# Deacidification and Reinforcement of Old Books Using Sodium Carbonate and Latex Composites

Huiming Fan, Mingfeng Guo, Hongyan Mou,\* Wei Shi,\* Jiahe Li, and Jianan Liu

Old books suffer from aging and deterioration spurred by acidification, oxidation, and other factors. To preserve the important historical documents, a de-acidification and reinforcement method was studied using ultrasonic atomization via deacidification by Na<sub>2</sub>CO<sub>3</sub> solution and styrene acrylic latex composite as reinforcing agent. These agents were atomized into micron-sized droplets and were absorbed by paper. In this study, the physical properties, internal structure, and surface morphology of the paper before and after aging were comprehensively studied for explaining the treatment mechanism. The paper pH, strength properties, brightness, color difference, and apparent morphology typically have been determined in detail as the important factors for evaluating the treatment effect of the preservation method for old paper. The analysis results showed that the pH of the paper after deacidification was successfully increased. Thus, even after aging, the pH of the deacidified paper was still higher than 7. The change of color difference of paper after treatment was not noticeable, meeting the requirement for the basic principle of an old book. Furthermore, the deacidification treatment had no clear influence on the breaking length and tear index of the paper. This study revealed a new perspective on the conservation of old books.

Keywords: Ultrasonic atomization; Old books; Deacidification; Reinforcement; Conservation

Contact information: State Key Laboratory of Pulp and Papermaking, School of Light Industry and Engineering, South China University of Technology, 381 Wushan Road, Tianhe District, Guangzhou, China, 510641; \*Corresponding authors: fehymou@scut.edu.cn; sww@scut.edu.cn

#### INTRODUCTION

Books are organic materials that will naturally age over time. In addition to being widely used for academic purposes, books are an integral part of many historical relic collections. As the years go by, the damage caused by natural aging, acidification, and oxidation processes results in aging that is increasingly becoming more serious (Area and Cheradame 2011). After nearly a hundred years of storage, the acidification of literature books can reach a very serious level, and some have been completely destroyed, resulting in permanent loss (Giorgi *et al.* 2002; Fan and Guo 2018). Removing acidic substances from paper is an important way to delay paper aging and extend the paper life. Natural aging occurs over time. The paper not only becomes acidic, but also turns yellow, brittle, and its mechanical properties will be degraded. Therefore, in the work of protection, if only the paper is deacidified, the repair effect would not be achieved. To extend the paper life, reinforcement is a necessary step for improving the mechanical performance of an old book to make it strong enough for holding/reading.

At present, the common practice for deacidification of paper is to use a basic substance to neutralize the acidic substances and to maintain a certain amount of alkali retention in the paper (Baty *et al.* 2010). Upon comparison of the gas phase method with

the liquid phase and the solid phase methods (Williams and Kelly 1976), inorganic deacidification reagents with low toxicity and good deacidification effect with water as solvent were selected. In the liquid phase method, unbound paper sheets have been conventionally deacidified through immersion in aqueous solutions containing a pHbuffering compound, such as magnesium carbonate, followed by drying under constraint to preserve flatness (Baty et al. 2010). In this method, the fiber was severely swelled, causing wrinkles and deformation of the paper after drying. In addition, some problems, such as handwriting and ink diffusion, were also observed. In early work at the British Library (Hon 1989; Hubbe et al. 2018) methanol was used as a nonaqueous solvent, and Ba(OH)<sub>2</sub> as the alkaline compound to extend the lifetime of paper. However, methanol has been found to solubilize some ink components that might do harm to paper protection. To solve the above problems, an alternate method, such as ultrasonic atomization, was investigated in this study. For inked paper, nanolime dispersions have been utilized for the deacidfication (Bastone et al. 2016), and also magnesium hydroxide nanoparticles have been used for deacidification of inked paper (Poggi et al. 2010). But both of them use nanoparticles, which makes the cost and preparation more complicated.

Because the ultrasonic atomization method can cause excellent atomization quality at a very low liquid transport speed (atomization effect is easy to control with the fine and uniform droplet size), the paper can slowly absorb the liquid agent. While the paper absorbs less moisture, the paper will not be wetted or deformed. The absorption is uniform, and the equipment requirements are not high, thus making the batch process easy. Therefore, the deacidification and strengthening treatment is completed *via* ultrasonic atomization. Through ultrasonic atomization, a convenient, efficient, and harmless mass conservation method was proposed.

To improve the deacidification efficiency, an ultrasonic atomizer that can make micro-particles (around 4  $\mu$ m to 5  $\mu$ m) would help to penetrate deacidifying and reinforcing agents into paper. Because it is more difficult to atomize the solid particles, the proposed method is suitable only for reagents with higher solubility. The operating principle of the ultrasonic atomization method requires the use of a relatively concentrated aqueous solution to obtain sufficiently high treatment levels in the paper without excessive moistening (Hanus et al. 2008). At the same time, considering that the deacidification agent should not cause damage to the paper, sodium carbonate is used as the deacidification agent in this paper. At present, more inorganic deacidification agents are generally used, such as carbonates, alkaline-earth carbonates, hydrogen carbonates, oxides, and hydroxides, etc. (Sequeira et al. 2006; Tan et al. 2013; Baglioni et al. 2014). In the early 2000s, alkaline nanoparticles were employed for deacidification; such work was based on an idea of easy penetration into the surface and interior of paper (Giorgi et al. 2005; He et al. 2019). Sodium carbonate is a salt formed from the reaction of a strong alkali with a weak acid. Hence, after hydrolysis it becomes alkaline. The hydroxide released from the hydrolysis of sodium carbonate might neutralize the acid in the paper.

In this study, a styrene acrylic latex compound with the advantage of non-toxicity is used as a reinforcing agent in the paper. The latex composite uses water as the dispersed phase, which can be easily ultrasonically atomized, and the formed film has good stability. The latex composite deposits on the surface of the paper, wraps and thickens the fibers, fills the fiber voids, forms a film, and finally improves the paper strength. Meanwhile, the color difference is controlled within 1.5, which can avoid being perceived to the naked eye (Chen and Huang 2018).

The aim of this work was to build a new perspective for old books conservation. It is important to stop paper acidification and consequently extend paper life. To solve the problems brought by immersion, such as fibers swelling, paper wrinkling, and deformation, the different method of ultrasonic atomization was studied. If the conditions permitted, some suitable removal of pollutants should be added before applying this process. By using this method, the uniform absorption of chemicals to paper was promoted. The treatment could be realized with low equipment requirements.

In this paper, the ultrasonic atomization was used to make paper absorb the deacidification agent and the latex compound in the designed atomization device separately (Fig. 1). The deacidification conditions and mechanism was investigated with the aim of achieving good conservation without any damage at room temperature and atmospheric pressure. By studying the changes of pH, mechanical strength, brightness, and color difference of paper before and after treatment, the deacidification and strengthening effects on paper properties were investigated. Moreover, the stability and aging resistance of paper after artificial aging were also analyzed.



The designed atomization device

Fig. 1. The designed atomization device and ultrasonic atomization

#### EXPERIMENTAL

#### Materials

The paper samples were taken from the third volume of the Selected Works of Marx and Engels, from 1972, from the library of South China University of Technology, Guangzhou, China. Sodium carbonate ( $Na_2CO_3$ ), hydrochloric acid, and ethanol were purchased from Guangzhou Chemical Co., Ltd. (Guangzhou, China). The styrene acrylic latex (Guangzhou Zhencheng Chemical Co., Guangzhou, China) was diluted to one-tenth of the as-received strength before use, with the viscosity of 4.69 cP after mixing at 180 rpm.

#### Original paper properties

The research object of this paper is paper literature of the Republic of China. The paper prepared in that time has unique acidic papermaking process conditions; thus there was an excess of acidic substances in the paper, and the aging degradation rate was faster than other specimens. For example, handmade paper made from mechanical pulp or sheets made under alkaline papermaking conditions generally last much longer (Fan and Guo 2018). However, it is not allowed to be used directly in experimental research because of its importance in heritage protection. Therefore, according to the needs of the experiment, paper with similar acidification degree to those of the paper literature in the Republic of China were selected. Consequently the third volume of the Selected Works of Marx and Engels published in 1972 was selected as a suitable object of study. The study can be used for other paper conservation as well. The paper has a basis weight of 51.9 g/m<sup>2</sup>. The paper was moderately acidified and yellowed with an average pH of approximately 5.8 for testing. The breaking length was approximately 1.2 km, and the tear index was approximately 2.7 mN·m<sup>2</sup>·g<sup>-1</sup>.

#### **Pattern Preparation**

The paper was prepared according to the standard GB/T 450-2008 (2008). Papers with no obvious stains and damaged surfaces were chosen, and the paper was cut in the middle. According to the ISO 187 (1990) standard, the prepared paper sample was suspended in a 23 °C constant temperature, and 50% relative humidity (RH) chamber for 24 h, so that the paper could obtain similar moisture before treatment. After treatment, the paper was also placed in a constant temperature and humidity room for at least 24 h, and then the paper performance was tested.

For the treatment purpose, the paper sample was suspended in the atomization reactor, and 0.4 mol/L Na<sub>2</sub>CO<sub>3</sub> solution was atomized (Ultrasonic atomization, WH-2000; Guangdong Yuehua Medical Instrument Factory, Guangzhou, China) for deacidification. For reinforcement, the deacidified paper was dried and hung in the atomization reactor, and styrene-acrylic latex was utilized. After the atomization was finished, the paper was dried naturally. According to different processing conditions, the processed paper samples were labeled as 1 (UT = blank samples), 2 (DA = deacidification samples), and 3 (DARF = deacidification and reinforcement samples), as shown in Table 1.

| Mark     | Processing Conditions  |
|----------|--|
| 1 (UT)   | Blank  |
| 2 (DA)   | Deacidification: ultrasonic atomization of 50 mL 0.4 mol/L<br>Na <sub>2</sub> CO <sub>3</sub>  |
| 3 (DARF) | Deacidification and reinforcement: ultrasonic atomization of 50 mL 0.4 mol/L Na <sub>2</sub> CO <sub>3</sub> , 30 mL styrene-acrylic latex |

Table 1. Mark and Processing Conditions of Treatment

#### Artificial Accelerated Aging

The International Organization for Standardization has proposed a dry heat accelerated aging standard, ISO 5630-1 (1991) and the accelerated aging conditions specified by this standard were a temperature 105 °C  $\pm$  2 °C. For air aging, the samples were freely suspended from the top of the oven (DHG-9053A; Shanghai Yiheng Technology Co., Ltd., Shanghai, China). After drying and aging for 72 h, it was placed in a constant temperature and humidity chamber to balance the moisture content for 24 h before testing the paper performance.

#### Methods

#### Determination of pH on paper surface

To avoid the destructive effects of measurements, such as cold extraction, the surface pH method was utilized in this study (Roberson 1976; Strlič *et al.* 2007). The pH value of the paper surface is an important indicator to evaluate the degree of deacidification (Strlič *et al.* 2007; Xingling *et al.* 2008). During the testing, a drop of distilled water (approximately 0.5 mL) was added on the surface of paper and then it was kept on the flat electrode surface of the pH meter (Planar pH composite electrode, Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China), each sample was tested three times to calculate the results. The Chinese standard GB/T 13528-92 (1992) was used to determine the pH of the sample. The average of the five measured values was used.

#### Calculation of paper color difference

The whiteness,  $L^*$ ,  $a^*$ , and  $b^*$  values before and after atomization were measured using the whiteness meter (L & W Elrepho 070, R457 D65; L&W, Stockholm, Sweden) using standard ISO 2470-1 (2009). The color difference was calculated according to Eq. 1,

$$\Delta E^* = (2\Delta L^* + 2\Delta a^* + 2\Delta b^*)^{\frac{1}{2}}$$
(1)

where  $\Delta L^*$  denotes the difference in lightness and darkness,  $\Delta a^*$  is the difference in red and green,  $\Delta b^*$  denotes the difference in yellow and blue, and  $\Delta E^*$  is the total color difference of the sample.

#### Determination of breaking length of paper

According to the ISO 1924-2 (2008) standard input parameters (L & W CE062; L&W, Stockholm, Sweden), the clamping distance, the distance between the clamps was set to 100 mm, the stretching rate was set at 20 mm/min. The average of the ten measured values was taken as the result. The breaking length was then calculated using Eq. 2,

$$L_a = \frac{1}{9.81} \times \frac{S}{g} \times 10^3$$
(2)

where  $L_a$  is the breaking length (km), S denotes the tensile strength (kN/m), and g is the basic weight (g/m<sup>2</sup>).

#### Determination of tear index of paper

This was measured according to ISO 1974 (2012) (L & W 009; L&W, Stockholm, Sweden). The dimensions of the sample used were  $(63 \pm 0.5) \text{ mm} \times (50 \pm 2) \text{ mm}$ . The number of testing layers was one. The average of five measurements was used. Tear index was calculated using Eq. 3,

$$X = F / g \tag{3}$$

where X represents tear index  $(mN \cdot m^2/g)$  and F denotes tear strength (mN).

#### Scanning electron microscopy (SEM) of paper

A scanning electron microscope (EVO18 type; Carl Zeiss, Jena, Germany) was used at a magnification of 10 kV accelerating voltage. The paper sample was scanned and photographed to observe the changes in the surface morphology of the paper.

#### Macroscopic surface morphology of paper

The macroscopic surface morphology of paper was scanned by a scanner (Epson Perfection V330; Epson, Shenzhen, China).

#### Paper surface, section element analysis

An X-ray energy dispersive spectrometer (EDS) was used for obtaining spectral characteristics using various X-ray energy levels. An electron beam was directed toward the sample to excite various elements to emit X-rays of different energies. The collection of the X-rays classifies them according to the size of the energy, and quickly displays the lines while simultaneously detecting those elements (Zeiss EVO18; Carl Zeiss, Jena, Germany). When analyzing the elements, the accelerating voltage was set at 20 kV. The samples in the selected area were scanned, and the required elements were selected to calculate their contents.

#### **RESULTS AND DISCUSSION**

#### Effect of Deacidification and Reinforcement Treatment on Paper pH

The deacidification treatment of old paper with Na<sub>2</sub>CO<sub>3</sub> was conducted to resolve the problem brought about by acidic hydrolysis. In addition, the deacidification mechanism was assumed to involve a neutralization reaction between the acidity in the paper and OH<sup>-</sup> ions formed from the Na<sub>2</sub>CO<sub>3</sub> hydrolyzed products. The changes in the surface pH values of paper before and after aging, as well as the aging change rate are shown in Fig. 2.



Fig. 2. Effect of deacidification and reinforcement treatment on paper pH

Figure 2 shows that the pH value of paper after treatment was higher than that of the blank paper, and the pH of the paper increased from 5.77 (UT) to 8.44 (DA) and 8.66 (DARF). Because the pH of paper was determined by being wetted with a drop of water, it is not possible to test local alkaline spots and local acidic spots (Hubbe *et al.* 2017). It was shown that the neutralization reaction effectively inhibited the acid hydrolysis of cellulose fibers. The increase in pH of the paper was due to the absorption of alkaline substances. The paper contains free hydroxyl groups that can cause adsorption of polar liquids such as water. At the same time, paper is a network of natural fibers and fillers. There are many gaps between fibers and also between the fibers and fillers, which bring out many pores.

These pores form a capillary adsorption effect on the liquid (He 1994), which makes the moisture of the paper susceptible to the RH of the environment. When the RH of the environment changes from low to high, the paper will absorb moisture. Therefore, the samples absorb moisture with the alkaline substances. The absorbed alkaline substance neutralizes the acidic substance in the paper, and as the alkaline substance accumulates, the pH of the paper gradually rises. The latex composite is weakly alkaline, so the pH of the deacidified paper reinforced with the latex composite was slightly elevated. According to the reported studies, the pH of the paper after deacidification should be between 7 and 10 (Bukovský 1999, 2005; Ahn *et al.* 2012). Therefore, the pH of the paper after Na<sub>2</sub>CO<sub>3</sub> treatment met the requirements for deacidification.

Compared with the change of pH of paper before and after aging, the decrease of pH of DA and DARF were lower than that of the original paper. The pH drop rate of UT, DA, and DARF after aging was approximately 13%, 5%, and 4%, respectively. This was because the latex composite adhered to the surface of the fiber, which not only inhibited the degradation of the fiber under dry heat aging conditions, but also reduced the area of contact between the fiber and oxygen in the air, acid gas (SO<sub>2</sub>, NOX, CO, *etc.*), and inhibited oxidative degradation of fibers. During the aging process, not only the acid degradation of the fiber occurs, but also oxidative degradation occurs, which accelerates the aging of the paper. Therefore, the pH of the paper treated by the deacidification and reinforcement was better than the simple deacidification.

### Effect of Dry Heat Aging on Brightness and Post Color Number of Neutral Paper

To evaluate the effect of treatment on the color of paper, which can be easily found by the naked eye, the changes in the color difference were determined, and the results are shown in Table 2.

|      | Color Difference | L*    | a*   | b*    |
|------|------------------|-------|------|-------|
| UT   |                  | 82.72 | 0.36 | 12.31 |
| DA   | 0.51             | 81.86 | 0.62 | 12.78 |
| DARF | 0.55             | 82.35 | 0.47 | 13.29 |

**Table 2.** Effect of Deacidification and Reinforcement Treatment on Paper Color

 Difference

Table 2 shows that the  $b^*$  value of the paper after deacidification and reinforcement treatment was larger than for the blank paper, indicating that the treatment slightly yellowed the paper. The change of color difference was related to the change of pH of the paper. A higher pH of the paper resulted in more deacidification agent that was absorbed. The lignin in the paper is sensitive to alkaline substances, which easily react to form chromophores (Xu and Zhu 2010), which in turn causes the color change in the paper. Chen *et al.* (1988) studied the color difference and human eyes' sensitivity, but with few evidence supported it. The whole treatment of Na<sub>2</sub>CO<sub>3</sub>-latex composite had little effect on the chromatic aberration of the paper, which kept the color change within a range that was hard to be perceived by the naked eye (Chen and Huang 2018).

## Effect of Deacidification and Reinforcement Treatment on Paper Breaking Length and Tear Index

The strength property is an important factor for extending the durability of old books. The effect of  $Na_2CO_3$ -latex treatment on paper breaking length and tear index is shown in Figs. 3 and 4, respectively.



Fig. 3. Effect of deacidification and reinforcement treatment on the breaking length of paper



Fig. 4. Effect of deacidification and reinforcement treatment on paper tear index

Figures 3 and 4 show that the breaking length and tear index of the paper after deacidification were changed only slightly. The strength of the fiber bonding force and the strength of the fiber itself are the most important factors affecting the strength of the paper. However, in the presence of acidic substances, the acid will catalyze the hydrolysis and breakage of the fibers, resulting in a rapid decline in the mechanical strength of the paper. Under neutral and weak alkaline conditions, the fibers will be relatively stable. As a result, the strength of the paper after deacidification was relatively stable, and the paper indicated better anti-aging properties after deacidification, while the mechanical strength of the base paper was rapid after artificial aging.

The strength of the DARF paper after deacidification and reinforcement was higher than that of UT and DA paper. The observed increase in strength can be understood possibly in terms of a localized wetting of spaces between cellulosic fibers. When a film of water was formed between solid surfaces, it can exert a capillary force that draws the surfaces together (Page 1993). As the water evaporates, the capillary forces draw the surface into molecular contact, allowing new hydrogen bonds to form between the cellulosic surfaces (Campbell 1959). The tear index decreased slightly after deacidification and reinforcement, indicating that the treated paper achieved some anti-aging properties. The latex composite itself has a certain heat aging resistance, which improved the strength of the paper after aging. Because the latex composite is easily wrapped on the surface of the fiber, the area of contact of the fiber with the air was reduced, thereby the oxidative degradation of the fiber was modified. Moreover, the paper retained some alkali residue after treatment. Through the aging, the formation of acidic substances inside the paper was suppressed, thereby greatly improving the anti-aging property of the paper.

### Effect of Deacidification and Reinforcement Treatment on the Macroscopic Surface Morphology of Paper

The macroscopic surface morphology of paper was scanned and the results are shown in Fig. 5.



**Fig. 5.** Effect of deacidification and reinforcement on paper macroscopic surface, ink quality, and handwriting: (a) UT; (b) DA; (c) DARF; (d) Ink quality and handwriting of UT; (e) Ink quality and handwriting of DA; and (f) Ink quality and handwriting of DARF

When the paper was subjected to deacidification treatment using the aqueous solution method, because the paper suffered water expansion, moisture expansion, and drying, there were problems, such as wrinkle deformation and ink diffusion, after the treatment. An important reason for choosing the ultrasonic atomization method was to solve the wrinkles and deformation problems that occur during conservation. Figures 5a, 5b, and 5c show that the paper after deacidification and reinforcement was basically free from any irregularities, wrinkles, and curls. Besides, there were no common moisture

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absorption and dehumidification problems on the edge of the paper. This was because of the slow speed addition of the deacidification agent by ultrasonic atomization. Thus, the paper moisture content was not high, and the paper was not wetted at the end of treatment. Additionally, the paper ink did not appear to spread and smudge, which was observed from Figs. 5a, 5b, and 5c. The red writing on the paper did not show obvious diffusion, and the color did not become lighter, indicating that the paper treated with ultrasonic atomization nearly maintained the original shape.

## Effect of Deacidification and Reinforcement Treatment on Microscopic Surface Morphology of Paper

Except for the macroscopic surface of paper, the morphology of the treated paper before and after aging were analyzed by SEM, and images are shown in Fig. 6.



**Fig. 6.** Effect of deacidification and reinforcement treatment on microscopic surface morphology of paper: (a) UT; (b) Aged UT; (c) DA; (d) Aged DA; (e) DARF; and (f) Aged DARF

Figure 6 shows that the fibers of original paper were closely interlaced, with a smooth surface, and a small amount of fine granular filler was seen attached to the surface. Comparing the original paper and deacidified paper, it was found in the deacidified paper that the fiber had no obvious changes like crack, roughness, or fracture, which was

basically consistent with the morphology of the untreated paper. The surface of the fibers showed cracks after the aging process, and the fibers displayed slight roughness. Thus, the paper fibers showed various degrees of aging degradations.

Because the latex composite is a microspheric-type material, it mainly adheres to the fiber surface by spherical dispersion. However, because the latex composite is also easy to flocculate, it can be observed that part of the latex composite was flocculated by multiple microspheres and part of the emulsion formed a film on the surface of fibers. The ball-like latex composite was seen wrapped on the surface to thicken the fiber. After aging, in Fig. 5f, the latex distributed on the fiber surface was not changed obviously, which could explain the increase of mechanical strength of the treated paper in Figs. 3 and 4.

### Effect of Deacidification and Reinforcement Treatment on the Dispersed Content of the Paper by SEM-EDS

Scanning electron microscopy and X-ray energy dispersive spectroscopy (SEM-EDS) were used to analyze the surface and cross-section elements of the original paper and treated paper, and their surface. The results further proved that the inside of the paper absorbed the ultrasonic atomization agent. The scanning figures and related data are shown in Fig. 7 and Table 4, respectively.



**Fig. 7.** X-Ray energy spectrum of the samples (SEM-EDS): (a) Surface of UT; (b) Surface of DA; (c) Cross-section of UT; and (d) Cross-section of DA

|         | Surface of | of Original | Surface of        |        | Cross-section of |        | Cross-section of  |        |
|---------|------------|-------------|-------------------|--------|------------------|--------|-------------------|--------|
|         | Paper      |             | Deacidified Paper |        | Original Paper   |        | Deacidified Paper |        |
| Element | Quality    | Atomic      | Quality           | Atomic | Quality          | Atomic | Quality           | Atomic |
|         | Score      | Ratio       | Score (           | Ratio  | Score            | Ratio  | Score             | Ratio  |
|         | (%)        | (%)         | %)                | (%)    | (%)              | (%)    | (%)               | (%)    |
| С       | 45.47      | 54.12       | 38.30             | 47.08  | 45.40            | 52.83  | 42.39             | 50.85  |
| 0       | 49.01      | 43.79       | 48.55             | 44.80  | 53.20            | 46.47  | 48.69             | 43.85  |
| Na      | 0          | 0           | 8.49              | 5.45   | 0                | 0      | 5.81              | 3.64   |

| Table 4. Electronic Spectrum Analysis Data of t |
|---|
|---|

The elemental analysis of the surface and sections of the original and deacidified papers were completed via SEM-EDS analysis to characterize the elemental changes of the paper after deacidification (Shepherd et al. 1998). Because the contents of some elements, such as copper (Cu), magnesium (Mg), aluminum (Al), and silicon (Si), were extremely small in the samples and had little effect on the paper absorption of the deacidification agent, they were not tested in this analysis. As shown in Fig. 7 and Table 4, the total content of carbon (C) and oxygen (O) on the surface of the original paper was 97.91%. Because SEM-EDS cannot analyze the hydrogen in the samples, only the carbon and oxygen contents of paper were analyzed. Therefore the above results were consistent with the chemical composition of cellulose (Sagar *et al.* 2016). Compared to the original paper (a) in Fig. 7, the sodium content appeared on the surface of deacidified paper (b) reached 5.45%, confirming that the deacidification agent was absorbed on the surface of the paper. In the paper cross-section, the deacidified paper (d) also revealed the Na element, indicating that the deacidifying agent penetrated inside of the paper and might have neutralized the acidic substance inside the paper. The surface and cross-sectional analysis of the deacidified paper all contained a Na element, but the content of Na element on the surface of the deacidified paper (b) was higher than the content of Na element in the crosssectional area (d). This was mainly due to the fact that the Na<sub>2</sub>CO<sub>3</sub> had a larger area of contact with the surface of the paper and a larger amount adhered to the surface of the paper. According to the influence of paper permeability and absorption rate, the agent penetrated into the inside of the paper at a slower rate than the surface of the paper, so the internal agent content was less than that on the surface.

#### CONCLUSIONS

In this study, the paper was deacidified and reinforced by Na<sub>2</sub>CO<sub>3</sub> and latex through ultrasonic atomization. The physical properties, internal structure, and surface morphology of the paper before and after aging were studied. The main conclusions are summarized below:

- 1. The results showed that  $Na_2CO_3$  latex was effective in the deacidification and reinforcement of paper. Even after aging, the pH of the paper was higher than 7, and the change of color difference was only slight; the naked eye could hardly detect the change.
- 2. The application of Na<sub>2</sub>CO<sub>3</sub> for deacidification treatment had no obvious effect on the breaking length and tear index of the paper. However, when using the Na<sub>2</sub>CO<sub>3</sub> and latex for the deacidification and reinforcement treatment, the breaking length and the tear

index of the paper were increased. The treated samples typically behaved better than the blank paper after aging, indicating that the durability of the paper after treatment was improved. Even the treatment had little effect on the morphology of the paper, the ink and handwriting were not diffused or smudged. This is important for applying this method on the old books in practice.

3. In this study, the SEM-EDS analysis afforded more scientific information on the Na<sub>2</sub>CO<sub>3</sub>-latex treatment mechanism. The deacidification agent was present not only on the surface of the paper, but it also penetrated into the inside of the paper, which neutralized the acidic substances. According to the SEM images, it was clearly observed that the latex composite mainly adhered to the surface of the fiber in a spherical structure, wrapping on the surface of the fiber to form a film, and consequently thickened the fiber. After artificial aging, the spherical-like latex composite particles became flat, and similarly spread to wrap the fibers, fill the fiber cracks, and thus prevented the fiber from degrading and breaking.

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#### **REFERENCES CITED**

- Ahn, K., Hennniges, U., Banik, G., and Potthast, A. (2012). "Is cellulose degradation due to β-elimination processes a threat in mass de-acidification of library books?," *Cellulose* 19(4), 1149-1159. DOI: 10.1007/s10570-012-9723-3
- Area, M. C., and Cheradame, H. (2011). "Paper aging and degradation: Recent findings and research methods," *BioResources* 6(4), 5307-5337. DOI: 10.15376/biores.6.4.5307-5337
- Baglioni, P., Chelazzi, D., Giorgi, R., and Carretti, E. (2014). "Commercial Ca(OH)<sub>2</sub> nanoparticles for the consolidation of immovable works of art," *Applied Physics A* 114(3), 723-732. DOI: 10.1007/s00339-013-7942-6
- Bastone, S., Chillura Martino, D. F., Renda, V., Saladino, M. L., Poggi, G., and Caponetti, E. (2016). "Alcoholic nanolime dispersion obtained by the insolubilisation-precipitation method and its application for the deacidification of ancient paper," *Colloids Surf. A: Physicochem. Eng. Aspects* 513(5), 241-249. DOI: 10.1016/j.colsurfa.2016.10.049
- Baty, J. W., Maitland, C. L., Minter, W., Hubbe, M. A., and Jordan-Mowery, S. K.
  (2010). "De-acidification for the conservation and preservation of paper-based works: A review," *BioResources* 5(3), 1955-2023. DOI: 10.15376/biores.5.3.1955-2023
- Bukovský, V. (2005). "The analysis of alkaline reserve in paper after de-acidification," *Restaurator* 26(4), 265-275. DOI: 10.1515/rest.2005.265
- Bukovský, V. (1999). "Is de-acidification a step to the rescue of historic newspapers?," *Restaurator* 20(2), 77-96. DOI: 10.1515/rest.1999.20.2.77
- Campbell, W. B. (1959). "The mechanism of bonding," *TAPPI Journal* 42(12), 999-1001.

- Chen, L., and Huang, X. X. (2018). "Aging behavior of non-aqueous MgO deacidification system in de-acidification of paper archives-A case study of writing paper," *Archives Science Bulletin* 2018(1), 97-102. DOI: 10.16113/j.cnki.daxtx.2018.01.021
- Chen, L., Wang, L. C., and Yan, Y. L. (1988). "Study on acid removal technology of magnesium methyl carbonate paper file," *Archives Research* 1, 47-51. DOI: 10.16065/j.cnki.issn1002-1620.1988.01.008
- Fan, H. M., and Guo, M. F. (2018). "Discussion on the preservation and repair of ancient books from the perspective of papermaking," *China Paper* 37(8), 61-65. DOI: 10.11980/j.issn.0254-508X.2018.08.011
- GB/T 450 (2008). "Determination of paper and paperboard specimens and determination of longitudinal, lateral and frontal surfaces of specimens," Standardization Administration of China, Beijing, China.
- GB/T 13528 (1992). "Determination of pH of paper and board surfaces," Standardization Administration of China, Beijing, China.
- Giorgi, R., Bozzi, C., Dei, L., Gabbiani, C., Ninham, B. W., and Baglioni, P. (2005). "Nanoparticles of Mg(OH)<sub>2</sub>: Synthesis and application to paper conservation," *Langmuir* 21(18), 8495-8501. DOI: 10.1021/la050564m
- Giorgi, R., Dei, L., Ceccato, M., Schettino, C., and Baglioni, P. (2002).
  "Nanotechnologies for conservation of cultural heritage: Paper and canvas deacidification," *Langmuir* 18(21), 8198-8203.
- Hanus, J., Bakos, D., Vrska, M., Jablonsky, M., Katuscak, S., Bajzikova, M., Bukovsky, V., and Rychly, J. (2008). "The Kniha project in Slovakia," in: 2<sup>nd</sup> International Symposium and Workshops, Liubjana, Slovenia, pp. 17-19.
- He, B. (1994). *Principles and Engineering of Papermaking*, China Light Industry Press, Beijing, China.
- He, B., Lin, Q. X., Chang, M. M., Liu, C. F., Fan, H. M., and Ren, J. L. (2019). "A new and highly efficient conservation treatment for de-acidification and strengthening of aging paper by *in-situ* quaternization," *Carbohydrate Polymers* 209, 250-257. DOI: 10.1016/j.carbpol.2019.01.034
- Hon, D. N. S. (1989). "Critical evaluation of mass deacidification processes for book preservation," in: *Historic Textile and Paper Materials II*, S. H. Zeronian, and H. L. Needles (eds.), American Chemical Society, Washington, DC, USA. DOI: 10.1021/bk-1989-0410.ch002
- Hubbe, M. A., Henniges, U., Potthast, A., Ahn, K., and Smith, R. D. (2018).
  "Nonaqueous solution deacidification treatments to prolong the storage life of acidic books: A review of mechanistic and process aspects," *BioResources* 13(3), 7096-7136. DOI: 10.15376/biores.13.3.Hubbe
- Hubbe, M. A., Smith, R. D., Zou, X., Katuscak, S., Potthast, A., and Ahn, K. (2017).
  "Deacidification of acidic books and paper by means of non-aqueous dispersions of alkaline particles: A review focusing on completeness of the reaction," *BioResources* 12(2), 4410-4477. DOI: 10.15376/biores.12.2.4410-4477
- ISO 187 (1990). "Paper, board and pulps -- Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples," International Organization for Standardization, Geneva, Switzerland.
- ISO 1924-2 (2008). "Paper and board Determination of tensile properties Part 2: Constant rate of elongation method (20 mm/min)," International Organization for Standardization, Geneva, Switzerland.

- ISO 1974 (2012). "Paper -- Determination of tearing resistance -- Elmendorf method," International Organization for Standardization, Geneva, Switzerland.
- ISO 2470-1 (2009). "Paper, board and pulps -- Measurement of diffuse blue reflectance factor -- Part 1: Indoor daylight conditions (ISO brightness)," International Organization for Standardization, Geneva, Switzerland.
- ISO 5630-1 (1991). "Paper and board-Accelerated aging. Part 1: Dry heat treatment at 105 °C," International Organization for Standardization, Geneva, Switzerland.
- Page, D. (1993). "A quantitative theory of the strength of wet webs," *Journal of Pulp and Paper Science* 19(4), J175-J176.
- Poggi, G., Giorgi, R., Toccafondi, N., Katzur, V., and Baglioni, P. (2010). "Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper," *Langmuir* 26(24), 19081-19084.
- Roberson, D. D. (1976). "The evaluation of paper permanence and durability," *TAPPI Journal* 59(12), 63-69.
- Sagar, J. T., Burgess, S. R., McCarthy, C., and Li, X. (2016). "Elemental characterization of sub 20 nm structures in devices using new SEM-EDS technology," *Microelectronics Reliability* 64, 367-369. DOI: 10.1016/j.microrel.2016.07.080
- Sequeira, S., Casanova, C., and Cabrita, E. J. (2006). "De-acidification of paper using dispersions of Ca(OH)<sub>2</sub> nanoparticles in isopropanol study of efficiency," *Journal of Cultural Heritage* 7(4), 264-272. DOI: 10.1016/j.culher.2006.04.004
- Shepherd, T. J., Ayora, C., Cendon, D. I., Chenery, S. R., and Moissette, A. (1998). "Quantitative solute analysis of single fluid inclusions in halite by LA-ICP-MS and cryo-SEM-EDS; complementary microbeam techniques," *European Journal of Mineralogy* 10(6), 1097-1108. DOI: 10.1127/ejm/10/6/1097
- Strlič, M., Cigić, I. K., Kolar, J., De Bruin, G., and Pihlar, B. (2007). "Non-destructive evaluation of historical paper based on pH estimation from VOC emissions," *Sensors* 7(12), 3136-3145. DOI: 10.3390/s7123136
- Tan, W., Cheng, L. F., and Fang, Y. X. (2013). "De-acidification of paper using supercritical carbon dioxide containing calcium propionate or magnesium bicarbonate," *Advanced Materials Research* 781-784, 2637-2640. DOI: 10.4028/www.scientific.net/AMR.781-784.2637
- Williams, J. C., and Kelly, Jr., G. B. (1976). "Method of de-acidifying paper," U.S. Patent No. 3969549.
- Xingling, T., Xiao, Z., and Feng, G. (2008). "Non-destructive testing and analysis technology in the field of cultural relics protection," *Non-destructive Testing* 2008(3), 178-182. DOI: 10.3969/j.issn.1000-6656.2008.03.013
- Xu, W. J., and Zhu, P. F. (2010). "Research on the causes of discoloration of paper artifacts and methods of decolorization," *Cultural Relics Protection and Archaeology* 22(2), 92-96. DOI: 10.3969/j.issn.1005-1538.2010.02.017

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