Journal of Cultural Heritage 15 (2014) 159–164

Available online at
SciVerse ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Original article

Deacidification of paper relics by plasma technology

Qinglian Li[a], Sancai Xi[b], Xiwen Zhang[a,b,*]

[a] Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
[b] Research Institute of Cultural Heritage, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 14 December 2012
Accepted 12 March 2013
Available online 22 April 2013

Keywords:
Plasma treatment
Deacidification
Paper
Tensile strength

ABSTRACT

With the acidification of paper and paper-containing relics becoming increasingly serious, a convenient, effective and harmless method for deacidification has become an urgent necessity in the protection of paper relics. In this research, a novel method for reducing the acidity of paper by plasma technology is presented, which can be used simply at room temperature and atmospheric pressure. The pH of the paper rises to alkalescence rapidly after treatment and remains stable with no color change, with a slight accompanying increase in the mechanical properties of the paper.

1. Introduction

Paper as a medium for written information is extremely important for transmitting and preserving knowledge and cultural history. However, with aging, more and more precious paper relics have become yellowed and brittle because of the acidification of paper. The main structure of paper consists of cellulose fibers. Cellulose is a polymer consisting of linear β(1-4)D-glucopyranosyl units which will hydrolyze in acidic conditions. Acidity from the absorption of atmospheric pollutants, oxidation of lignin and additives from the papermaking process can all act as catalysts in the process of acid hydrolysis of paper [1]. These hydrolysis catalysts penetrate the paper fiber and cause glucosidic bond scission, which results in the degradation of cellulose. Furthermore, the hydrolysate contains additional acidic substances, which make this process a vicious cycle which ultimately results in a significant decrease in the mechanical strength of paper. Therefore, the removal or prevention of acidity is one of the most significant problems to be addressed in paper reinforcement and conservation.

There are currently several methods for paper deacidification being applied in conservation and restoration [2], but they have several unavoidable drawbacks [1,3]. For example, direct contact with chemical deacidification reagents which are mostly based on non-environmentally friendly solvents [4,5], will lead to paper crinkle, and visual appearance altering. Some other methods have very rigid deacidification conditions [6]. Thus, an efficient, convenient and environmentally friendly method for deacidification of paper is urgently needed.

Non-equilibrium plasma chemistry (often known as cold plasma chemistry) which has been used to modify macromolecular surfaces via various high-energy ions, electrons, free radicals and photons, is a dry and clean process without environmental concerns, such as use of hazardous reagents and solvents. It has been successfully applied in a number of processes, such as plasma cleaning, etching and coating. One of the main advantages of the plasma approach is that any resulting modifications are limited only to the material surface, leaving unaffected the bulk properties [7]. Thus, for the specific case of paper relics, treatment by the plasma method should guarantee the paper protection against surface damage.

When considering alkaline reagents for deacidification, the water-soluble inorganic compounds are much better than complex metallo-organic compounds, due to their lower toxicity and polluting effects [3], as well as cost. When comparing some alkaline inorganic salts, calcium compounds, in general, show better performance than the other commonly used reagents like sodium and magnesium compounds which are considered to be significant in the yellowing of the treated paper [8–10]. The neutralization reaction between an acid substance and OH^- from the $Ca(OH)_2$ can occur directly in the environmental humidity. As a result, some of the free calcium ions deep in the fiber can bond to the carboxyl anions in the oxidized cellulose and decelerate the degeneration rate of the cellulose, while other calcium ions on the surface could transform into $CaCO_3$ for further protection [11,12]. Since many ancient papers with higher calcium carbonate content exhibit a longer-term stability, the use of $Ca(OH)_2$ would be a better choice of alkaline reagent for their conservation.

In this paper, a cold plasma system has been used with a deacidification reagent consisting of saturated $Ca(OH)_2$ solution

* Corresponding author. Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China.
E-mail address: zhangxw@zju.edu.cn (X. Zhang).

1296-2074/$ – see front matter © 2013 Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.culher.2013.03.004

to impregnate alkaline groups into the paper fibers and to modify the fiber surfaces. Parallel investigations using traditional chemical deacidification treatments were carried out, using the same apparatus but without activating the plasma system, so that paper was only treated by $Ca(OH)_2$, similar to the traditional aqueous deacidification method. Measurements of pH and tensile strength of the paper samples were also made in each case. Moreover, different kinds of colored paper were treated to measure the corresponding color change after plasma treatment. In addition, scanning electron microscopy was used to analyze the fiber surfaces of both treated and untreated samples, and the elemental content of the samples was measured by energy-dispersive X-ray spectroscopy [1].

2. Experimental

2.1. Preparation of paper samples

Machine-made paper manufactured in different years, from the 1920's to 1990's, eight kinds of hand-made paper which are Chinese art paper from Jiajiang, bamboo paper from Liangping, raw, mixed moso bamboo paper (#15), raw, mixed bitter bamboo paper (#30), clinker, mixed bitter bamboo paper (#42), clinker, pure bitter bamboo paper (#48), pelure paper from Wenzhou, straw paper were chosen, six kinds of colored machine-made paper (blue, red, yellow, pink, light green, green) and A4 paper samples covered with different pigments (vermilion, Chinese ink, printing ink, malachite, eosin, phthalocyanine blue) were chosen as deacidification test samples. Each sample was cut into pieces of dimensions 130 mm × 150 mm, and maintained under room conditions of 23 ± 1 °C, 50 ± 2% humidity for at least one day prior to testing.

2.2. Plasma processing

The experimental apparatus for plasma processing consists of an arc plasma gun, RF power supply (120–260 W, 0–20 kHz), a conical flask to provide alkaline reagent, gas with valve and a flow meter, which is depicted in schematic form in Fig. 1. The saturated $Ca(OH)_2$ solution firstly fills the plasma gun in vapor form, together with argon. The intensity of the plasma can be controlled by adjusting the flow rate of gas and the power of the generator. The arc plasma gun is connected to a computer numerical control electromotor in order to allow it to move on a designated route at a certain speed, so that every part of the paper placed in the attainable region of the plasma gun can be treated directly in the plasma zone for a certain period of time.

The experiments were carried out under the following working conditions: temperature 20–25 °C, atmospheric pressure, output voltage 75 V, arc power 100 W. The gas used was argon with the rate of 4 L/min, pH of alkaline agent was 12.48, the longitudinal speed of the plasma gun was 35 mm/s and the transverse distance was 2 mm each time.

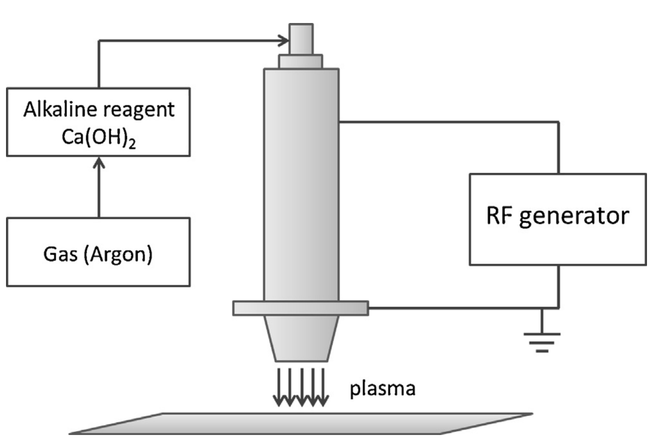

Fig. 1. Schematic of the specially designed plasma treatment apparatus.

2.3. Traditional parallel test method

A parallel test simulating a traditional aqueous deacidification method was made using the same experimental apparatus without activating the plasma system, so that the alkaline agent saturated $Ca(OH)_2$ solution sprayed directly onto the paper samples from the inactive arc plasma gun. In this case, the samples were treated only by alkaline agent with all the other factors the same as for the plasma treatment process.

2.4. Accelerated aging procedure

The stability of the deacidification samples was investigated by moisture-heat-accelerated aging using an aging oven. Artificial aging was performed in the aging oven at a temperature of 80 °C and humidity of 65% for 72 hours, which corresponds to 25 years of natural aging [1].

2.5. Tensile tests

Tensile strength tests on paper sheets were performed on a computer controlled tensile testing machine with an extensometer gauge of 25 mm and a test speed of 5 mm/min. At least ten specimens, which were 100 mm long and 15 mm wide, were tested for each type of paper sheet in order to check for repeatability.

2.6. pH tests

The current surface method of evaluating the pH of paper using a flat electrode is known to be flawed, as it is really the pH of the solution that moistens the paper surface [13]. A more accurate but destructive method is cold extraction measurement [14]. For this method, paper samples are cut into pieces and dispersed in cold deionized water. Accordingly, 1 g of the paper samples was added to 40 ml of cold, deionized water for 1 hour and the pH of the water after the extraction time was deemed to be the pH of paper. For the present study, we used the non-destructive surface pH measurement technique to measure the pH of the paper relics, and the cold extraction method for ordinary samples.

2.7. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis

The surfaces of both untreated and plasma-treated samples were coated by evaporation with gold for 80 seconds before examination. A scanning electron microscope (Hitachi-TM3000) was used to investigate the surface morphologies and determine the content of the specified elements at the same time.

3. Results and discussion

3.1. Measurement of properties before and after plasma deacidification

3.1.1. pH and tensile strength variation

After the deacidification treatment by plasma, both machine-made (Table 1) and hand-made (Table 2) paper samples experienced an increase in pH. Since there will be a long-term consumption of the alkaline compound, the pH achieved after treatment should be above neutral but not high enough to cause alkaline depolymerization. The optimal value was in the 8.0 range, as the