Journal of Cultural Heritage 18 (2016) 250–257

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Original article

Calcium hydroxide nanoparticles in hydroalcoholic gelatin solutions (GeolNan) for the deacidification and strengthening of papers containing iron gall ink

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ARTICLE INFO

Article history:
Received 15 July 2015
Accepted 29 October 2015
Available online 26 November 2015

Keywords:
Alkaline nanoparticles
Deacidification
Paper
Cellulose
Calcium hydroxide
Gelatin
Nanocomposite
Iron gall inks
Lamination
GeolNan

ABSTRACT

A severe decay process, catalyzed by acidity and metal ions, affects cellulose in historical manuscripts and books that contain iron gall inks. The inhibition of this process can be achieved by alkaline-earth nanoparticles dispersions in alcohols, which create a neutral environment in which both oxidation and depolymerization of cellulose are hindered. As a result of the degradation process, paper in historical manuscripts and books is fragile and very difficult to handle. A reinforcement intervention with gelatin and Japanese tissue could be used for the strengthening of historical manuscripts, even if this method could not prevent paper degradation due to iron gall inks. Therefore, a new method, combining a deacidification treatment based on calcium hydroxide nanoparticles and a reinforcement process using Japanese tissue has been developed and tested on mockups containing iron gall inks. The protective action arising from the combined treatment was evaluated by performing cellulose viscosimetric degree of polymerization (DPv) and pH measurements on artificially aged systems. Scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX) was used for the evaluation of calcium distribution from the deacidification agent within samples cross section. Determinations of DPv clearly showed that the degradation of untreated inked paper was significantly slowed down by the combined treatment. The method was also tested on original manuscripts from 16th and 18th century. SEM-EDX maps showed that the applied treatment, which raised the pH to an appropriate value, is homogenously distributed over the treated surfaces.

1. Research aims

Cellulose in historical manuscripts is subjected to several decay processes that may lead to irreversible degradation and to the ultimate loss of valuable information. The presence of metal or iron gall inks in manuscripts is responsible for cellulose corrosion due to the synergistic action of acid-catalyzed hydrolysis and metal-catalyzed oxidation. It has been recently demonstrated that alkaline-earth nanoparticles dispersions in alcohols neutralize manuscripts acidity, raising the pH and therefore inhibiting the catalytic activity of metal ions. Unfortunately, the loss of the mechanical properties of degraded manuscripts, which is an irreversible process, makes their manipulation very difficult. In order to ease the manipulation of highly corroded manuscripts, in the restoration laboratory of the Archive of the Crown of Aragon, a reinforcement intervention is carried out using Japanese tissue and gelatin. Nevertheless, this strengthening treatment is not capable of stabilizing the degradation process due to the concomitant action of acidity and metal ions. With the aim of expanding the palette of available treatments for paper conservator, a new method, combining a deacidification treatment based on calcium hydroxide nanoparticles and a reinforcement with Japanese tissue, was tested on mockups and on real 16th and 18th century manuscripts, showing that the method could overcome the limit of a traditional methodology, improving

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http://dx.doi.org/10.1016/j.culher.2015.10.005
1296-2074/

the useful life of historical manuscripts and granting at the same time their manipulation.

2. Introduction

Cellulose is a linear polymer consisting of several hundred to over ten thousand D-glucose units linked to each other by a β-(1,4)-glycosidic bond. Depending on the plant species, the degree of polymerization (DP) of native cellulose can vary between 7000 and 15,000 [1].

In the interconnected supramolecular structure of cellulose, which is created by both intermolecular and intramolecular hydrogen bonds, two zones can be identified:

- the crystallites, highly crystalline sites, having a compact structure that makes them resistant to degradation;
- the amorphous zones, less oriented and more prone to be degraded by chemical reagents.

Acidic compounds catalyze the hydrolysis of β-(1,4)-glycosidic bonds, leading to the depolymerization of the polymer, therefore reducing the mechanical properties of cellulose-based materials [2]. The hydrolysis reaction takes place at room temperature and can be described as a three steps mechanism [3,4] resulting in a self-accelerating reaction [5,6]. Several factors including pH, temperature, moisture content and degree of crystallinity, affect the depolymerization of cellulose.

Deacidification is probably the most diffused method for the preservation and conservation of cellulose-based artifacts, considering the primary role of acid-catalyzed hydrolysis in the degradation of these artworks. Due to their high compatibility, carbonates and hydroxides of alkaline-earth elements, such as calcium and magnesium, are commonly used for the deacidification of cellulose-based artworks. Several solutions based on colloids and materials science have been recently proposed for overcoming the main issues of traditional methods [7–9]. For instance, dispersions of alkaline nanoparticles, mainly calcium and magnesium hydroxide in non-aqueous solvents, have been used for the pH-control of several cellulose-based works of art, such as paper [10–12], manuscripts [13,14] and archeological wood [15,16]. These nanoparticles are highly reactive due to their high specific area: they neutralize the present acidity and, if in excess, provide a stable environment by rapidly turning into carbonates.

Acidity is often interconnected with oxidation in promoting the degradation of cellulose, by creating the so-called “spiraling effect” [17,18]. A well-known conservation issue of manuscripts is the corrosion of paper due to the presence of iron gall inks that promote the concomitant oxidation and hydrolysis of cellulose. The colouring complex of iron gall inks is iron(III)-pyrogallate formed by the reaction of gallic acid, extracted from gall nuts, with iron(II) sulfate (i.e. vitriol, as reported in historic recipes) [19,20]. A by-product of this reaction is sulfuric acid that is responsible for the acid-catalyzed hydrolysis of cellulose in manuscripts featuring iron gall inks. Inks prepared according to the old recipes are often unbalanced [21]. Under these conditions, unbound transition metal ions are free to catalyze cellulose oxidation through a radical mechanism, involving the formation of hydrogen peroxide in situ [21]. As a consequence of acid-catalyzed hydrolysis and concomitant metal-induced oxidation, manuscripts often show severe browning, a general loss of the typical mechanical properties of paper, i.e. elasticity and tensile strength and, in some extreme cases, the perforation of inked areas [22,23].

Metal ion-catalyzed oxidation is enhanced by acidity; as a matter of fact, this process is favored at pH below 4.5, and it reaches the minimum in the 5.5–6.5 pH range [24]. An ideal deacidification treatment should stabilize the pH of manuscripts around neutrality, to hinder both acid-catalyzed hydrolysis and metal-catalyzed oxidation [25]. It has been recently demonstrated that the application of alkaline-earth metal hydroxide nanoparticles dispersed in non-aqueous solvents can successfully inhibit the two different degradation mechanisms of metal gall ink through a single, simple and safe treatment, that gradually takes to a neutral pH, which results in a significant increase of inked paper resistance to aging [13,14]. Non-aqueous treatments prevent the leaching of original writing fluids and allow an efficient distribution of the deacidifying nanoparticles within the substrate.

In the restoration laboratory of the Archive of the Crown of Aragon, the reinforcement of manuscripts and books containing iron and metal gall inks is carried out using Japanese tissues and hydroalcoholic gelatin solutions, creating the so-called “lamination” of the corroded paper sheets. This operation is aimed at easing the manipulation of historical documents, whose mechanical strength is reduced during natural aging by the presence of iron and metal gall inks.

In this paper, the effects of a combined treatment, based on deacidification with calcium hydroxide nanoparticles and reinforcement with gelatin, are investigated. This new method, applied to paper in a hydroalcoholic medium, is aimed at slowing down the degradation of cellulose, and, at the same time, at increasing the mechanical properties of the original paper. The combined treatment has been tested on mockup samples containing iron gall ink. Deacidification efficacy was assessed by pH and viscosimetric determinations of polymerization degree of cellulose (DPv) upon an aging cycle at high temperature and relative humidity (T = 80 °C, RH = 75%). The penetration of nanoparticles within the cross section has been evaluated by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDX). The proposed method was also tested on original manuscripts from 16th and 18th century, which show severe corrosion and fragility due to the presence of the metal gall inks. On these samples, a complete restoration intervention has been conducted, including the lamination of the paper using Japanese tissue (3 g/m^2) and the combined treatment for concomitant deacidification and strengthening. On real samples, pH measurements were performed and SEM images and elemental maps were acquired in order to evaluate the treatment efficacy.

3. Materials and methods

3.1. Chemicals

Arabic gum, and gall nuts were provided by Zecchi, Art Shop in Florence. Iron(II) sulfate heptahydrate (Ph. Eur.; chlorides < 300 ppm, Zn < 500 ppm, heavy metals < 50 ppm, Fe(III) < 0.5%, Mn < 0.1%) was supplied by Fluka Chemicals, as well as the other reagents for the preparation of iron gall ink, i.e., ethyl alcohol (99.8%) and acetic acid (99.5%). Type B gelatin, extracted in alkaline environment from bovine skin and connective tissues, was supplied by Helm Iberica. Ethanol absolute (99.8%, Fluka), *n*-propanol (99.5%, Sigma-Aldrich), and metal granular calcium (99%, Aldrich) were used for nanoparticles syntheses. For DP determination via viscosimetric measurements, bis(ethylenediamine)copper(II) hydroxide solution (Sigma-Aldrich) was used. Highly pure water (having a resistivity of 16 MΩcm) produced by a Millipore Milli-Q UV system was used during the experiments.