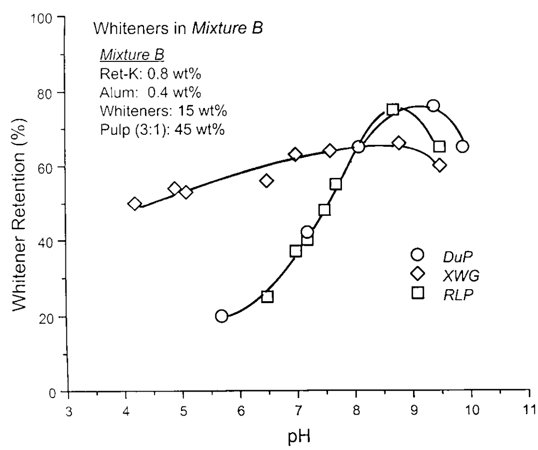

Fig. 6 Retention of whiteners DuP, XWG, and RLP as a function of the pH in mixture B

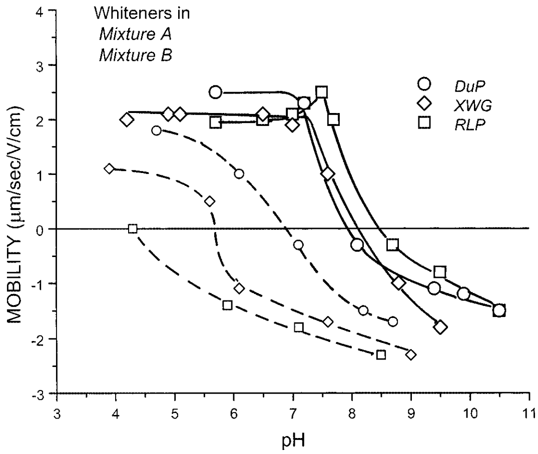

Fig. 7 Electrophoretic mobilities of whiteners DuP, RLP2, and XWG as a function of the pH in mixture A (- - - -) and in mixture B (——), respectively

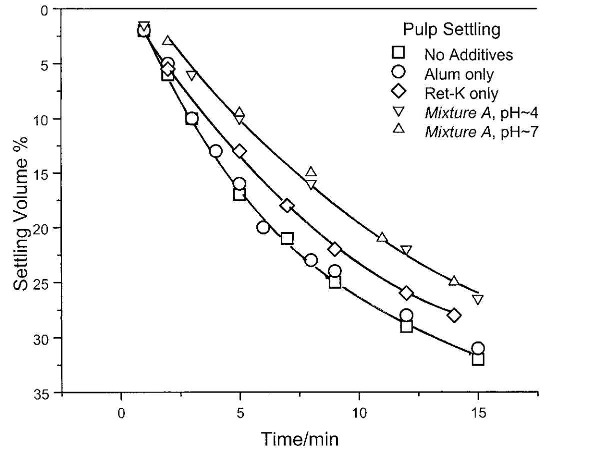

Fig. 8 The effect of the retention aids on the pulp settling volume of cellulose containing no additives (□), 10 mg dm^{-3} Ret-K (○), 0.01 mmol dm^{-3} alum (◇), and mixture A at pH 3.9 (△) and 7.1 (▽), respectively

Discussion

The systems described in this study contain polyamine (Ret-K) as the retention aid and alum, in addition to pulp and pigment. Thus, the results need to be reviewed by considering all components of the mixtures. Figure 3 clearly shows the uptake of the pigment to be strongly dependent on the amount of Ret-K, while keeping all other components the same. The mixture also contains alum, which has been one of the most commonly used nonfibrous materials in the paper industry since the nineteenth century. The beneficial effect of alum in pigment retention is revealed in Fig. 4, which also shows that above a given dose the effect is reversed, i.e., the uptake is greatly reduced. This finding is most likely related to the coagulation effect of alum on the whitener above a critical ionic strength, resulting in a fast settling rate of the flocculated pigment. As a result, less entrapment in the fiber mat takes place. It is interesting to speculate on the role of alum in the system studied. It is a well-known fact that over the pH range of interest aluminum ions hydrolyze and the resulting complex species strongly adsorb on lyophobic colloids such as silver halides or polymeric latex, causing their charge to be reversed from negative to positive [5, 24, 25]. However, cellulose behaves quite differently, i.e., no charge reversal could be established when the aluminum salt was added to the microcrystalline cellulose over the entire pH range [26]. It would seem that hydrolyzed aluminum ions in aqueous media may condense with some hydroxy groups of the pulp fibers, essentially causing them to partially dehydrate, which then makes it easier for the Ret-K molecules to approach the fiber and interact with the surface sites.

Figure 8 shows that the settling rate of cellulose fibers depended of the composition of the pulp additives. With the addition of Ret-K and alum (mixture A), the settling rate was much reduced. The mechanical forces induced by shear activate the unfolding of native structures, resulting in swelling. The extent of swelling is promoted by the addition of the retention aid, which penetrates into the microfibrils, causing a loosening of fiber–fiber bonds. This effect is also synergistic, because its effectiveness was much less in the presence of a single additive. Probably, the most revealing finding is summarized in Figs. 5 and 6, which demonstrates a significant effect of the concentration of Ret-K on the retention of all three whiteners as a function of the pH. A comparison with the corresponding electrokinetic data shows that the maximum retention took place at pH values at which the whiteners were negatively charged, i.e., the retention was favorable in the acidic pH region in the presence of a low content of Ret-K and in the basic region when a higher amount (8 times) of the retention aid was added. Thus, in these examples the electrostatic effects seem to dominate, since the cellulose fibers were positively charged owing to the presence of Ret-K (Fig. 2).

However, there is a marked difference in the behavior of titania-coated silica (XWG) when compared to the other two pigments. The XWG particles are much larger in size with a lower density and dispersity, so they are more readily trapped by the fiber matrix.

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