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Properties of Papers Sized with Rosin under Acidic to Alkaline Papermaking Conditions

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Effects of the new rosin sizing method with a rosin emulsion, alum and polyvinylamine (PVAm) on the properties of the sized papers were investigated in terms of basis weight, sizing degree, pH value, brightness and folding endurance of the papers. The MIT folding endurances of the sized papers were much larger than that of the control paper due to the use of PVAm in the sizing. The pH values of papers Nos. 1 to 5 sized at pHs 5 to 8 were in acidic region varying from pH 5.5 to 5.8, and the papers lost dramatically their brightnesses and folding endurances. The pH values of papers Nos. 6 to 10 containing different amounts of CaCO₃ varied from pH 7.9 to 8.3, and the papers retained their permanence well during the accelerated aging. These results illustrate that although the new sizing method was effective under neutral-alkaline papermaking conditions, the sized papers were acidic and exhibited poor permanence. The use of CaCO₃ in the rosin sizing could make the sized papers alkaline so that the papers showed good permanence.

INTRODUCTION

Internal sizing in paper manufacture is an important process to provide paper and paperboard with resistance to liquid wetting, penetration and absorption. Rosin with alum has been a dominant sizing agent since 1807. Papers sized with rosin and alum, however, generally become yellow and brittle when they age. This has been a serious problem for the preservation of library materials (Luner, 1969; Roberson, 1976; Usuda, 1984; Oye, 1988). Previous studies have illustrated that paper acidity due to alum is one of major causes responsible for the deterioration of the papers (Dixon and Nelson, 1962; Kim *et al.*, 1988; Lyne, 1995). Although alkaline sizing is a remedy to the problem, the alkaline sizing agents, for example alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA), are expensive and difficult to deal with compared with rosin sizes. The use of familiar rosin sizes to papermaking under neutral-alkaline conditions has been studied by many investigators in the past decade (Biermann, 1992; Nakajima, 1993; Tahara *et al.*, 1996).

In the previous papers (Wu and Tanaka, 1995; 1996; 1997), we reported that conventional rosin sizes with alum and polyamines exhibited effective sizing in the region from pH 4 to 8. Since alum is still used in the sizing, it is necessary to evaluate the effects of the new sizing method on properties of the sized papers. This paper deals with basis weight, sizing degree, pH value, brightness and folding endurance of the papers. The permanence of the papers, in addition, was investigated by means of accelerated aging carried out at 105°C, 0% RH for 30 days.

MATERIALS AND METHODS

Materials

A commercial bleached hardwood kraft pulp was used. The pulp was beaten to a Canadian Standard Freeness (CSF) of 410 ml in a TAPPI (Technical Association of the Pulp and Paper Industry) standard beater. Polyvinylamine (PVAm) was prepared based on the method (Tanaka and Senju, 1976). The average molecular weight of the PVAm was 320,000 (Wu and Tanaka, 1995). Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 16 \sim 18\text{H}_2\text{O}$) was obtained from Tokyo Kasei Kogyo Co. Ltd.. The rosin emulsion size (RE) was kindly provided by the size maker.

Preparation of rosin sized papers

A pH value of an aqueous pulp slurry at consistency of 1.1% was adjusted to the desired pH. Alum (20 mg/g pulp), PVAm (1 mg/g pulp) and RE (5 mg/g pulp) were added to the slurry, sequentially, with stirring. Then the slurry was diluted with water previously adjusted to the desired pH, and handsheets were formed according to TAPPI Test Method T2050m-88. The wet sheets were pressed at 350 kPa for 5 min, and dried at 105°C for 10 min. The dry sheets were conditioned at 20°C and 65% RH for more than 12 h. Sizing degrees were evaluated according to JIS P 8122.

When calcium carbonate was used, it was added to a pulp slurry before the other additives. The slurry was prepared and dilute with tap water (pH 7.7).

Procedure for accelerated aging of the sized papers

Accelerated aging of the sized papers was carried out according to TAPPI Test Method T4530m-89. The papers were heated in a convection oven at 105°C. The samples were taken at desired times, and conditioned at 20°C, 65 RH%.

The MIT folding endurances under the tension of 50 kPa and pH values of the samples were measured according to JIS P 8115 and JIS P 8133, respectively. The brightnesses of the samples were measured with a MINOLTA CR-200 photoelectric reflectance photometer.

Quantitative analysis of rosin in the sized papers

The quantity of sizing agents in the papers was determined by pyrolysis-gas chromatography (Py-GC) combined with on-line methylation (Yano *et al.*, 1992; Ishida *et al.*, 1994). A vertical microfurnace-type pyrolyzer (Shimadzu PYR-4A) was directly attached to a gas chromatography (Shimadzu GC-17A) equipped with a flame ionization detector. About 500 µg of the milled paper sample was exactly weighed using a platinum sample cup, and then 4 µL of tetramethylammonium hydroxide (TMAH) was added to the cup. A fused silica capillary column (Shimadzu CBP₅-M25-025) was used. The flow rate of carrier gas (He) was reduced from 50 mL/min at the pyrolyzer to 1.0 mL/min at the capillary column by means of a splitter. The column temperature was initially set at 80°C, and then programmed up to 300°C at a rate of 5°C/min.

RESULTS AND DISCUSSION

Properties of the papers sized with RE at different pHs

Table 1 gives the properties of the papers sized with the rosin emulsion size (RE), PVAm and alum from pH 5 to 8. The basis weights of the papers (Nos. 1 to 5) increased from 61 g/m² at pH 5 to 72 g/m² at pH 8. This may be explained by the fact that more fines in a pulp slurry can be retained in a sheet at neutral pHs because fibers in the slurry at higher pHs were more swollen.

Although the papers Nos. 1 to 5 were formed at pH 5.0 to 8.0, their pH values were in an acidic region from pH 5.2 to 5.8. It was reported that the extractable acidity of a sheet is not a simple function of the stock pH, and an aluminum sulfate solution remains sensibly constant over most of the range of neutralization (Reynolds and Linke, 1963). Since alum in a pulp slurry at pH 5.0–8.0 is mostly retained in a sheet (Aoki *et al.*, 1995; Wang *et al.*, 1997) and the papers Nos. 1 to 5 contained about 6.5% of water, the buffering effect of the alum retained in Nos. 1 to 5 may explain the small change in their pH values. The pH values of the papers containing CaCO₃ (Nos. 6 to 10), however, were in a weak alkaline region from pH 7.9 to 8.3. The presence of small amount of CaCO₃ (16 mg/g pulp) in No. 6 made the paper pH rise to 7.9, compared with pH 5.2 to 5.8 of Nos. 1 to 5. From the standpoint of paper preservation, a neutral-alkaline paper is desirable. The results described above illustrate that the use of CaCO₃ in rosin sizing can make sized papers neutral-alkaline.

The sizing degrees of Nos. 1 to 10 covered the range from 42 s to 18 s, illustrating that conventional rosin sizes with alum and PVAm exhibit effective sizing in a wide pH region

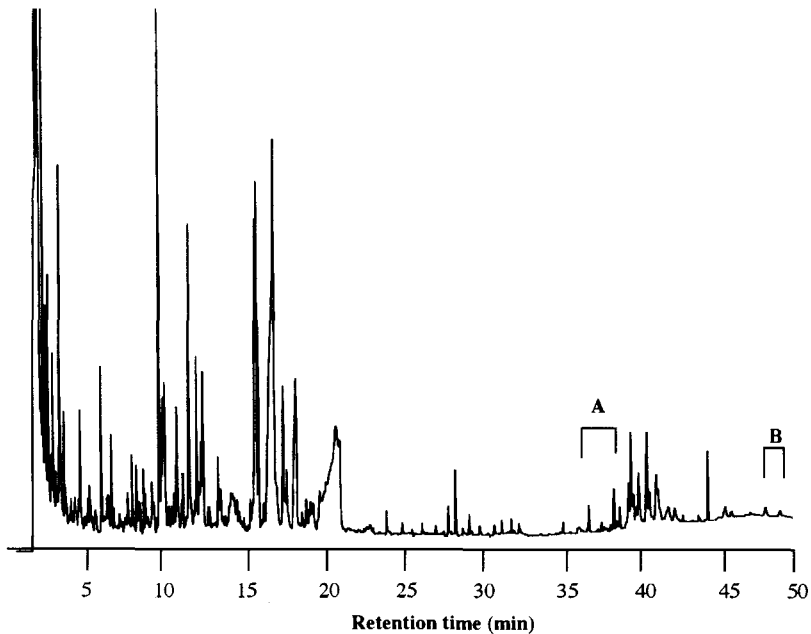


Fig. 1 The pyrogram of the rosin sized paper No. 1.

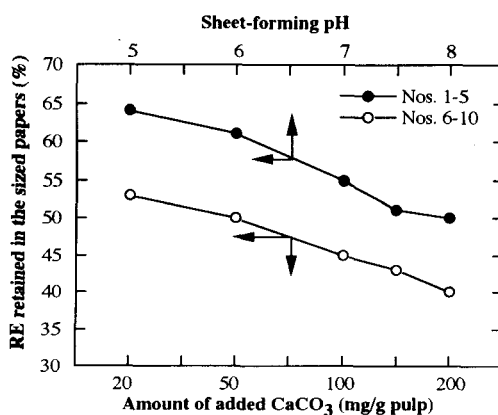


Fig. 2 Effect of sheet-forming pH and the amounts of added CaCO₃ on the retention of rosin size (RE) in the sized papers.

(Wu and Tanaka, 1995; 1996; 1997). To clarify effects of the sheet-forming pHs on the sizing degrees of the papers, the amounts of RE retained in the papers were determined by Py-GC. Figure 1 shows the pyrogram of the paper No. 1. The peak A (retention time, 36 to 38 min) and B (47–49 min) are assigned for RE (Ishida *et al.*, 1994; Wu and Tanaka, 1998). The RE retention decreased from 64% of No. 1 at pH 5 to 49% of No. 5 at pH 8 (Fig. 2). The sheet-forming pHs significantly influenced the RE retention. The comparison of the values in Table 1 and Fig. 2 shows that the decrease in the sizing degrees of Nos. 1 to 5 is in agreement with that in the RE retention. On the other hand, the increase in amounts of added CaCO₃ from 20 mg/g pulp to 200 mg/g pulp reduced the RE retention from 53% of No. 6 to 40% of No. 10. The sizing degrees (Table 1) decreased from 30 s of No. 6 to 18 s of No. 10. A higher sheet-forming pH and larger amount of added CaCO₃ may result in a less RE retention and a smaller sizing degrees of the papers.

As shown in Table 1, the control sheet which was formed at pH 7.7 was slightly brighter than the sheets Nos. 1 to 4, and the brightness (96%) of No. 1 was 2 point smaller than that (98%) of No. 5. The comparison of the brightnesses and the RE retention shows that a larger RE retention is correlated with a smaller brightness, indicating that the sizing may cause a little brightness losses of the papers. The application of CaCO₃ to the rosin sizing enhanced appreciably the brightnesses of Nos. 7 to 10. This is also a reason for rapid increase in use of calcium carbonate in papermaking.

Effects of the rosin sizing on mechanical properties of Nos. 1 to 10 was evaluated in terms of MIT folding endurance. The folding endurances of Nos. 1 to 5 were much larger than 42 folds of the control paper (Table 1). This may be attributed to the strengthen effect of PVAm and high molecular weight surfactant in RE on the folding endurances of the papers (Wu). With increase of sheet-forming pH from 5 to 8, the folding endurances of the sheets increased from 112 folds of No.1 to 195 folds of No. 5, due to the increase in their basis weights with increasing pH.

Table 1 Properties of the papers sized with the rosin emulsion size at pH 5 to 8^a.

No.	pH of sheet-forming	CaCO ₃ added (mg/g pulp)	Basis weight (g/m ²)	Paper properties			
				pH	Sizing degree (s)	Brightness ^{b)} (%)	Folding endurance (folds)
Control	7.7	–	63	7.5	–	98	42
1	5.0	–	61	5.2	42	96	112
2	6.0	–	66	5.4	42	96	120
3	7.0	–	66	5.5	39	96	161
4	7.5	–	71	5.7	35	97	192
5	8.0	–	72	5.8	31	98	195
6	7.7	20	66	7.9	30	98	171
7	7.7	50	68	8.1	25	98	112
8	7.7	100	72	8.1	22	101	60
9	7.7	150	74	8.3	19	102	29
10	7.7	200	79	8.3	18	103	27

a) The amounts of RE, alum and PVAm added in Nos. 1 to 5 were 5, 20 and 1 mg/g pulp, respectively. The level of PVAm added in Nos. 6 to 10 was raised to 5 mg/g pulp.

b) Relative values of the brightnesses of the papers to that of a standard white plate.

Deterioration of the sized papers during accelerated aging

As described above, one of the main problem for rosin sizing is natural deterioration of the sized papers during storage. It is important to evaluate effects of a new sizing method on permanence of the sized papers because the permanence of paper has become an important property for many users to choose paper products. According to "Dictionary of Paper" (Michael, 1996), the permanence of paper refers to the retention of significant use properties, particularly folding endurance and color, over prolonged periods. The permanence of the papers Nos. 1 to 10, therefore, is evaluated in terms of brightness and MIT folding endurance according to TAPPI Test Method T453om-89.

Upon heating, the papers suffered brightness losses to different extends as shown in Figs. 3 and 4. The papers Nos. 1 to 5 lost 5% of their brightnesses after being heated for 7 days, compared to 2% of the control paper. Significant differences in brightness can be seen among the papers heated for 30 days. The control paper remained 91% of its brightness, while No. 1 lost 14% of its brightness. The brightness losses in papers prepared under neutral pHs were smaller than those in the papers under the acidic conditions during the accelerated aging. The differences in the RE retention may be an explanation for the results. The rosin sizing caused brightness losses of the papers during the aging.

When CaCO₃ is present in the papers, brightness losses of the papers is smaller (Fig. 4). After being heated for 30 days, No. 9 and No. 10 retained 92% and 93% of their brightnesses, respectively. These values are larger than 91% of the control paper. It can be seen from Fig. 4 that the brightness losses decreased with the increases in amounts of CaCO₃. This may be explained by the facts that rosin contents is lower in the papers

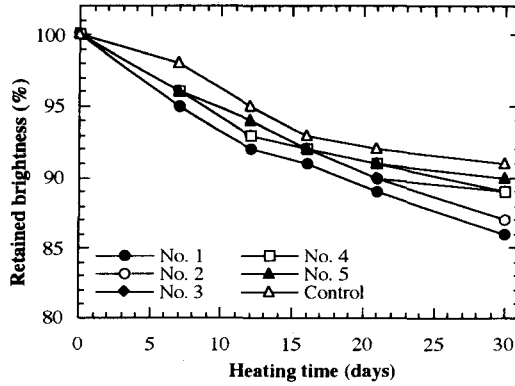


Fig. 3 Effect of sheet-forming pH on the brightnesses of the rosin sized papers during accelerated heating.

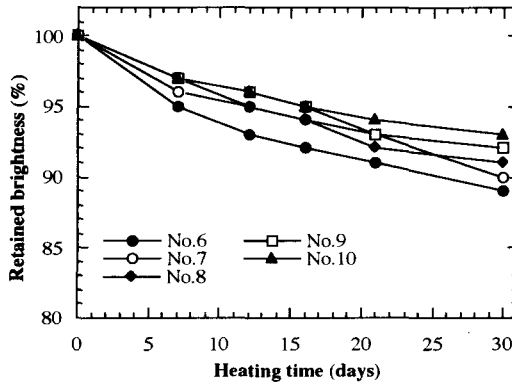


Fig. 4 Effect of the amounts of added CaCO_3 on the brightnesses of the sized papers during accelerated aging.

containing more CaCO_3 , and that CaCO_3 is stable during the heating.

Figure 5 shows effects of sheet-forming pH on the MIT folding endurance of the rosin sized papers Nos. 1 to 5 during the accelerated aging. Nos. 1 to 5 heated for 30 days lost half of their folding endurance, compared to 31% of the control paper. This may be attributed to the acidities of the papers, illustrating that the rosin sizing of RE with alum and PVAm also caused significant losses in the folding endurance of the sized papers. As shown in Fig. 6, however, the rosin sized papers Nos. 6 to 10 retained their endurance

well during the aging. After being heated for 30 day, No. 10 lost 30% of its endurance, compared to 31% of the control paper. This may be due to the fact that the pH values of Nos. 6 to 10 were in the neutral region.

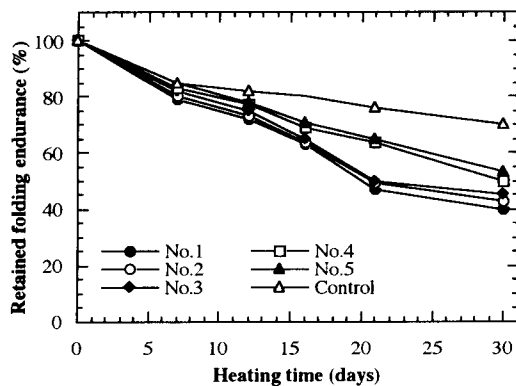


Fig. 5 Effect of sheet-forming pH on the MIT folding endurance of the rosin sized papers during the accelerated aging.

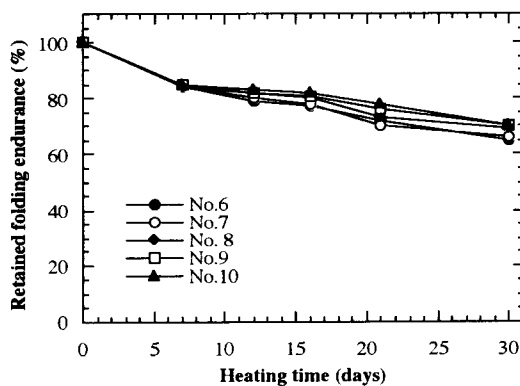


Fig. 6 Effect of the amounts of added CaCO_3 on the MIT folding endurance of the rosin sized papers during accelerated aging.

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