

The Effect of Aluminum Ions on the Acidification and Aging of Paper

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Abstract. Paper documents provide important records of human civilization and so understanding the causes of paper document aging is very important to delay the process and prolong the lifespan of paper. This study used an anionic rosin as a sizing agent and aluminum sulphate as a fixing agent, to produce paper with different amounts of aluminum sulphate. The effect of different contents of aluminum ions on the acidification and aging of the paper was studied by accelerated aging experiments. The results showed that the presence of aluminum ions in paper could accelerate the acidification and aging process, and the higher the content of aluminum ions, the worse the durability of paper. In the process of accelerated aging, with increasing aluminum ion content, the rate of decline in the strength and whiteness of paper increased whilst the pH value decreased. Accelerated aging under the same conditions for 15 days caused the pH value, whiteness, tensile index and tear index of paper without aluminum ions to decrease by 14.77%, 3.15%, 7.99% and 11.70% respectively. In comparison, paper which had aluminum sulphate added to 30 kg per ton of paper, showed the decreases of pH, whiteness, tensile index and tear index by 22.62%, 4.35%, 24.66% and 31.07% respectively.

1. Introduction

Paper documents provide important records of human civilization, which are affected by time and environmental conditions. Paper aging leads to yellowing, brittleness and even crushing of paper, which seriously affects the lifespan of paper documents[1-2]. Paper aging is significantly affected by air properties[3-5] such as moisture[6-8], temperature[9-10], sunlight[11] and mold[12]. Other factors such as ink[13] and acid substances[14] present in paper can cause acidification and aging. Studies have shown that transition metal ions from inks and pigments, such as $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Cu}^{+}/\text{Cu}^{2+}$, and Mn^{2+} , catalyze the production of carbonyl or aldehyde groups from cellulose, leading to oxidation reactions and cellulose degradation[15-18]. Ute Henniges et al. [19-20], proved the aging degradation effect of ink on cellulose using carbazole-9-carbonyl oxygen amine (CCOA) notation, and demonstrated the oxidation process using a carbonyl fluorescence labeling method. The study also showed that new carbonyl groups and reductive ends were produced after accelerated aging of the paper samples that contained copper ion pigments. However, since the invention of gum rosin in 1807 by Illing[21], the aluminum-alum sizing system has allowed for internal sizing which has been widely used in large-scale acid paper manufacturing. Few reports have focused on the aging characteristics of this kind of paper. The current study used anionic rosin as sizing agent and aluminum sulfate as fixing agent to produce paper with different amounts of aluminum sulfate. Through an accelerated aging experiment, the influence of aluminum ion content on acidification and aging of paper was studied.



2. Experimental Methods

2.1. Materials

Bleached eucalyptus kraft pulp with a beating degree of 40.5°SR was obtained from Zhuhai Hongta Renheng Packing Co., Ltd.

Anionic rosin with a solid content of 40% was obtained from Guangxi Wuzhou Arakawa Chemical Industries, Ltd. Aluminum sulphate was obtained from, AR, CALMAX Chemical Inc. USA.

2.2. Paper Making

According to ISO 5269/2, paper samples were made in the laboratory with a basis weight of 70 g/m², a diameter of 20 cm and an area of 0.0314 m². Paper with different amounts of Al₂(SO₄)₃ (based on oven dry stock) was made by varying the amount of Al₂(SO₄)₃ from 0 kg/ ton to and 30 kg/ ton, whilst keeping the amount of anionic rosin constant at 18 kg/ ton paper. Al₂(SO₄)₃ solution and anionic rosin emulsion were added successively after the pulp (concentration was 0.5%) was digested. After each reagent was added, the reaction was fully stirred for 2 min. The paper was then made using an automatic paper making system (RK3A-KWT, PTI, Austria). After vacuum drying, the paper was placed in a constant temperature and humidity room (relative humidity was 50 ± 5%, temperature was 23 ± 1 °C) to balance moisture for more than 24 hours. The paper was then used for subsequent treatments and performance measurements.

2.3. Accelerated Aging of Paper

According to the standard GB/T 464-2008, paper samples were subjected to a dry-heat accelerated aging test. A certain amount of paper from the different experimental groups was extracted and hung inside the oven. At 105 °C, dry heat aging was carried out. Paper samples were taken every 5 days for performance testing.

2.4. Performance Test and Characterization of Paper

The pH value of the paper samples was determined according to GB/T 450 and GB/T 1545.2-2003. Tensile index was determined according to GB/T 453-2002. The whiteness of the paper was determined according to GB/T 7974-2002.

The degree of polymerization (DP) was determined by weighing a paper sample (with an accuracy of 0.005 g) and then adding the paper sample into 50 ml of polyethylene solution. 2-3 pieces of red copper were then added and a pipette used to absorb 25 ml of deionized water into the solution before the bottle was capped and vigorously shaken. 25 ml of ethylene diketamine hydroxide solution was injected into the bottle and glass beads were added until the solution filled the bottle to eliminate the excess air. The bottle was then placed at a 25 °C constant-temperature shaking table and shaken violently until the sample had completely dissolved. The solution bottle was removed and placed in a thermostat of automatic circulation heat preservation and kept at 25 °C for 10 min. Finally, the outflow time of the solution was determined at 25 ± 1 °C in triplicate and the average value recorded. The relative viscosity was calculated according to the formula $\eta_r = \eta_n \cdot t_n$. The characteristic viscosity η , and the pulp degree of polymerization were calculated according to the formula $DP_{0.905} = 0.75[\eta]$.

The thermostability of the paper samples was determined by weighing 5 mg of the paper samples and placed them onto a platinum crucible. Nitrogen was used as carrier gas with a gas flow rate of 40 mL/min. The temperature rise rate was 20°C /min, and the temperature increases from room temperature to 600 °C. The thermogravimetric (TG) curves of the paper samples were obtained by processing the data collected automatically by the system.

3. Results and Discussion

3.1. Effect of Aluminum Sulphate Content on pH Value of Aged Paper

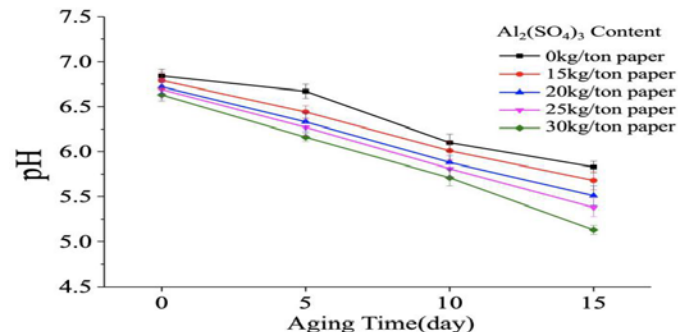


Figure 1. The Effect of $\text{Al}_2(\text{SO}_4)_3$ Content on the pH Value of Aged Paper

Figure 1 shows the effect of $\text{Al}_2(\text{SO}_4)_3$ content on the paper pH values after aging for 5, 10 and 15 days. It can be seen that the pH value of all papers manufactured under acidic conditions was greater than 6.5. With increasing aging time, paper acidification and the degree of aging increased, whilst pH value was gradually reduced. The amount of $\text{Al}_2(\text{SO}_4)_3$ had a major influence on the pH value of the aged paper. At the same aging times, the higher the amount of $\text{Al}_2(\text{SO}_4)_3$, the higher the content of aluminum ions in the paper, and the more obvious the reduction in pH value. After aging for 15 days, the pH values of the paper manufactured with different contents of $\text{Al}_2(\text{SO}_4)_3$ (0 kg/ ton paper, 15 kg/ ton paper and 30 kg/ ton paper) decreased by 14.77 %, 16.35% and 22.62 %, respectively. The results show that under the same aging times, the presence of aluminum ions accelerate paper acidification.

3.2. Effect of Aluminum Sulphate Content on the Physical Properties of Aged Paper

The main components of paper are cellulose, hemicellulose and lignin. The aging process is accompanied by the hydrolysis or oxidation of cellulose, hemicellulose and lignin, which consequently alters the mechanical properties of paper. Figure 2 show the effect of $\text{Al}_2(\text{SO}_4)_3$ content on the tensile index of aged paper and the decline rate of the tensile index of aged paper under different $\text{Al}_2(\text{SO}_4)_3$ contents. According to these data, as aging time increases, the tensile index of paper decreases to different degrees. The higher the amount of $\text{Al}_2(\text{SO}_4)_3$, that is, the higher content of aluminum ion in paper, the faster the decline in the tensile index of the aged paper. After 15 days aging, the tensile index of paper without aluminum ions decreased by 7.99%, whilst the paper tensile index when $\text{Al}_2(\text{SO}_4)_3$ contents are 15 kg/ton paper and 30 kg/ton paper decreased by 11.07% and 24.66%, respectively. These results show the presence of aluminum ions accelerates the aging of paper: the higher the content of aluminum ions, the faster the aging of paper.

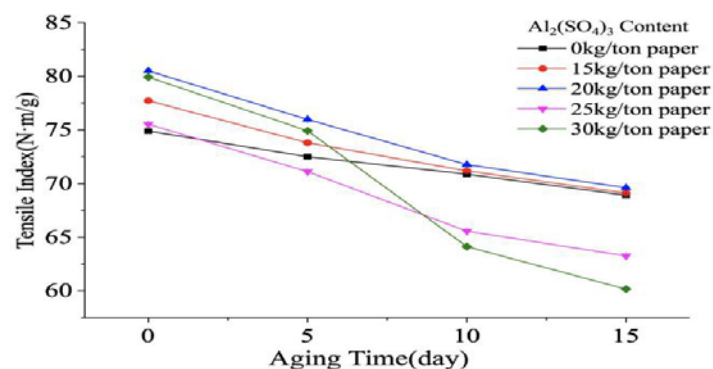


Figure 2. Effect of $\text{Al}_2(\text{SO}_4)_3$ Content on the Tensile Strength of Aged Paper

3.3. Effect of Aluminum Sulphate Content on the Whiteness of Aged Paper

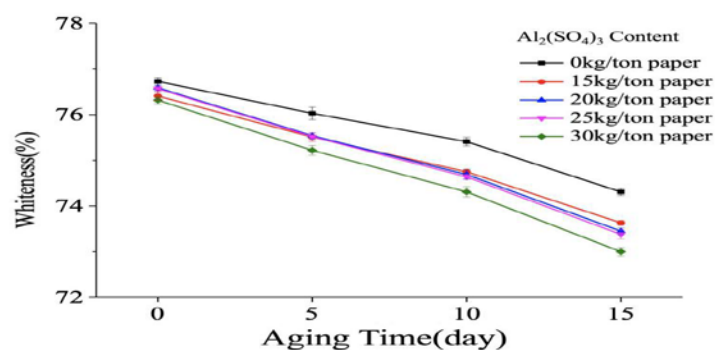


Figure 3. Effect of $\text{Al}_2(\text{SO}_4)_3$ Content on the Whiteness of Aged Paper

Paper aging is displayed as paper yellowing macroscopically, and the higher degree aging, the more serious the paper yellowing. Changes in paper whiteness are used to measure the yellow degree of paper, which reflect aging and durability. From figure 3, it can be seen that with increasing aging time, the whiteness of the paper gradually decreased. After 15 days of aging, the whiteness of the paper at $\text{Al}_2(\text{SO}_4)_3$ contents of 0, 15 and 30 kg/ ton paper decreased by 3.15%, 3.64% and 4.35% respectively. The results show the presence of aluminum ions in paper can accelerate the aging and yellowing of paper which worsens the durability of paper.

3.4. Effect of Aluminum Sulphate Content on Polymerization Degree of Aged Paper

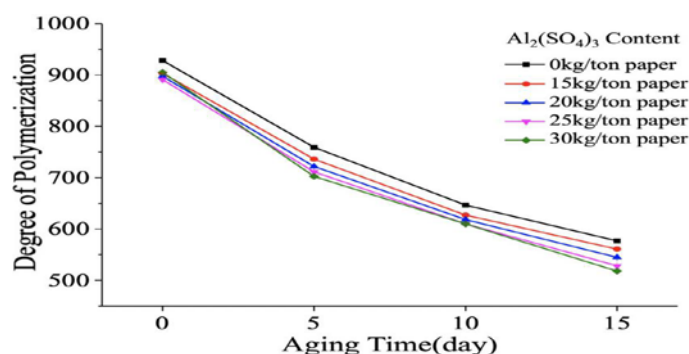


Figure 4. Effect of $\text{Al}_2(\text{SO}_4)_3$ Content on the Degree of Polymerization of Aged Paper

The average length of cellulose chains could be characterized by the DP in paper. With aging, the cellulose chain broke and the DP decreased. Therefore, the change in the DP of cellulose reflects the degradation of plant fibres during the aging process and can better explain the change in the paper strength properties. Figure 4 shows that the DP of cellulose decreased after aging. Under the same aging times, the paper with higher $\text{Al}_2(\text{SO}_4)_3$ contents, showed a greater DP decline in cellulose after aging. For example, after 15 days of aging, the DP of cellulose when the content of $\text{Al}_2(\text{SO}_4)_3$ was 15 kg/ ton paper, reduced by 37.90 % from 903.2 to 560.8, whilst the DP decreased by 42.77% from 905.1 to 518.0 in paper with $\text{Al}_2(\text{SO}_4)_3$ at 30 kg/ ton. The results showed that the higher the content of aluminum ions in paper, the more seriously the cellulose was degraded during the aging process. Aluminum ions in paper may accelerate the degradation of paper cellulose and so the higher the aluminum content, the more obvious the degradation.

4. Conclusions

The presence of aluminum ions in paper accelerates the acidification and aging of paper: the higher the content of aluminum ions, the worse the durability of paper. During the aging process, with increase

content of aluminum ions, the DP of cellulose gradually decreased, and the decline rate in paper strength and whiteness increased, and the pH value is lower. After 15 days of accelerated aging under the same conditions, the pH value, whiteness, tensile index and tear index in the paper without aluminum ions were reduced by 14.77 %, 3.15 %, 7.99 % and 11.70 %, whilst for the paper with an aluminum sulphate content of 30 kg/ ton, the corresponding reductions were 22.62 %, 4.35 %, 24.66 % and 31.07 %.

5. Acknowledgement

Thanks to the support of Science and Technology Plan Special Project of Guangzhou, China (No. GZDD201808).

6. References

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