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Original article

Deacidification of paper using dispersions of $Ca(OH)_2$ nanoparticles in isopropanol. Study of efficiency

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Abstract

The efficiency of a recently described non-aqueous method for paper deacidification using $Ca(OH)_2$ nanoparticles in isopropanol was evaluated by pH and colorimetric measurements and by the analysis of the degree of polymerization (DP). Samples of plain paper and paper with iron gall ink were tested. The results were compared with non treated samples and samples submitted to the traditional treatment with saturated aqueous $Ca(OH)_2$ solution. By comparing the two conservation methods, the aqueous one shows higher neutralization reaction kinetics than the non-aqueous one. The iron gall ink samples maintain their coloration closer to the original after the non-aqueous $Ca(OH)_2$ nanoparticles treatment, in contrary to the aqueous treatment that changes the ink aesthetics considerably. Artificial aging tests revealed a general increase in the aging stability of deacidified paper samples. The $Ca(OH)_2$ nanoparticles treatment can be an alternative for papers who can not be treated by the classical aqueous treatment, e.g. papers with water soluble components.

Keywords: Paper; Nanoparticles; Calcium hydroxide ($Ca(OH)_2$); Deacidification; Iron gall ink

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1. Introduction/research aims

The acid catalyzed depolymerization of cellulose is one of the major problems in paper conservation. Since about the middle of the 17th century, oxidizing and acid components have been introduced in the papermaking processes, in order to save time and/or money or to improve the paper initial appearance. At long term, these additives contribute to the degradation of the paper since an acid pH leads to the breaking of the chemical bonds that connect the cellulose polymer units (Fig. 1)—depolymerization of cellulose—in a continuous and consecutive process, resulting essentially in the progressive lost of tensile strength and color change of the paper [1]. The oxidation of cellulose also contributes for the raising of acid concentration in paper, since through photo-oxidation, the primary alcohol groups in the cellulose polymer are oxidized to aldehyde and later to carboxyl groups—acid species (Fig. 2) [2,3]. One way to stop the cycle of acid catalyzed reactions described above is to neutralize the protons (H^+) responsible for the low pH by reaction with an alkaline compound—deacidification of cellulose. Currently in conservation and restoration, several methods for paper deacidification are being applied but their effectiveness is not complete. The major drawbacks of these treatments are the fact that they are either restricted to papers with insoluble inks and paints (e.g. aqueous treatments), that they often lead to the accumulation of by-products that alter the visual appearance of the treated documents (e.g. non-aqueous treatments based in magnesium compounds), and that, with a few exceptions [4] they are frequently based on non-environmentally friendly solvents [5,6].

The main aim of this research was to produce and evaluate a new non-aqueous paper deacidification method, which consists in the application of nanometric $Ca(OH)_2$ particles, dispersed in iso-propanol, by spraying (having this way the potentiality of being applied in mass deacidification). This conservation treatment was developed in Florence University and published in 2002 [7]. The neutralization reaction between one of the

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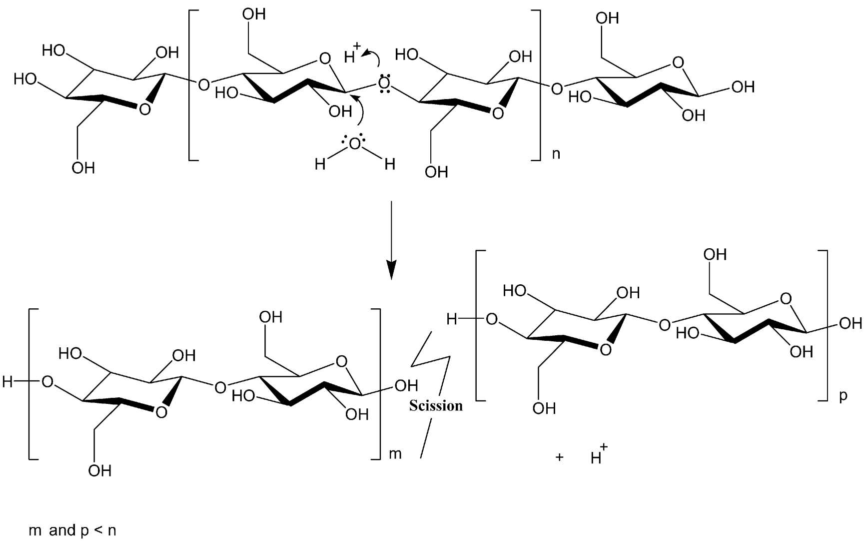

Fig. 1. Acid catalyzed hydrolysis of the 1,4-glycosidic bond in cellulose (hydrolysis can occur at any glycosidic bond in the chain).

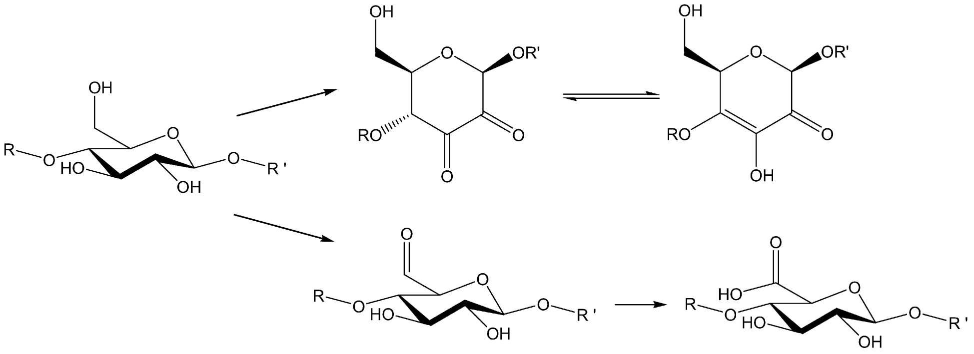

Fig. 2. Cellulose oxidation mechanisms.

hydroxyl groups of the $Ca(OH)_2$ and the proton of the acid species [reaction 1], occurs in the particle surface through a water layer from environmental humidity. Free calcium ions (Ca^{2+}) can also connect to the carboxyl anions (deprotonated by the hydroxyl group) when these are present in the oxidized cellulose (Fig. 2) and its charge balance may be maintained by OH^- anions [8]. The $Ca(OH)_2$ at the particles surface which did not react with any protons will carbonate by reaction with carbon dioxide from the atmosphere, forming calcium carbonate [reaction 2]—an alkaline reservoir that will neutralize the upcoming acid species [reaction 3].

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \text{ [reaction 1]}$$
$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l) \text{ [reaction 2]}$$
$$CO_3{}^{2-}(s) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l) \text{ [reaction 3]}$$

When compared to the other commonly used non-aqueous deacidification methods, the main advantage of this method is the employment of nanoparticles. Since the specific surface area of a solid increases exponentially with the decrease of its volume, these nanoparticles have a much superior surface area of the alkaline compound ($Ca(OH)_2$ in this case) available to react with the acid groups, than the microparticles generally used, ensuing in a superior capacity of neutralization. Besides, these nanometric particles also have a better ability to penetrate in the cellulose fiber net, reaching more easily to all the thickness of the paper, not forming white glazing films at the surface, which would affect the appearance of the paper, its readability and/or its aesthetic value.

This is also the first non-aqueous deacidification treatment using $Ca(OH)_2$ as the alkaline compound. Since the ancient papers that are in better conservation conditions are the ones who exhibit higher calcium carbonate ($CaCO_3$) content [1,9], pointing out to a long-term physicochemical stability between calcium and cellulose, and the magnesium compounds usually employed in the non-aqueous methods cause yellowing of the treated paper [10–12], the use of calcium would be a better conservation choice. Comparatively to the aqueous deacidification methods, the non-aqueous ones allow a faster and easier application, as they use a more volatile medium and can be applied by spraying. In the case of paper with water soluble components (for example inks), a non-aqueous treatment would be a reasonable alternative.

The evaluation reported here consists in a comparison between both the non-aqueous $Ca(OH)_2$ nanoparticles deacidification method and the traditional aqueous $Ca(OH)_2$, with assessment of long lasting results through artificial aging tests. The efficiency of both treatments is compared in terms