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Original article

Preservation of aged paper using borax in alcohols and the supercritical carbon dioxide system

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ABSTRACT

Selecting an appropriate paper deacidification agent is very important for the deacidification of paper. The use of three deacidification agents (i.e., iso-butylamine, calcium propionate, and borax) is studied for the deacidification of paper using the immersion treatment by investigating the paper surface pH, alkaline residue, paper whiteness, strength, and other performance indicators. Results show the deacidification by borax solution not only results in the promotion of a proper pH range, high level of alkali reserves, and ignorable influence to paper appearance, but also to the enhancement of the mechanical intensities of paper even after artificial aging. Supercritical carbon dioxide (CO_2SCF), as a solvent system, is used in the deacidification of acidic papers using the borax solution of water and alcohol. CO_2SCF improved the deacidification process by significantly improving the pH value and the base residual value. The borax in supercritical fluids can be better combined with cellulose hydroxyl to improve the mechanical properties of paper substantially. The treatment of borax in CO_2SCF could be an alternative for acidic papers. Aside from improving the pH and depositing a sufficient alkaline residual, CO_2SCF also strengthens the mechanical properties of treated papers.

1. Introduction and research aims

Numerous archives and libraries all over the world, including China, have focused on a large number of decrepit and damaged documents. Many precious documents, such as archive materials, books, manuscripts, prints, and paintings on paper, are affected by the hydrolytic breakdown of cellulose catalyzed with acids [1]. Acids are mainly derived from four aspects, namely, the product of photo-oxidation, oxidation, inorganic acid from air, organic acid from bio-deterioration, and additives, such as aluminum sulfate [2]. Since the mid-19th and 20th centuries, more and more papers, especially most newspapers, have been industrially manufactured from mechanical pulp containing large amounts of additives, which can lead to the accumulation of acidic substances [3]. Thus, these manufactured papers have been facing serious acidification, and they would also evoke the acid-induced depolymerization of cellulose fibers through hydrolysis. Currently, more and more researchers have been contributing to the conservation, particularly deacidification, using their scientific knowledge to create solutions that could increase the expected lifetime of documents.In general, the final pH value of papers should be in the range of 7.0–8.5 after the deacidification treatments. If the pH value of the paper surface is too high, it would undergo alkaline depolymerization, leading to the decrease in the chain lengths of the cellulose [4]. Moreover, many deacidification treatment processes are suspects for diminishing paper strength and degrading paper because they damage the fiber structures and inks [5–7]. Borax dissolves in water to form boric acid and mono-borate [reaction (1)]. The boric acid/borate solution is a buffer, which can be propitious to deacidification treatments not only in controlling the pH of the paper in a reasonable range, but also in ensuring that there is no further alkaline hydrolysis in cellulose fibers.

$$[B_4O_5(OH)_4]^{2-} + 5H_2O = 2H_3BO_3 + 2[B(OH)_4]^{-} \quad \text{[reaction 1]} \qquad (1)$$

Borax, as an antibacterial agent, is known to effectively control the growth of microorganisms in the paper, which is also favorable for the long-term preservation of papers. Borax has been drawing considerable interests as mild and moderate alkaline agent. Moreover, it has shown a remarkable ability to accept electrons and form molecule interplay among the polyhydroxy cellulose molecules that can make papers stronger [8–11].

In the recent 30 to 40 years, CO_2SCF has been successfully used either as a nontoxic or an excellent inflammable solvent in other applications. CO_2SCF can be used at relatively low costs and just above room temperature, and it does not cause any deterioration in

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Table 1
Characteristic parameters of original and blank treatment paper samples.

Parameters	NYT	N-IM	N-IM after aging 3 days	Standard
Grammage ($g \cdot m^{-2}$)	45–50	–	–	ISO 536:1995
pH of the paper surface	3.45–3.65	3.77–3.92	3.30–3.52	GB/T 13528–92
Alkali reserve ($mol \cdot kg^{-1}$)	–	0.0002–0.0010	–	ISO 10716:1994
Tensile strength ($kN \cdot m^{-1}$)	1.72–1.82	1.78–1.89	1.45–1.62	ISO 1924–2:2008
Stretch (%)	0.81–0.93	0.83–0.97	0.70–0.75	ISO 1924-2:2008
Folding endurance (times)	4–6	5–6	3–4	ISO 5626:1993
Tear (mN)	100.2–120.2	110.3–134.2	100.0–110.5	ISO 1974:1990
Colorimetric measurements				
L	76.80–77.80	76.2–77.5	72.38–75.22	ISO 11476
a	2.87–3.87	2.91–3.55	3.42–4.35	
b	8.90v9.90	8.73–9.84	9.87–11.23	

inks, pictures, adhesives, or leather bindings of books [12,13]. Fortunately, the processing of paper in CO_2SCF has been verified highly efficient, safe, and practices wasteless conservation in the neutralizing treatment of acidic paper [14,15] because of the different deacidification agents, and its efficiency showed quite a difference. In the current study, three representational agents were selected for the immersion treatment, CO_2SCF treatment, and kinetics of accelerated aging to simultaneously find a suitable deacidification agent and method, and improve the mechanical properties of aged paper. Moreover, the effects of the three agents on the pH value, chromatic changes, mechanical properties, and alkali reserve of papers were investigated.

2. Experimental

2.1. Materials and methods

The conventional notations for the deacidification treatments and paper samples are as follows:

- NYT: samples of the New York Times newspaper, 1989;
- IB: AR iso-butylamine, $C_4H_{11}N$;
- CP: AR Calcium propionate, $(CH_3CH_2COO)_2Ca$;
- BX: AR borax, $Na_2B_4O_7 \cdot 10H_2O$;
- N-IM: the paper sample immersed in water and ethanol (volume ratio 50:50) solutions;
- IB-IM: the paper sample immersed in distilled water and ethanol (volume ratio 50:50) solutions of AR iso-butylamine;
- CP-IM: the paper sample immersed in distilled water and ethanol (volume ratio 50:50) solutions of AR calcium propionate;
- BX-IM: the paper sample immersed in distilled water and ethanol (volume ratio 50:50) solutions of AR borax;
- BX-CO_2SCF: the paper sample immersed in distilled water and ethanol (volume ratio 50:50) solutions of AR borax CO_2SCF.

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

2.1.1. Sample parameters

Table 1 shows the parameters of the NYT samples used in the investigation. A study on the other types of paper is currently undergoing.

2.1.2. Immersion treatment of basic agents

Paper samples were immersed in distilled water and ethanol solutions (volume ratios 50:50) of borax. The alcohol-water solvents of iso-butylamine and calcium propionate were also tested for comparisons. In these experiments, a standard sample of paper was immersed into a 0.0001 mol/g to 0.0020 mol/g (paper) of basic agent solution and was allowed to stand for 40 min.

2.1.3. Treatment with CO_2 SCF

Fig. 1 shows the scheme of the proposed experimental device for paper treatment using a basic agent in CO_2SCF. Rolled paper samples (about 20 g) were treated with CO_2SCF in reactor 1, which could be heated up to 80 °C. Gaseous CO_2 was introduced from cylinder 4, then cooled to liquid by cooler 6, and then compressed to the working pressure. An alkali alcoholic solution was introduced in portions into the mixing chamber during CO_2 pumping. The introduced alcoholic solution of a basic agent was mixed with the CO_2SCF fluid in mixer chamber 3 equipped with a magnetic stirrer. The pressure was monitored with pressure gauges and a backpressure regulator. In the segregator, the pressure and temperature decreased to the critical condition of CO_2, and CO_2 was separated from the alkali

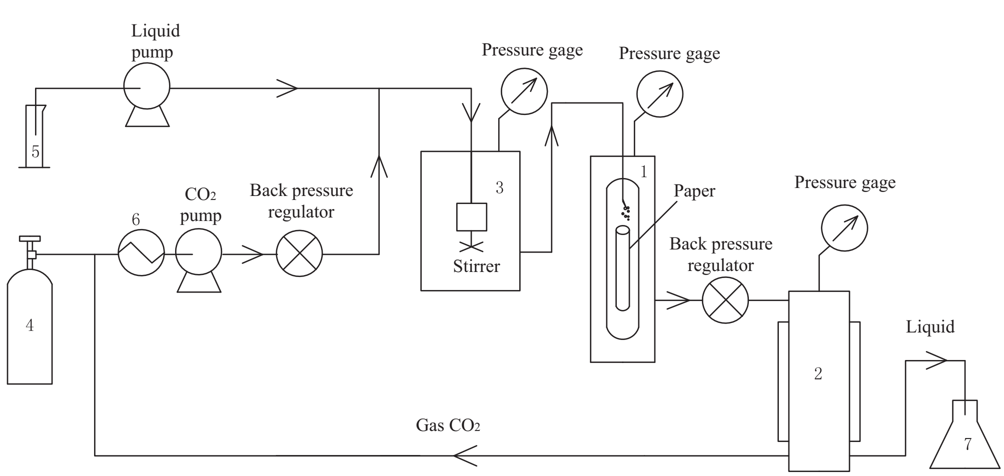

Fig. 1. Scheme of the experimental device of CO2SCF treatment for paper: (1) reactor, (2) segregator, (3) mixer, (4) CO2 cylinder, (5) alkali, (6) cooler, and (7) recover.