

ORIGINAL ARTICLE

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Retention behavior of size and aluminum components in handsheets prepared in rosin soap size–alum systems*

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Abstract Handsheets were prepared with rosin soap size and aluminum sulfate under various conditions, and the retention behavior of the rosin size and aluminum components in the handsheets was studied. Pyrolysis–gas chromatography and X-ray fluorescence analysis were used to determine the size and aluminum contents in the handsheets, respectively. When the addition level of rosin soap size varied from 0% to 4% and that of aluminum sulfate was fixed at 2%, the rosin size content increased with the increase in the size addition level, whereas aluminum and calcium contents were roughly constant. Under these conditions, handsheets prepared from fines-free pulp had aluminum contents less than those for the original beaten pulp, probably because the former pulp had a carboxyl content less than that of the latter pulp. Not only the conventional rosin retention mechanism but also mechanism proposed below must exist in the rosin soap size–alum systems. That is, some aluminum compounds originating from aluminum sulfate are adsorbed on pulp fibers immediately after the aluminum sulfate addition. These adsorbed aluminum compounds form cationic sites on pulp fibers, and free rosin acid components with anionic charges are then adsorbed onto the cationic sites of pulp fibers at the wet-end.

Key words Rosin soap size · Aluminum sulfate · Retention · Sizing · Paper

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Introduction

Rosin soap size–alum systems were developed for internally sizing paper about 200 years ago. Some new techniques using rosin emulsion sizes and rosin ester sizes have been developed on the basis of the traditional rosin soap size–alum systems and have become predominant for producing papers under weakly acidic or neutral conditions. Even now, however, the rosin soap size–alum systems are used in part for producing some acidic paper at pH 4–5. The retention mechanism of rosin size in the rosin soap size–alum systems at the wet-end and its sizing mechanism after drying the paper have been extensively studied. The studies mainly focused on surface charges and chemical structures of colloidal size precipitates, which are formed from rosin soap sizes by the addition of alum or acid solutions in either deionized water or pulp suspensions.

When an alum solution is added to an alkaline rosin soap size solution, colloidal precipitates are formed in the solution, and its pH is decreased. Because (1) surface charges of these precipitates were cationic at pH 4–6, (2) they consisted of aluminum dirosinate and free rosin acid (about 1:1 by molar ratio), and (3) powdered pulp fibers always had anionic surface charges in water even after alum addition, adsorption of cationic rosin–aluminum precipitates on anionic pulp fibers by electrostatic interactions at the wet-end seems to have been well established as the predominant retention mechanism of rosin size in the rosin soap size–alum systems.[1–5] In contrast to the above result (3),[2,4] amorphous pulp particles prepared by regeneration from nonaqueous pulp solutions had cationic surface charges in water for some time after adding aluminum sulfate.[6] Microparticles (about 0.1 μm in diameter), presumably owing to the rosin–aluminum precipitates, were observed on handsheet surfaces by scanning electron microscopy (SEM).[7] Strazdins[8,9] pointed out that not only the electrostatic interactions but also van der Waals forces between hydroxyl groups of pulp fibers and rosin–aluminum precipitates were important for the retention of the rosin size components in paper. As to the size retention sites on pulp fibers, abundant hydroxyl groups and small amounts of carboxyl groups originating from uronic acids of hemicellulose in pulps were their candidates.[9] Effects of calcium ions in pulp suspensions and maleopimaric acid components in fortified rosin soap sizes on sizing performance were studied in terms of aluminum rosinate formation in dried paper.[10,11] Analyses of solvent extracts from rosin-sized handsheets indicated that aluminum components formed polyaluminum compounds in the handsheets, and these compounds formed coordinate bonds with rosin acids and hydroxyl groups of pulp.[12]

Because it had been generally difficult to determine rosin size content in paper samples (e.g., by extraction–gas chromatography methods), relations between rosin size content and sizing degree were not studied systematically for a long time. Lindström and Söderberg[13] first tried to elucidate the relation between them using a radioactive fortified rosin soap size prepared from ^{14}C-labeled fumaric acid and rosin acids, in terms of amounts of rosin soap size and alum added, pulp consistency, effects of calcium ions in pulp suspensions, and other factors. Their results showed that retention values of rosin size were less than 50% when the handsheets were prepared with 1%–2% (based on the dry weight of pulp) rosin soap size and 1%–2% (based on the dry weight of pulp) alum at 0.045%–2.000% pulp consistency.[13–15] Furthermore, the effect of the stirring conditions of pulp suspensions, the additions of cationic polymers and fillers, the addition sequences of size and alum, the temperatures of the pulp suspensions, and the presence of fines fraction and anionic trashes on retention of rosin size and sizing performance of the handsheets were studied using similar techniques to determine the rosin size content.[16–19] However, the technique using ^{14}C-labeled fortified rosin size cannot be applied to paper samples prepared under practical conditions; and aluminum contents, which must be significant for rosin size retention, have not been determined easily. On the other hand, more accurate and facile determination methods of rosin size and aluminum contents in handsheets have become possible by pyrolysis–gas chromatography and X-ray fluorescence analysis, respectively.[20–24]

In this study, therefore, handsheets were prepared from a beaten pulp and its fines-free pulp with a rosin soap size and aluminum sulfate under various conditions; and the rosin size and aluminum contents in the handsheets were determined. Furthermore, the retention mechanism of rosin size in the rosin soap size–alum system was discussed on the basis of the retention behavior of rosin size and aluminum components in the handsheets.

Materials and methods

Materials

A commercial bleached hardwood kraft pulp was beaten to 450ml Canadian Standard Freeness with a PFI mill. A fines-free pulp was obtained from the above beaten pulp in 79% yield using a fiber classifier by removing the fines fraction according to the Tappi test method.[25] A fortified rosin soap size used was a commercial product (completely saponified with KOH) (Japan PMC Co.). Aluminum sulfate and other chemicals used were of special grade (Wako Chemicals Co., Japan). The tap water used for handsheet production contains Ca and Mg ions at 0.60mEq/L and 0.22mEq/L, respectively.

Handsheet production

Certain amounts of the rosin soap size and aluminum sulfate were added in 1% solutions to a 0.15% pulp suspension with continuous stirring. Then a 0.1N HCl solution was added to the pulp suspension to adjust it to pH 4.5. The interval between the size and aluminum sulfate additions and that between the aluminum sulfate and 0.1N HCl additions were set to 30s. After stirring for 30s, the pulp suspensions were subjected to the preparation of handsheets with a basis weight of 60 g/m^2 using tap water according to the Tappi test method.[26] Wet-pressed handsheets were dried at 20°C and 65% relative humidity for 1 day. A part of the handsheets were then heated at 105°C for 20min in an oven.

Analyses

Carboxyl contents of pulps were determined according to the Tappi test method.[27] The distribution of pulp fiber length was measured using an automatic fiber length analyzer (FS-200, Kajaani Electronics, Finland) and expressed as weight average fiber lengths. Brunauer-Emmett-Teller (BET) specific surface areas of freeze-dried pulps were measured using a nitrogen adsorption apparatus (Omnisorp 100CX, Coulter Co., USA). Rosin size contents in the handsheets were determined by pyrolysis–gas chromatography (PY-GC) using the on-line methylation technique with tetramethylammonium hydroxide.[20–23] A scanning electron microscope (SEM) (S-4000; Hitachi Co., Japan) was used for observing the surfaces of the handsheet samples after Pt-Pd coating. An X-ray fluorescence analyzer (XFA) (MESA 500, Horiba Co., Japan) was used to determine aluminum and calcium contents in the handsheets under the conditions reported in a previous paper.[24]

Results and discussion

Effect of size addition level on size and aluminum contents in handsheets

Figure 1 shows the distributions of fiber length of the original beaten pulp and the fines-free one. Weight average fiber lengths of the original beaten pulp and the fines-free one were 0.73mm and 0.80mm, respectively (Table 1). Although the BET specific surface areas of the two pulps, which were determined by the nitrogen adsorption method, were roughly equal to each other, their carboxyl contents were clearly different. The fines fraction had a carboxyl content of about 0.11 mEq/g when calculated on the basis of the carboxyl contents of the pulps and their weight percentages. This value was more than twice as much as that of the coarse fiber fraction in the beaten pulp.

When the addition level of aluminum sulfate was 2% (based on the dry weight of the pulp), sizing degrees of the handsheets increased with increasing the level of rosin soap size added from 0 to about 1% (based on the dry weight of pulp); they reached plateau levels at a size addition level of more than about 1% (Fig. 2). The heat treatment brought about higher sizing degrees. The handsheets prepared from the fines-free pulp had higher sizing degrees than those prepared from the original beaten pulp, but this difference was ascribed to handsheet thickness. The handsheets prepared from the fines-free pulp were thicker than those for the original beaten pulp when they had the same basis weight. In fact, the sizing degrees became roughly equal between the handsheets prepared from the two pulps after correction using their thickness values on the basis of the Lucus-Washburn equation.[28]

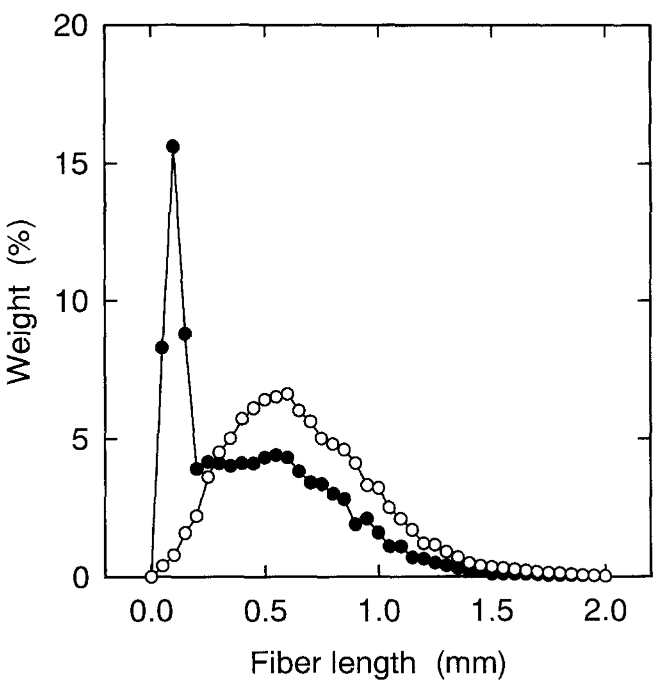

Fig. 1. Distribution of fiber length of the original beaten pulp (*filled circles*) and the fines-free pulp (*open circles*) used in this study

As shown in Fig. 3, rosin size contents in the handsheets increased with an increasing amount added in a manner similar to that for the two pulps. The results of Figs. 2 and 3 indicate that a rosin size content of more than 2 mg/g was necessary for the appearance of sizing features on the handsheets when this rosin soap size–alum system was used. On the other hand, because the sizing degree reached plateau levels at a rosin size content of more than about 5 mg/g, excess rosin size components of more than 5 mg/g did not contribute to sizing development. Retention values of the rosin size were less than 50% in the whole range of the size addition level examined in this study.

Figure 4 shows the aluminum and calcium contents in the handsheets prepared with 0%–4% (based on the dry weight of pulp) rosin soap size and 2% (based on the dry weight of pulp) aluminum sulfate at pH 4.5. The aluminum and calcium contents were roughly constant to the addition level of the rosin soap size in the range of 0.5%–4.0% (based on the dry weight of pulp). The handsheets prepared from the fines-free pulp had aluminum contents about 20% less than those of the handsheets prepared from the original beaten pulp. This difference in aluminum contents between the handsheets prepared from the two pulps must be ascribed to the difference in carboxyl contents between them rather than that in their BET specific surface areas (Table 1). The tap water used in this study for handsheet production contains Ca and Mg ions at 0.60 and 0.22 mEq/L, respectively, and these ions may be entrapped in the handsheets as counterions of the retained rosin acids. As shown in Fig. 4, however, the calcium content in the handsheets was roughly constant based on the size addition level for the handsheets prepared from the two pulps. Nearly no magnesium ions were entrapped in the handsheets. These results on the aluminum and calcium contents in the handsheets provide some information concerning the retention mechanism of rosin size in the rosin soap size–alum systems (described later).

Effect of alum addition level on size and aluminum contents in handsheets

Figure 5 shows the sizing degrees of the handsheets prepared with 1% rosin soap size and 0%–2.2% (all percents

Table 1. Properties of the original beaten pulp, its fines-free pulp, and the fines fraction

Sample	Weight ratio (%)	Average fiber length (mm)	Carboxyl content (mEq/g)	BET specific surface area (m^2/g)
Original beaten pulp	100	0.73	0.0625	0.7
Fines-free pulp	79	0.80	0.0489	0.7
Fines fraction	21[a]	0.48[a]	0.1104[a]	0.7[a]

BET, Brunauer-Emmett-Teller

[a] These values are indirectly obtained by calculation on the basis of the data for the original beaten pulp and fines-free pulp

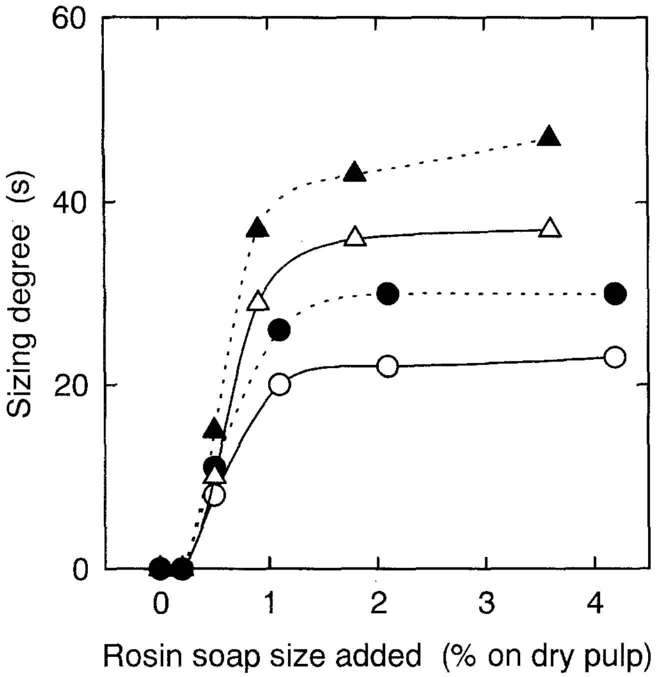

Fig. 2. Sizing degree of handsheets prepared from the original beaten pulp (*circles*) and the fines-free pulp (*triangles*) with 0%–4.2% (based on the dry weight of the pulp) rosin soap size and 2% (based on the dry weight of the pulp) aluminum sulfate at pH 4.5. *Solid lines*, dried at 20°C; *dashed lines*, cured at 105°C for 20 min

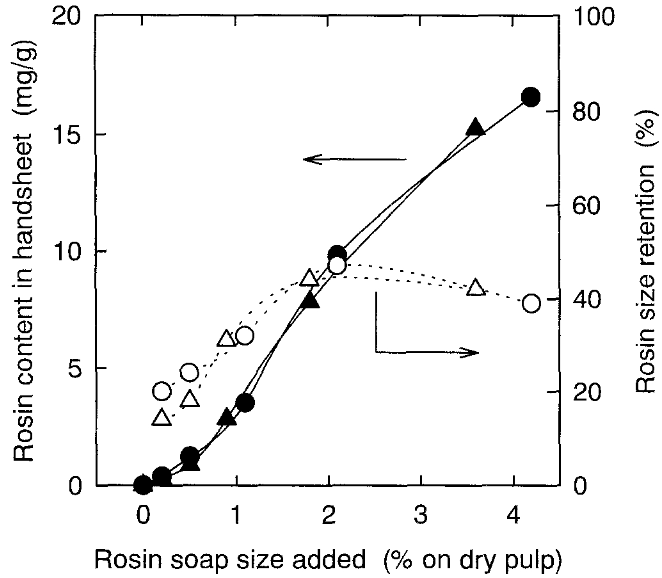

Fig. 3. Rosin size content in handsheets prepared from the original beaten pulp (*circles*) and the fines-free pulp (*triangles*) with 0%–4.2% (based on dry weight of pulp) rosin soap size and 2% (based on dry weight of pulp) aluminum sulfate at pH 4.5. Right axis shows retention values of rosin soap size in handsheets. See legend to Fig. 2 for other explanations

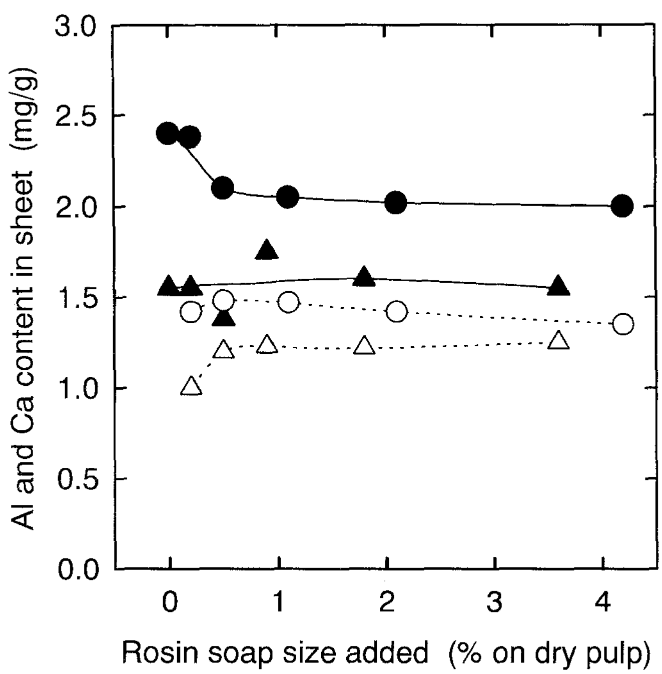

Fig. 4. Aluminum (*filled symbols*) and calcium (*open symbols*) contents in handsheets prepared from the original beaten pulp (*circles*) and its fines-free pulp (*triangles*) with 0%–4.2% (based on dry weight of pulp) rosin soap size and 2% (based on dry weight of pulp) aluminum sulfate at pH 4.5

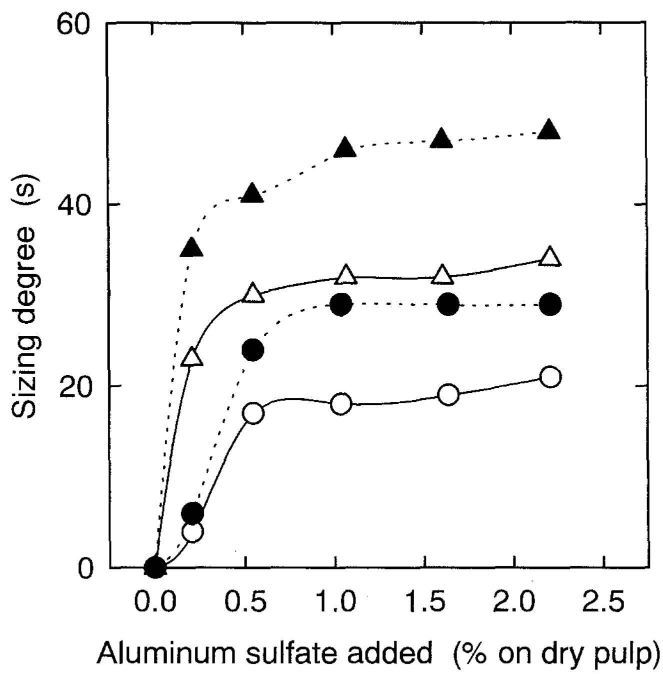

Fig. 5. Sizing degree of handsheets prepared from the original beaten pulp (*circles*) and its fines-free pulp (*triangles*) with 1% (based on dry weight of pulp) rosin soap size and 0%–2.2% (based on dry weight of pulp) aluminum sulfate at pH 4.5. *Solid lines*, dried at 20°C; *broken lines*, cured at 105°C for 20 min

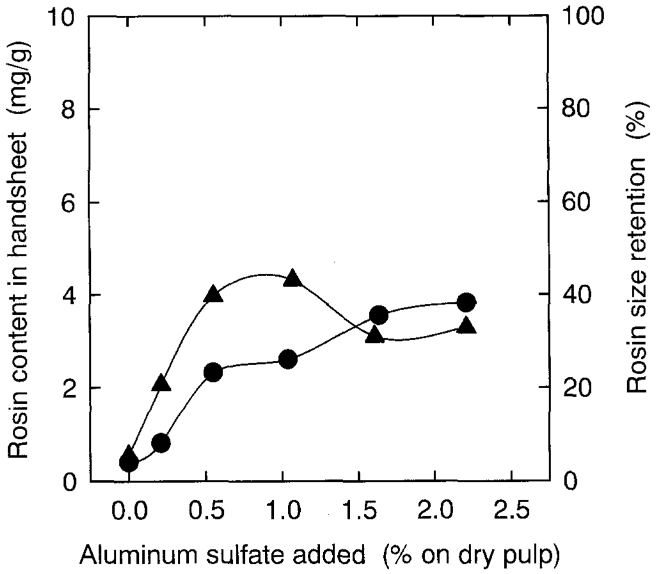

Fig. 6. Rosin size content in handsheets prepared from the original beaten pulp (*circles*) and its fines-free pulp (*triangles*) with 1% (based on dry weight of pulp) rosin soap size and 0%–2.2% (based on dry weight of pulp) aluminum sulfate at pH 4.5. Right axis shows retention values of rosin soap size in handsheets

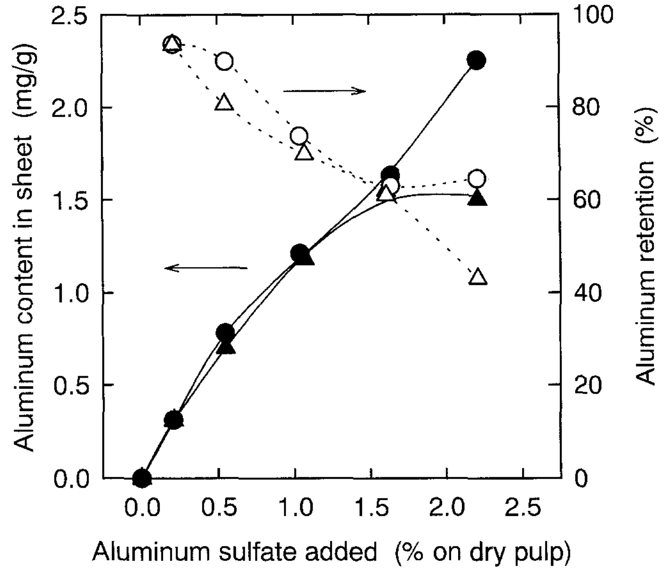

Fig. 7. Aluminum content in handsheets prepared from the original beaten pulp (*circles*) and its fines-free pulp (*triangles*) with 1% (based on dry weight of pulp) rosin soap size and 0%–2.2% (based on dry weight of pulp) aluminum sulfate at pH 4.5. Right axis shows retention values of aluminum compounds in handsheets. See legend to Fig. 2 for other explanations

here and hereafter are based on the dry weight of pulp) aluminum sulfate at pH 4.5. Sizing degrees sharply increased with increasing addition levels of aluminum sulfate up to about 0.5% and then increased gradually or reached plateau levels. In these cases also, the handsheets prepared from the fines-free pulp had higher sizing degrees than those for the original beaten pulp, which was simply reflected by the thickness effect of the handsheets.

Rosin size contents in the handsheets increased with an increasing addition level of aluminum sulfate up to about 0.5% (Fig. 6). Thus, at these addition levels, aluminum compounds added as aluminum sulfate to the pulp suspensions clearly played a role in retaining rosin size components in the handsheets. However, adding aluminum sulfate to more than about 0.5% did not bring about clear increases in the size content. Thus, no more than 50% of the rosin soap size added to the pulp suspensions could be retained in the handsheets even by adding excess aluminum sulfate, so long as this rosin soap size–alum system was used in the handsheet production.

Figure 7 illustrates the aluminum contents in the handsheets prepared with 1% rosin soap size and 0%–2.2% aluminum sulfate at pH 4.5. As the addition level of aluminum sulfate increased, the aluminum content in the handsheets increased in those prepared from the original beaten pulp. In the case of the fines-free pulp, the aluminum content increased up to about 1.5 mg/g and then leveled off, presumably because this fines-free pulp had a carboxyl content about 20% less than that of the original beaten pulp (Table 1). Retention values of aluminum were high at low addition levels of aluminum sulfate and then decreased when the addition level was increased.

Retention mechanisms of rosin size components

The results described in the previous sections provide information concerning the retention mechanism of the rosin size in the rosin soap size–alum systems at the wet-end. As shown in Fig. 3, the rosin size content in the handsheets increased with increasing size addition levels for both pulps. On the other hand, neither the aluminum nor the calcium content in the handsheets clearly increased with increasing rosin size content in the handsheets (Fig. 4). If cationic rosin–aluminum (and rosin–calcium) precipitates are formed and then are adsorbed on anionic pulp fibers, as many researchers have proposed,[1–5] the aluminum (and calcium) content(s) in the handsheets should increase with an increasing size content. The results in Fig. 4, however, indicate that not only the above conventional hypothesis about the size retention mechanism but also the following one is applicable to the rosin soap size–alum systems.

1. A part of the aluminum compounds originating from aluminum sulfate is adsorbed on pulp fibers immediately after aluminum sulfate is added to the pulp suspensions and forms cationic sites on pulp fibers.
2. Free rosin acid components with anionic charges at either the single molecular level or the colloidal particle level are then adsorbed on the cationic sites of pulp fibers at the wet-end.

Figure 8 shows SEM images of surfaces of the handsheets prepared from fines-free pulp with 1% rosin soap size and 2% aluminum sulfate at pH 4.5. Microparticles with 0.01–0.50 μm diameter were observed on the pulp fiber surfaces of the handsheet, and these particles maintained their shapes after heating the handsheet at

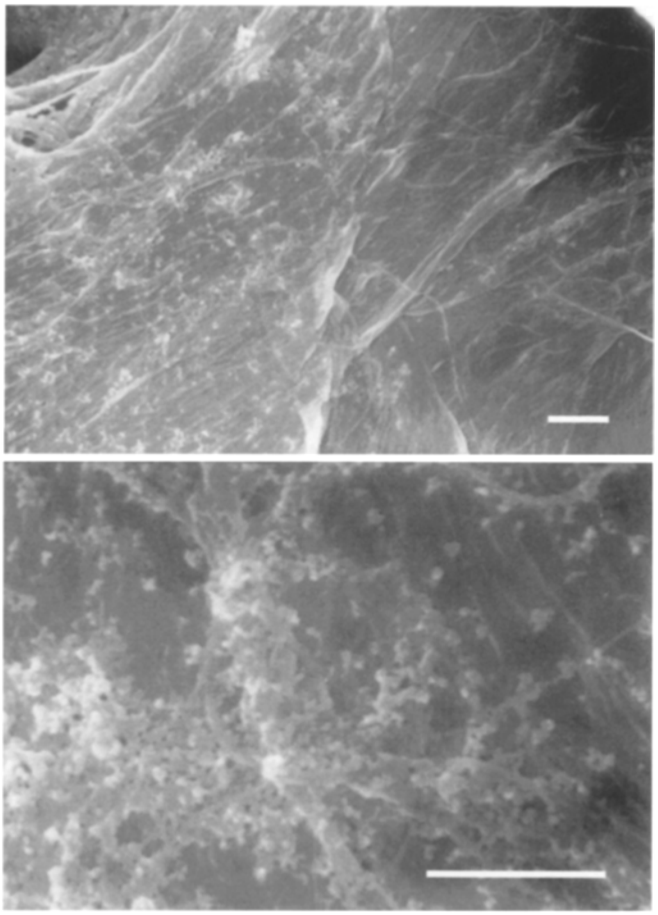

Fig. 8. Scanning electron microphotographs of surfaces of handsheets prepared from fines-free pulp with 1% rosin soap size and 2% aluminum sulfate at pH 4.5. Bar to 1 μm

105°C for 20 min. These particles observed by SEM have been regarded as size precipitates consisting of a mixture of aluminum dirosinate and free rosin acids.[6] Similar particles were also observed on the surfaces of the handsheets prepared from the fines-free pulp with aluminum sulfate alone (without adding the rosin soap size),[24] so these particles might be aluminum flocs formed from $Al_2(SO_4)_3$ in pulp suspensions and adsorbed on pulp fibers at the wet-end. Thus, it is difficult to distinguish between rosin–aluminum precipitates and aluminum flocs by SEM alone. So far there have been no reports directly proving that such particles are not aluminum flocs but are the rosin size precipitates.

Although rosin size content increased with an increase in its addition level, sizing degrees were leveled off at the rosin size content of more than 5 mg/g (Fig. 3). On the other hand, heat treatment led to clear sizing developments (Fig. 2). The SEM observation did not show any evidence of melting and spreading behavior of the size components in the heated handsheets. At this point, therefore, it is unknown whether the effect of heating on sizing development was due to melting and spreading of the rosin size components in small areas on pulp fiber surfaces or some changes in the chemical structure of the rosin size components, such as aluminum rosinate formation. Further studies are necessary to elucidate the retention and sizing mechanisms of rosin size in the rosin soap size–alum systems.

Conclusions

Pyrolysis–gas chromatography and X-ray fluorescence analysis can evaluate rosin size and aluminum contents in handsheets prepared under various conditions in the rosin soap size–alum system. The following conclusions in terms of retention behavior of rosin size and aluminum components in the handsheets were obtained.

1. When the addition level of rosin soap size varied from 0% to 4% and that of aluminum sulfate was fixed at 2%, the rosin size content increased with an increase in the size addition level, whereas aluminum and calcium contents remained roughly constant.
2. Under the above conditions, handsheets prepared from fines-free pulp had aluminum contents about 20% less than those for the original beaten pulp, probably because the former pulp had a carboxyl content about 20% less than that of the latter pulp.
3. Because neither the aluminum nor the calcium content in the handsheets increased with increasing rosin size content in the handsheets under the above conditions, some aluminum compounds originating from aluminum sulfate may be adsorbed on pulp fibers immediately after the addition of aluminum sulfate. These adsorbed aluminum compounds form cationic sites on pulp fibers, and free rosin acid components with anionic charges are then predominantly adsorbed on the cationic sites of pulp fibers at the wet-end.
4. Only limited rosin size components of the rosin soap size added to pulp suspensions are adsorbable on pulp fibers and fines at the wet-end, even after addition of excess aluminum sulfate.
5. Although microparticles (about 0.1 μm in diameter) were observed on pulp fiber surfaces in the handsheets by SEM, it is unknown whether these particles were rosin–aluminum precipitates or only aluminum flocs.

References

1. Thode EF, Gorham JR, Atwood RH (1953) Surface properties of rosin size precipitate. I. Factors affecting formation of rosin-aluminum sulfate complex. Tappi J 36:310–314
2. Thode EF, Htoo S (1955) Surface properties of rosin size precipitate. III. Electrokinetic properties of rosin-sized wood pulp fibers. Tappi J 38:705–709
3. Thode EF, Gorham JR, Humler RW, Woodberry NT (1955) Surface properties of rosin size precipitate. IV. Influence of the electrokinetic potential of rosin-size precipitate on sizing efficiency. Tappi J 38:710–716
4. Guide RG (1959) A study of the sodium aluminate sodium abietate size precipitates. II. The relationship between the physicochemical properties of the size precipitate and sizing. Tappi J 42:740–746
5. Davison RW (1964) The chemical nature of rosin sizing. Tappi J 47:609–616
6. Isogai A, Onabe F, Usuda M (1992) Changes in zeta potentials of amorphous cellulose particles with aluminum sulfate. Sen'i Gakkaishi 48:649–654

7. Hock CW (1954) Studies of rosin sizing by means of autoradiography and electron microscopy. Tappi J 37:427–430
8. Strazdins E (1965) Critical phenomena in the formation of the rosin-aluminum sizing complex. Tappi J 48:157–164
9. Vandenberg EJ, Spurlin HM (1967) Mechanism of the rosin sizing of paper. Tappi J 50:209–224
10. Strazdins E (1977) Mechanistic aspects of rosin sizing. Tappi J 60:102–105
11. Cobb RMK, Low DV (1955) The coordinate role of alum in sizing of paper. Tappi J 38:49–65
12. Kamutzki W, Krause T (1984) Neues über Reaktionen und Mechanismen bei der Harzleimung. Das Papier 38(10A):V47–V55
13. Lindström T, Söderberg G (1983) Studies on internal rosin sizing. Part 1. A method based on ^{14}C radioactive labeling for determination of rosin size retention in paper. Svensk Papperstidning 86:R22–R24
14. Lindström T, Söderberg G (1983) Studies on internal rosin sizing. Part 2. Studies on abietic acid retention in handsheets using ^{14}C fumaropimaric acid. Svensk Papperstidning 86:R25–R30
15. Lindström T, Söderberg G (1984) Studies on internal rosin sizing. Part 3. The effects of pH, electrolyte concentration and concentration of calcium-lignosulfonate on size retention. Svensk Papperstidning 87:R2–R7
16. Davison RW (1988) Retention of rosin sizes in papermaking systems. J Pulp Paper Sci 14:J151–J159
17. Marton J, Marton T (1983) Effect of fillers on rosin sizing of paper. Tappi J 66(12):68–71
18. Marton J, Kurrle FL (1987) Retention of rosin size. J Pulp Paper Sci 13:J5–J9
19. Marton J (1989) Fundamental aspects of the rosin sizing process: mechanistic differences between acid and soap sizing. Nordic Pulp Paper Res J 4:77–80
20. Ishida Y, Ohtani H, Kano T, Tsuge S, Yano T (1994) Determination of rosin sizing agents in paper by pyrolysis-gas chromatography combined with on-line methylation. Tappi J 77:177–183
21. Kitaoka T, Isogai A, Onabe F (1995) Sizing mechanism of emulsion rosin size–alum systems. Part 1. Relationship between sizing degrees and rosin size or aluminum content in rosin-sized handsheets. Nordic Pulp Paper Res J 10:253–260
22. Kitaoka T, Isogai A, Onabe F (1997) Sizing mechanism of emulsion rosin size-alum systems. Part 2. Structure of rosin size components in sheet. Nordic Pulp Paper Res J 12:26–31
23. Ito K, Isogai A, Onabe F (1999) Retention behavior of size and aluminum components on handsheets in rosin-ester size/alum systems. J Wood Sci 45:46–52
24. Kato M, Isogai A, Onabe F (1998) Retention behavior of aluminum compounds on pulp fibers at wet-end. J Wood Sci 44:361–368
25. Tappi Test Methods (1995) Fines fraction of paper stock by wet screening. T261 om-94
26. Tappi Test Methods (1995) Forming handsheets for physical test of pulp. T205 om-88
27. Tappi Test Methods (1995) Carboxyl content of pulp. T237 om-93
28. Washburn EW (1921) Dynamics of capillary flow. Phys Rev 17:374–375