ULTRASOUND-ASSISTED DEACIDIFICATION OF AGED PAPER USING BORATES

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As a paper deacidification agent, borax has been used in ancient paper protection. In order to study the deacidification effects of borax compounds, a series of paper immersion experiments have been done. The pH, whiteness and strength of treated paper were investigated. The results showed that lithium tetraborate and potassium tetraborate can not only maintain the pH in a proper range, but also strengthen the mechanical parameters of paper, and have similar deacidification effects to those of borax. The effect of lithium tetraborate was slightly better than those of potassium tetraborate and borax. Ultrasonic technology was applied to assist deacidification of ancient paper with the mentioned deacidification agents. SEM and FTIR analyses were carried out to analyze the damage of paper. The results indicated that the deacidification time decreased due to the effects of the mechanical action and cavitation of ultrasounds, and the ultrasound-assisted deacidification did not affect the properties of the paper.

Keywords: paper, lithium tetraborate, potassium tetraborate, deacidification, ultrasound (US), mechanical properties

INTRODUCTION

Ancient literature manuscripts are an important part of our historical and cultural heritage. Unfortunately, valuable ancient manuscripts are damaged over time because of acidity, oxygen, pollutants or biodeterioration.[1] Cellulose in paper fibers undergoes acid-catalyzed hydrolysis, which is considered a major factor of deterioration.[2] Therefore, stopping this deterioration mechanism is an urgent problem to solve.

Many researchers have contributed to finding effective reagents or processes of deacidification, which could reduce the deacidification time and prolong the expected lifetime of documents. At present, liquid phase and gas phase processes are the main deacidification methods known. A number of scientists prefer liquid phase deacidification rather than the unsafe gas phase process.[3] However, some liquid phase deacidification solutions are harmful to human health, such as barium hydroxide methanol and methoxymethyl carbonate.[4] Moreover, some non-toxic deacidification reagents, such as calcium propionate and magnesium bicarbonate, have a poor deacidification effect.[5,6] Therefore, finding a more effective deacidification reagent has gradually become a hot research topic. Wang *et al*. demonstrated the efficient use of borax for the purpose of deacidification.[7] Firstly, it can keep the final pH value of papers between 7.0 and 8.5.[8] Secondly, it does no harm to people's health. Aqueous solutions of borate salts can control the pH in an appropriate range due to their strong buffering capacity.

In the present study, borax and other borate compounds, such as lithium tetraborate and potassium tetraborate, which have similar characteristics to those of borax, have been

investigated. These salts were applied for the deacidification of aged paper. The properties of paper after deacidification, such as pH, chromatic changes and mechanical properties, were studied.

However, the main objectives of our study were not only to find deacidification reagents with good performance, but also to improve the deacidification rate. Ultrasonic technology was developed in the 20th century and has been widely used in electronics, machinery, light industry and other domains to increase reaction rates.[9,10] This technology mainly depends on the interaction of ultrasounds with media. The most common interaction mechanisms involve mechanical action, cavitation effects and heat effects. In the present study, the ultrasonic technology has been used to assist deacidification reagents in deacidifying paper. The effects of ultrasound waves on the deacidification of paper were assessed. The pH value, chromatic changes and mechanical properties of paper were also investigated after the deacidification treatment.

EXPERIMENTAL

Materials

The following notations were conventionally used to denote the deacidification treatments and paper samples:
BSD: Samples of "Beauty Star Daily" journal, 1982;
BX: AR borax, $Na_2B_4O_7 \cdot 10H_2O$;
LT: AR lithium tetraborate, $Li_2B_4O_7$;
PT: AR potassium tetraborate, $K_2B_4O_7 \cdot 5H_2O$;
BSD-IM: paper sample immersed in distilled water solution;
BX-IM: paper sample immersed in distilled water solution of AR borax;
LT-IM: paper sample immersed in distilled water solution of AR lithium tetraborate;
PT-IM: paper sample immersed in distilled water solution of AR potassium tetraborate;
BX-US: deacidification process of BX-IM assisted by ultrasound;
LT-US: deacidification process of LT-IM assisted by ultrasound;
PT-US: deacidification process of PT-IM assisted by ultrasound;

All chemicals were Aladdin products, with a purity higher than 99 wt%.

Sample parameters

Table 1 shows the characteristics of the initial BSD samples used in the investigation, as well as those of the samples treated with a blank solution.

Immersion treatment with basic agents (alkali treatment)

Paper samples were immersed in a distilled water solution of LT and PT, respectively. A water solution of BX was also tested for the sake of comparison. The concentration of the basic agent solutions were varied from 0.0001 molg^{-1} to 0.0020 molg^{-1}. The paper samples were kept in the solution for 20~40 minutes.[11]

Table 1
Characteristics of original paper samples and samples treated with a blank solution

Parameters		BSD	BSD-IM	BSD-IM after aging for 3 days	Standard
Grammage (g^{-2})		-	-	-	ISO 536:1995
pH of paper surface		3.72-3.92	4.05-4.12	3.62-3.85	ISO6588-1:2005
Tensile strength (kNm^{-1})		1.519-1.615	1.588-1.695	1.268-1.432	ISO1924-2:2008
Stretch (%)		0.41-0.52	0.43-0.55	0.30-0.38	ISO1924-2:2008
Folding endurance (times)		4-6	5-6	3-4	ISO 5626:1993
Tear index (mN)		100.0-120.0	110.0-128.0	100.0-116.2	ISO 1974:1990
Colorimetric measurements	*L'*	73.26-74.26	72.65-73.25	70.28-72.85	ISO 11476
	a'	8.06-9.06	8.10-8.68	8.65-9.89	
	b'	20.23-21.23	20.05-21.18	21.19-22.32	

Ultrasonic treatment

The specimens of paper were put in a beaker containing the respective deacidification solution and subjected to ultrasonic treatment (KH2200B). The ultrasound-assisted deacidification procedure was operated in an inox jug (23×14 cm) with a maximal capacity of 3 L and a transducer. At the bottom of jug, the beaker was operated at 40 kHz with an input power of 80 W. The ultrasound temperature was kept at 25 °C and the treatment time was varied between 10 and 20 minutes. Then, the beaker was removed rapidly from the ultrasonic cleaning device, the paper samples were taken out, placed flat on a table and left in the air for more than 24 h.

Kinetics of accelerated aging

It was reported that 3 days of accelerated aging corresponded to about 25 years of natural aging,[12] and the mechanical properties of paper samples would change

over time.[13,14] Before aging experiments, the samples were treated by immersion and ultrasonication at 23 °C and 50% RH for 24 h.[15] Then, BSD paper samples were exposed to accelerated aging procedures to simulate the long-term degradation processes for an appropriate duration. Thermal aging of paper samples was conducted at 105±2 °C in a thermostat chamber under forced air circulation for 72 h (ISO5630-1:1991).[16]

Measurement

The main characteristics of paper samples (pH of the paper surface and physico-mechanical parameters), with and without ultrasound treatment, were determined by standard techniques listed in Table 1.[17]

pH measurement

The pH of paper surface was determined according to ISO 6588-1:2005, which depends on the uniformity of the immersion treatment with basic agents.

Colorimetric measurement

The colorimetric value was measured by a Color Reader CR-10 Konica Minolta® colorimeter. Each value was calculated from 10 sets of data with an error in the range of ±10% (ISO11476:2000). Colorimetric measurements CIE (*L'*, *a'*, *b'*) focused on standard chromatic coordinates. Parameter *L* represents the lightness of the color between white and black (the smallest value meaning black), *a* means the color between yellow and blue (the smallest value meaning blue), and *b* represents the color between red and green (the smallest value meaning green).

Physico-mechanical performance

Before the tests, the samples were kept at 23 °C and 50% RH for 24 h. The tests were performed according to the international standards listed in Table 1. The values of tensile strength, stretch, folding endurance and tear were calculated from 10 sets of measurements with an error in the range of ±10%, while the mean values of folding endurance were evaluated from 20 sets of measurements with an error in the range of ±15%. Relative losses (%) of mechanical properties of the paper samples were measured after artificial aging for 72 h.

Scanning electron microscopy (SEM)

The morphological analysis of the surfaces of untreated and treated paper samples were observed by SEM (S-3400N, Hitachi Ltd., Japan).[18]

Infrared spectroscopy

Pellets of *cca.* 2 mg of cellulosic samples were prepared. FTIR spectra were recorded using a Nicolet 380 spectrometer, equipped with a detector, with 4 cm^{-1} resolution and 64 scans per sample.[19]

RESULTS AND DISCUSSION

Evolution of pH of the paper surface after immersion treatment and accelerated aging

A standard sample of paper was immersed into 0.0001 $molg^{-1}$ to 0.0020 $molg^{-1}$ (paper) of alkaline reagent water solution,[20] for 0~60 minutes. From Figure 1, it may be noted that, after the deacidification treatment, the pH value of all the paper samples increased with increasing duration of the treatment and leveled off after 20 minutes. The evolution of the pH values of LT-IM, BX-IM and PT-IM showed a similar tendency, and the final pH value reached was below 8.5. Meanwhile, the pH of the paper samples treated with the blank water solution was still below 4.5. According to previous research, a pH value of paper between 7 and 8.5, after treatment, would prevent the paper from acid and alkaline depolymerization.[21] In our study, the pH value of LT-IM, BX-IM and PT-IM was maintained in that range. Aqueous solutions of borate salts have a strong buffering capacity and can control the pH in an appropriate range, which will contribute to a long-term preservation of paper.

According to Figure 2, samples LT-IM, BX-IM and PT-IM showed a similar decrease in the pH after accelerated aging for 3, 6, 9, 12 and 20 days. After 15 days of aging, the pH of LT-IM, BX-IM and PT-IM was 7.02, 7.08 and 7.08, respectively. Thus, it can be estimated that the pH of the paper samples will be still in a safe range after 125 years. After 20 days of aging, LT-IM, BX-IM and PT-IM samples showed pH values of 6.05, 6.06 and 6.09, respectively. These findings allow concluding that the deacidification treatment of paper samples with borate salts could preserve them for at least 125 years.

Mechanical performance of paper samples after immersion and ultrasound treatments

It is known that the tensile strength of paper depends on the bonding strength among fibers, average fiber strength, fiber crisscross coefficient and internal organization direction. Folding endurance depends on fiber length, strength, flexibility and adhesion strength. Stretch and tear index can be related to the ability of paper to conform and maintain conformance to a particular contour. After the deacidification treatment, all the

mechanical properties of the samples were improved. The samples could be ranked with regard to their tensile strength, stretch, folding endurance, and tear index as follows: LT-IM > BX-IM > PT-IM (Table 2). The results thus reveal that lithium tetraborate has a better effect on the mechanical performance of paper, compared to the other two deacidification reagents.

Chromatic changes upon deacidification

After immersion treatments with PT, BX and LT, the chromatic changes of the paper samples were assessed. The values obtained for the colorimetric coordinates of paper samples, before and after deacidification treatment, are listed in Table 3. The data demonstrate that there were no obvious changes in the *L'* and *b'* coordinates, which indicates that the three deacidification solutions under study had no influence on the chromophores in the paper. Compared with the changes in *L'* and *b'*, it may be observed that the variation of amplitude of *a'* was a little higher. This may be related to the paper itself. Also, the red ink applied on the paper migrated to the interior of the sample, which can be attributed to the soluble red ink applied in newspapers.[22]

After accelerated aging, the evolution of colorimetric coordinates of paper samples was compared with their initial values for untreated samples. The results revealed that PT, BX and LT could largely prevent the degradation and oxidation of cellulose, all three deacidification agents are suitable for treating paper.

Ultrasonic treatment

Ultrasonic energy refers to mechanical waves in the frequency range from 20 kHz to 10^6 kHz. Its effects include mechanical action, cavitation and heating in the process of interaction with media.[23]

The application of ultrasonic technology has been widely used in various fields, such as sewage disposal, petrochemical industry, electric industry, nanomaterials, medical diagnosis *etc*. Other application fields include organic synthesis, catalyst manufacture and regeneration, extraction of materials, separation, scattering, crystallization, atomization, dry heat transfer and others.[24] However, to the best of our knowledge, no published studies have reported on the use of ultrasound technology to assist the deacidification of paper so far.

Therefore, in the present study, ultrasonic technology has been applied in paper deacidification in order to test our hypothesis that it could determine an improvement in the efficiency of the process. Setting an overly long time or a too high power for the ultrasonic treatment may influence the structure of the paper. Hence, a series of experiments were done to investigate this assumption.

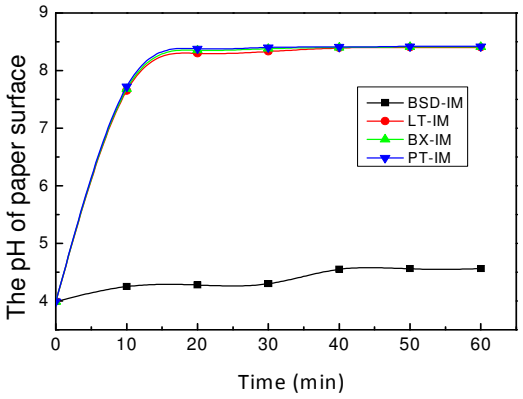

Figure 1: pH values of paper samples as a function of immersion treatment time

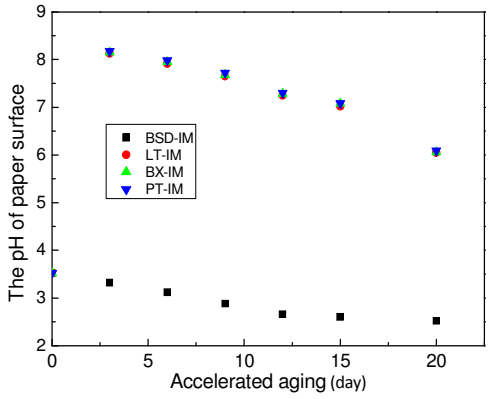

Figure 2: pH values of paper samples after 3-20 days of accelerated aging

Table 2

Physico-mechanical properties of paper samples subjected to immersion and US treatments, with or without deacidification and artificial aging

Properties		PT-IM	BX-IM	LT-IM	LT-US
Tensile strength (kNm^{-1})	Before treatments	1.489±0.10	1.475±0.06	1.480±0.08	1.460±0.05
	Deacidification	1.642±0.02	1.668±0.05	1.790±0.06	1.780±0.08
	Accelerated aging	1.550±0.08	1.558±0.06	1.583±0.05	1.590±0.02
	D–B[a]	10.27	13.08	20.95	21.92
	A–D[b]	-5.60	-6.59	-11.56	-10.67
Stretch (%)	Before treatments	0.92±0.05	0.89±0.02	0.82±0.01	0.8±0.05
	Deacidification	1.15±0.08	1.18±0.06	1.29±0.06	1.25±0.02
	Accelerated aging	1.01±0.01	1.05±0.05	1.08±0.02	1.10±0.08
	D–B	25	32.58	57.32	56.25
	A–D	-12.17	-11.02	-16.28	-12
Folding endurance (times)	Before treatments	5±1	6±1	5±1	5±1
	Deacidification	8±2	9±2	10±3	10±3
	Accelerated aging	7±1	8±2	8±1	8±1
	D–B	60.00	50.00	100.00	100.00
	A–D	12.5	11.11	20.00	20.00
Tear index (mN)	Before treatments	80.2±10.2	78.8±10.3	79±10.2	78±8.5
	Deacidification	120.2±11.2	125.6±9.5	132.8±9.8	130.5±6.6
	Accelerated aging	112.8±8.8	115.2±8.8	118.6±8.5	116.9±7.9
	D–B	49.88	59.39	68.10	67.3
	A–D	-6.16	-8.28	-10.69	-10.42

[a]Percentage (%) variation in mechanical properties after deacidification to the values obtained before treatments
[b]Percentage (%)variation in mechanical properties after accelerated aging to the values obtained with deacidification

Table 3
Colorimetric coordinates of paper subjected to immersion and ultrasound treatments before and after deacidification and artificial aging

Colorimetric measurements		PT-IM	BX-IM	LT-IM	LT-US
Before	*L'*	73.20±0.55	73.22±0.33	73.18±0.25	73.32±0.36
	a'	8.25±0.32	8.29±0.20	8.22±0.55	8.30±0.32
	b'	21.08±0.55	21.03±0.45	21.05±0.42	21.02±0.35
After deacidification	*L'*	73.15±0.24	72.62±0.33	72.83±0.32	72.80±0.33
	a'	8.78±0.22	8.72±0.35	8.68±0.40	8.45±0.25
	b'	20.72±0.52	20.25±0.42	19.98±0.28	19.99±0.32
After artificial aging	*L'*	72.75±0.22	72.40±0.45	72.05±0.55	72.02±0.62
	a'	7.88±0.25	7.92±0.32	7.95±0.28	7.85±0.45
	b'	20.99±0.36	20.55±0.29	20.02±0.33	20.03±0.35

The results proved that when the ultrasonic treatment time was set within 20 minutes and the power at 100 W, there was little influence of the treatment on the ink, fiber adhesion and strength of paper.

Effects of ultrasound treatment time upon deacidification

To study the influence of ultrasound treatment time on the deacidification of paper samples, paper samples were immersed into PT, BX or LT solutions, respectively, and subjected to ultrasound exposure for 5 to 30 minutes. The ultrasound power was set to 80 W. It is well known that tensile strength and stretch are two important physical parameters in judging the strength of paper. For this reason, these properties were tested in the experiment. The results showed that when the ultrasound treatment time was set to about 10 minutes, the tensile strength and stretch achieved better values than those obtained at other treatment durations.

Colorimetric tests were performed as well (Table 4). The paper samples were immersed into the LT solution and subjected to ultrasounds for 5 to 30

minutes. The results indicated that when the ultrasound exposure time lasted for 10 minutes, the paper sample was much whiter than when exposed to other ultrasound treatment times. Therefore, it could be concluded that an ultrasound exposure time of 10 minutes was the most suitable. According to the previously performed series of tests, the ideal deacidification time with LT without ultrasound treatment was 20 minutes. Therefore, in the following experiments, the deacidification of LT-IM for 20 minutes was compared with that of LT-UT for 10 minutes.

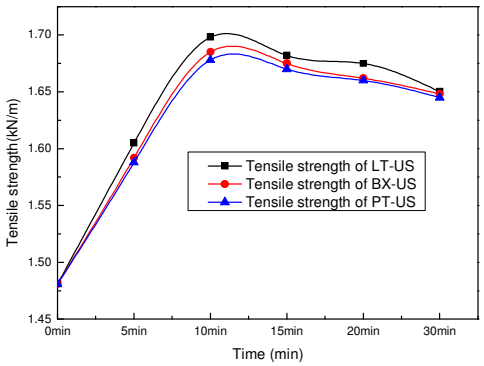

Figure 3: Effect of ultrasound treatment time on tensile strength

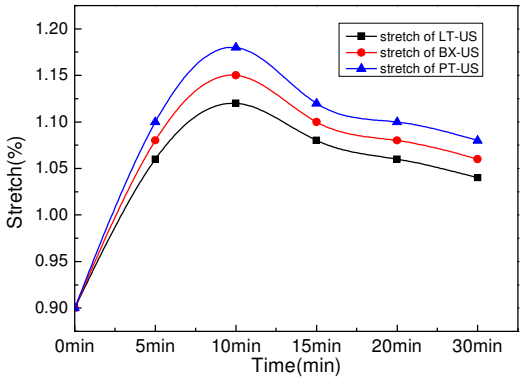

Figure 4: Effect of ultrasound treatment time on stretch

Table 4
Effect of ultrasound treatment time on colorimetric coordinates of paper samples

Coordinate	0 min	5 min	10 min	15 min	20 min	30 min
L'	72.10	71.75	72.20	72.18	72.05	72.02
a'	8.23	8.32	8.45	8.42	8.35	8.32
b'	21.02	20.88	20.40	20.35	20.28	20.15

Chromatic changes of paper upon ultrasound treatment

Paper sample LT-IM exhibited no obvious changes in the *L'* and *b'* coordinates (Table 4) after exposure to ultrasounds. Moreover, under the action of ultrasounds, the deacidification time could be significantly shortened. This is due to the mechanical action and cavitation effect of ultrasounds, which facilitate faster penetration of the agent into the fibers and more uniform impregnation of the the paper, which could decrease the diffusion of ink in the paper. As can be seen in Table 4, the ultrasound-assisted deacidification did not cause any evident color changes in the paper samples, compared with the immersion treatment alone. This demonstrates that the ultrasound technology is suitable for treating paper with the purpose of deacidification under controllable conditions.

After the accelerated aging tests, the deacidification effect of the aged paper samples subjected to ultrasound exposure was higher than that of the samples treated by immersion only. As a result, the former showed less yellowing and higher brightness than the latter. Compared with the initial unaged ultrasound treated samples, the *L'* and *a'* values of the aged ultrasound treated ones decreased only by 1% and 7%, respectively, while the *b'* value increased by 0.2%.

Paper strengthening upon ultrasound treatment

It could be noted from Table 2 that the percentage variation in the tensile strength, stretch, folding endurance and tear index of sample LT-IM, after deacidification to the initial values, amounted to 20.95%, 57.32%, 100% and 68.1%, respectively, while the corresponding values of LT-US reached 21.92%, 56.25%, 100% and 67.3%, respectively. Compared with the values for LT-IM, the changes occurring in LT-US are minor. However, after artificial aging, the percentage variation in the

tensile strength, stretch, folding endurance and tear index of LT-US reached -10.67%, -12%, 20%, -10.42%, respectively, indicating that the ultrasound treated sample was less affected by artificial ageing than the aged sample LT-IM, treated by immersion only. Thus, using ultrasound technology to assist LT deacidification is a reasonable choice: it shortened the deacidification time, and led to better mechanical properties of the paper after artificial ageing.

SEM analysis

In order to further study the effect of ultrasound-assisted deacidification, SEM was used to characterize the morphology of the samples. SEM images in Figure 5 show the surface of the untreated paper (Fig. 5 a and b), of sample LT-IM treated by simple immersion for 20 minutes (Fig. 5 c and d) and of sample LT-US treated by ultrasound-assisted immersion for 10 minutes (Fig. 5 e and f). Images a, c and e were magnified 500 times, while images b, d and f have a magnification of 3000 times.

As can be seen in Figure 5 a and b, the surface of the fiber of the untreated paper sample was wizened. Compared to the untreated sample, the paper deacidified with LT for 20 minutes presented a much softer fiber surface (Fig. 5 c and d). Judging by the images in Figure 5 e and f, ultrasound-assisted deacidification for 10 minutes did not affect negatively the fiber surface. It may be concluded from our SEM observation[25,26] that the deacidification process had a positive effect on the fibers on the paper surface, while the ultrasonic treatment did not alter this positive effect.

FTIR analysis

FTIR analysis was performed to detect any changes in the structure of fibers under the influence of the ultrasonic treatment (Fig.6). The characteristic absorption peaks of cellulose may be noted around 2900 cm^{-1} and 3400 cm^{-1} in the spectra of all the samples, with a strong peak at 3338 cm^{-1} assigned to the vibration of –OH. The peaks at 2907 cm^{-1} and 1663 cm^{-1} are related to CH stretching vibrations and carbonyl (C-O) stretching, respectively. The band near 1245 cm^{-1} corresponds to the-C-O-C- bond in the cellulose chain. Thus, the FTIR spectra of the three samples reveal insignificant changes among them, which allows concluding that ultrasound-assisted deacidification does not affect the structure of the fibers of paper.[27,28]

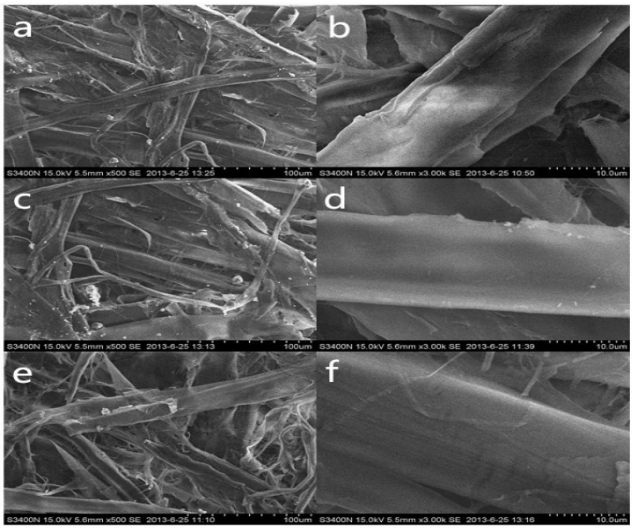

Figure 5: SEM images of paper samples (a-b – untreated paper, c-d – sample LT-IM treated for 20 min, e-f – sample LT-US treated for 10 min)

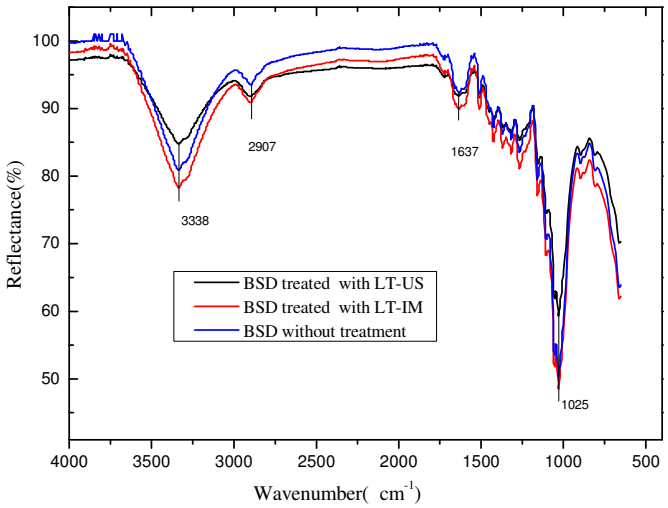

Figure 6: FTIR spectra of papers in the wavenumber range 4000-500 cm^{-1}

CONCLUSION

Our study demonstrated that both lithium tetraborate and potassium tetraborate, similarly to borax, can control the pH of paper in a proper range. Moreover, lithium tetraborate can achieved better results, even when a small amount of reagent is added.

In order to increase the deacidification rate of aged paper, ultrasound technology was used to assist the deacidification process. It could be observed that, when using ultrasounds to assist paper deacidification, a shorter deacidification time was necessary. Moreover, ultrasound-assisted paper deacidification has a minimum to no negative impact on the paper, with regard to its tensile strength, folding endurance, tear index and color.

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REFERENCES

[1] S. Sequeira, E. J. Cabrita and M. F. Macedo, *Int. Biodeter. Biodegrad.*, **74**, 67 (2012).
[2] R. D. Smith, *The Library Quarterly*, **36**, 273 (1966).
[3] U. S. Patent 3472611, 1966.
[4] R. Giorgi, D. Chelazzi and P. Baglioni, *Appl. Phys. A*, **83**, 567 (2006).
[5] A. Bluher, *Chimia*, **55**, 981 (2001).
[6] A. L. Dupont, B. Lavedrine and H. Cheradame, *Polym. Degrad. Stabil.*, **95**, 2300 (2010).
[7] Y. J. Wang, Y. X. Fang and W. Tan, *J. Cult. Herit.*, **14**, 16 (2013).
[8] Q. Haisong, T. Liebert and F. Meister, *Macromol. Symp.*, **294**, 125 (2010).
[9] J. A. Gallego-Juareza, G. Rodriguez-Corrala, J. C. Gálvez Moraleda and T. S. Yang, *Dry. Technol.*, **17**, 597 (1999).
[10] A. Mizrach, *Postharvest Biol. Tech.*, **48**, 315 (2008).
[11] W. Tan, L. F. Cheng and Y. X. Fang, *Adv. Mater. Res.*, **781**, 2637 (2013).
[12] B. Havlinova and V. Brezova, *J. Mater. Sci.*, **37**, 303 (2002).
[13] X. Zou, T. Uesaka and N. Gurnagul, *Cellulose*, **3**, 243 (1996).
[14] H. Ial, in *Procs. 64th IFLA General Conference*, Amsterdam, Netherlands, August 16-21, 1998, pp. 114-115.
[15] B. Havlínová, S. Katuščák, M. Petrovičová, A. Maková and V. Brezová, *J. Cult. Herit.*, **10**, 222 (2009).
[16] E. Ardelean, E. Bobu, Gh. Niculescu and C. Groza, *Cellulose Chem. Technol.*, **45**, 97 (2011).
[17] Q. L. Li, S. C. Xi and X. W. Zhang, *J. Cult. Herit.*, **15**, 159 (2014).
[18] E. Formo, M. S. Yavuz, E. P. Lee, L. Lane and Y. N. Xia, *J. Mater. Chem.*, **19**, 3878 (2009).
[19] D. Ray and B. K. Sarkar, *J. Appl. Polym. Sci.*, **7**, 1013 (2001).
[20] Y. J. Wang, W. Tan and C. Y. Liu, *Adv. Mater. Res.*, **347**, 504 (2012).
[21] S. Zervos and I. Alexopoulou, *Cellulose*, **22**, 2859 (2015).
[22] S. Sequeiraa, C. Casanovab and E. J. Cabritac, *J. Cult. Herit.*, **7**, 264 (2006).
[23] T. J. Mason, L. Paniwnyk and J. P. Lorimer, *Ultrason. Sonochem.*, **3**, 253 (1996).

[24] F. Chemat, Z. Huma and M. K. Khan, *Ultrason. Sonochem.*, **18**, 813 (2011).
[25] H. Zhao, J. H. Kwak, Z. C. Zhang, H. M. Brown, B. W. Arey *et al.*, *Carbohyd. Polym.*, **68**, 235 (2007).
[26] M. Das and D. Chakraborty, *J. Appl. Polym. Sci.*, **102**, 5050 (2006).
[27] L. A. Pothan, C. Bellman, L. E. Kailas and S. Thomas, *J. Adhes. Sci. Technol.*, **16**, 157 (2002).
[28] M. A. Sawpan, K. L. Pickering and A. Fernyhough, *Compos. A-Appl. Sci.*, **42**, 888 (2011).